In addition, certain aspects of the invention relate solely to the preparation and use of boxime-modified doxime, nanoscale metal oxide nanoparticles. I

A suspension of magnetite nanoparticles is dispersed in an aqueous medium. A suspension of a metal oxide nanoparticles modified with 2-pralidoxime is added to the suspension. The resulting suspension is then added to an aqueous medium that is mildly acidic. The oxime-modified magnetite nanoparticles are stable and can be separated from the medium using a magnetic field. The oxime-modified magnetite nanoparticles can be used as a probe to detect nerve agents in an aqueous environment.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.
CATALYTIC NANOPARTICLES FOR NERVE-AGENT DESTRUCTION

Background of the Invention

The presence of organophosphate esters (OPE) in industrial and agricultural drain waters, spills, runoffs, and drifts, as well as OPE agent-based chemical munitions that may be released in case of warfare or terrorist attack, pose great risks to human health and the environment. The number of exposures to OPE due to pesticides and insecticides is estimated at some 3,000,000 per year, with the total number of deaths and casualties over 300,000 per year worldwide. Eyer, P. "The role of oximes in the management of organophosphorus pesticide poisoning," *Toxicol Rev.* 2003, 22(3), 165-190. Numerous OPE pesticides, insecticides and warfare agents, such as sarin, soman, and VX, in addition to being carcinogenic, act as nerve poisons which may cause cumulative damage to the nervous system and liver. The primary mechanism of action of the OPEs is irreversible inhibition of acetylcholinesterases, resulting in the accumulation of the neurotransmitter acetylcholine at nerve synapses. Structures of the nerve poison sarin and a model analog used in this study, diisopropyl fluorophosphate (DFP), are given in Figure 1.

Some of the first OPE decontaminating agents were oxidizers, such as bleaching powders. See Yang, Y. C. *et al.* Yang, Y. C.; Baker, J. A.; Ward, J. R. "Decontamination of chemical warfare agents," *Chem. Rev.* 1992, 92(8), 1729-1943. However, it has been observed that the activity of bleaches decreases upon long-term storage; to have the desired effect, copious amounts of bleach must be used. Moreover, because bleaches are quite corrosive, they are not compatible with many surfaces.

At present, the decontamination solutions of choice are DS-2 (a non-aqueous liquid composed of diethylenetriamine, ethylene glycol, monomethyl ether, and sodium hydroxide) and STB (super tropical bleach). Although DS-2 is generally not corrosive to metal surfaces, it damages skin, paints, plastics, rubber, and leather materials. STB, while effective, has the same environmental problems as bleaches and cannot be used on the skin. Consequently, personal decontamination equipment typically consists of packets of wipes containing such chemicals as sodium hydroxide, ethanol, and phenol. These chemicals are selected to provide a nucleophilic attack at the phosphorous atom of nerve agents.

Alternatives to oxidizers have focused on the development of processes for the catalytic destruction (CD) of nerve agents and pesticides. Chiron, S. *et al.* "Pesticide chemical oxidation: state-of-the-art," *Water Research* 2000, 34(2), 3ββ-2 ll; and Russell, A.
J. et al. "Biomaterials for mediation of chemical and biological warfare agents," *Annu. Rev. Biomed. Eng.* 2003, 5, 1-27. It was first recognized in the 1950s that certain metal ions, especially Cu(II), had the ability to catalyze the hydrolysis of nerve agents and their simulant. The catalytic activity of such chemicals was significantly enhanced when Cu(II) was bound to certain ligands. For example, diisopropyl phosphorofluoridate (DFP) has a hydrolytic half-life of approximately 2 days in water, 5 hours in water when CuSO₄ is added, and just 8 minutes in water when Cu(II) bound to either histidine or N,N'-dipropylidyl is added in an approximately 2:1 ratio of metal complex to substrate. Sarin was found to be even more susceptible to metal-based catalysis with a half-life of only 1 minute in the presence of tetramethyl-ED A-Cu(II) complex (1:1 metal complex to substrate). However, the use of free copper-ligand complexes for catalyzing the degradation of nerve agents also has disadvantages. First, the nerve agent must be brought into contact with a solution of the metal-ion-containing catalyst. Second, the ratio of metal to chelate must be carefully controlled. Third, solubility issues can still limit the pH range and choice of chelates for use in a particular environment.

In addition, researchers have begun to look at enzymes stabilized by attachment to polymeric support as catalysts for the degradation of nerve agents. These enzymes, variously known as organophosphorous acid anhydrases, phosphotriesterases, sarinase, or others, are extracted either from microorganisms, such as *Pseudomonas diminuta*, or from squid. The enzymatic approach shows promise but is limited by the specificity of the proteins for their substrates, e.g., a parathion hydrolase would not be effective against another nerve agent. Further, the enzymes require a very specific range of conditions, e.g., pH, to function properly, in addition, field conditions can involve concentrated solutions of nerve agents, which can overwhelm the relatively low concentration of enzymes which can be immobilized on a support.


Summary

The present invention provides compositions and methods for sorbing (e.g., adsorption and chemisorption) and destroying organophosphate chemical agents. To this end, the invention contemplates the use of finely divided, modified nanoscale metal oxide particles.

In one embodiment, a suspension of magnetite (Fe₃O₄) nanoparticles modified with 2-pralidoxime or its polymeric analog, poly(4-vinylpyridine-N-phenacyloxime-co-acrylic acid), catalyzes the hydrolysis of organophosphate compounds at a neutral pH. In another related embodiment, organophosphate compounds can be catalytically hydrolyzed by magnetite (Fe₃O₄) nanoparticles modified with poly(1-vinylimidazole-co-acrolein oxime-co-acrylic acid). In another related embodiment, organophosphate compounds can be catalytically hydrolyzed by magnetite (Fe₃O₄) nanoparticles modified with oximated humic acid.
The modified magnetite particle of the invention serve as a nano-sized particulate carrier with a powerful $\alpha$-nucleophile, e.g., an oximate group, immobilized on its surface. These modified magnetite nanoparticles are colloidally stable within a wide pH range and are readily recovered for reuse from the aqueous milieu by high-gradient magnetic separation methods with no loss of catalytic activity. In certain embodiments, the adsorbent nucleophilic particles of the instant invention may be fabricated in the form of filters, sponges, wipes, powder or any other form suitable for use in a decontamination process. For example, the particles of the invention may be used in gas masks, wearable protective garments, air filtration systems, and the like.

Certain aspects of the invention relate to the preparation and use of the $\alpha$-nucleophile containing compound, or polymer, without a metal nanoparticle.

**Brief Description of the Figures**

**Figure 1** depicts the chemical structures of [A] diisopropyl fluorophosphate (DFP) and [B] sarin.

**Figure 2** depicts the chemical structures of certain oxime-containing species employed for magnetite particle modification described herein: [A] 2-pralidoxime bromide and [B] poly(4-vinylpyridine-N-phenacyloxime-co-acrylic acid) [p(VPOX-AA)]$_n$ where m, n and p are integers.

**Figure 3** depicts the effect of pH on $\zeta$-potential and hydrodynamic diameter of magnetite particles modified with 2-pralidoxime (PAM/M) and poly(4-vinylpyridine-N-phenacyloxime-co-acrylic acid) [p(VPOX-AA)]$_n$. Open and filled points show $\zeta$-potential and diameter, respectively. The temperature was 25 °C; and the buffer used was 10 mM Tris buffer with its pH adjusted by 1 M NaOH or HCl.

**Figure 4** depicts the potential-time response of fluoride-selective electrode to various DFP concentrations in the absence (1) and the presence (2, 3) of 1 mg/mL magnetite particles modified with PAM. DFP concentration is 0.54 mM (1, 2) or 2 mM (3). The temperature was 25 °C; and the buffer used was 10 mM Tris buffer at a pH of 7.0.

**Figure 5** depicts the observed kinetic constants ($k_{obs}$) of the DFP hydrolysis versus the effective concentration of additives (T = 25 °C; pH 7.0; 10 mM Tris buffer).

Designations M, PAM, PAM/M, p(VP-AA)/M, and p(VPOX-AA)/M stand for magnetite, 2-pralidoxime, and magnetite modified with pralidoxime, poly(4-vinylpyridine-co-acrylic acid), and poly(4-vinylpyridine-N-phenacyloxime-co-acrylic acid), respectively.
**Figure 6** depicts a postulated mechanism for the hydrolysis of DFP with oxime-modified particles.

**Figure 7** depicts the initial rate of DFP hydrolysis \( (\nu) \) versus concentration of the oxime groups \(([\text{Ox}])\) in suspensions of magnetite modified with PAM (1) or p(VPOX-AA) (2) or solutions of PAM (3). \([\text{DFP}]_0=4\, \text{mM}, \, T=25\, ^\circ\text{C}, \, 10\, \text{mM Tris buffer, pH 7.0.}\)

**Figure 8** depicts the Lineweaver-Burk plots of the initial rate of DFP hydrolysis \((1/\nu)\) versus initial DFP concentration \((1/[\text{DFP}])\) in suspensions of magnetite modified with PAM (1) or p(VPOX-AA) (2) or solutions of PAM (3). Initial oxime concentrations were 1.7, 7.3, and 1.5 \( \mu\text{M} \) on plots 1, 2, and 3, respectively. \( T=25\, ^\circ\text{C}, \, 10\, \text{mM Tris buffer, pH 7.0.}\)

**Figure 9** depicts the effect of recycling on the performance of magnetite modified by p(VPOx-AA) in DFP hydrolysis \((T=25\, ^\circ\text{C}; \, \text{pH 7.0}; \, 10\, \text{mM Tris}; \, \text{initial DFP concentration in all cycles was 1.33 mM})\). Cycle #1 comprised the first use of the particles; cycle #2 comprised the first magnetic recovery and resuspension of the particles at 1 mg/mL; and cycle #3 comprised the second magnetic recovery and resuspension of the particles at 1 mg/mL. Solid lines show linear fits \((R^2\) greater than or equal to about 0.99 in all cases).

**Figure 10** depicts a schematic showing the decomposition of diisopropyl fluorophosphate (DFP) by 2-pyridinealdoxime (PAM).

**Figure 11** depicts electrode response curves showing the potential-time response of fluoride-selective electrode to various treated and untreated PET film concentrations. Numbers stand for effective concentrations of PAM/M particles in the buffer solution, in mg/mL. In the case of untreated films, no PAM/M particles was added. \( T=25\, ^\circ\text{C}, \, \text{pH 7.0.}\)

**Figure 12** depicts a graph showing the dependence of the observed nerve gas hydrolysis kinetic constants \((k_{\text{obs}})\) on the effective concentration of magnetite modified with pralidoxime (PAM/M) particles in the system. The particles were added via soaking of the PAM/M-treated PET film in the buffer solution. \( T=25\, ^\circ\text{C}, \, \text{pH 7.0.}\)

**Figure 13** depicts a schematic of a protective composite fabrics modified with nanoparticles. Protective layer is water-permeable; reactive layer: nanoparticles capture and destroy toxins; adsorptive layer: products of decomposition are captured. The composite fabric is user-friendly and can be utilized in the military, industrial, and outdoor markets.

**Figure 14** depicts electrode response curves showing the potential-time response of fluoride-selective electrode to various treated and untreated Polartec® films. Numbers stand
for effective concentrations of PAM/M particles in dry fabric, in mg/mg. In the control experiment, only untreated fabric was used and no PAM/M particles was added. T=25°C, pH 7.0.

**Figure 15** depicts a graph showing the dependence of the observed nerve gas hydrolysis kinetic constants ($k_{\text{obs}}$) on the effective concentration of magnetite modified with pralidoxime (PAM/M) particles in the Polartec® fabric. T=25°C, pH 7.0.

**Figure 16** depicts the schematic of an oxime-containing specie employed for magnetite particle modification described herein: a p(VIm-AcOx-AA) copolymer. Variable x, y and z are integers.

**Figure 17** depicts a graph showing the effect of pH on $\zeta$-potential and hydrodynamic diameter of magnetite particles modified with p(VIm-AcOx-AA). T=25°C; 10 mM Tris buffer with pH adjusted by 1 M NaOH or HCl.

**Figure 18** depicts electrode response curves showing the potential-time response of fluoride-selective electrode to 0.6 mM DFP concentration in the presence of varying concentrations of magnetite particles modified with p(VIm-AcOx-AA). T=25°C; 10 mM Tris, pH 7.0. Numbers stand for particle concentrations in mg/mL. Addition of DFP to a suspension of oxime-containing particles, resulted in the rapid appearance and accumulation of the fluoride ions, as is seen from the response of the ion-selective electrode. The electrode potential was converted to the time-dependent fluoride concentration ($C_t$) readings, using electrode calibration curves in sodium fluoride solutions. The initial slope of the $C_t$ vs $t$ kinetic curves corresponds to the initial rate of the DFP hydrolysis ($v_0$). The observed rate constant for the DFP hydrolysis ($k_{\text{obs}}$) was obtained from the experimental data.

**Figure 19** depicts the catalytic stability of magnetic nanoparticles modified by p(VIm-AcOx-AA) indicated by essentially unchanged kinetic profiles observed for DFP hydrolysis when the particles are recovered, washed, and reused. T=25°C, pH 7.0, 10 mM Tris; initial DFP concentration in all cycles, 0.6 mM. Cycle 1 denoted the first use of the particles, Cycle 2 the first magnetic recovery and resuspension of the particles at 1 mg/mL, and Cycle 3 the second magnetic recovery and resuspension of the particles at 1 mg/mL. The straight line illustrates the average slope of the kinetic curves used to calculate the $k_{\text{obs}}$

**Figure 20** depicts a graph showing dependence of the observed DFP hydrolysis kinetics constants ($k_{\text{obs}}$) on the effective initial concentration of the oxime groups ([Ox]$_0$) in suspensions of magnetite modified with p(VIm-AcOx-AA). T=25°C; 10 mM Tris, pH 7.0,
[DFP]₀ = 0.6 nm. Broken line shows k_{obs} for the spontaneous hydrolysis of DFP in the buffer solution alone.

**Figure 21** depicts an FTIR spectra of the oximated humic acid (OHA)-modified magnetite and in humic acid (HA)-modified magnetite taken in KBr.

**Figure 22** depicts a graph of the response of a fluoride-selective electrode to the addition of diisopropyl fluorophosphate (DFP) to suspensions containing either humic acid-modified magnetite or oximated humic acid-modified magnetite in 10 nm Tris buffer at pH 7.0 and 25 °C. Initial DFP concentration, 3 mM; effective particle concentration in each experiment, 10 mg/mL.

**Detailed Description of the Invention**

**Overview**

The present invention relates to compositions and methods for destroying dangerous substances, such as chemical and biological agents. Organophosphorus pesticides and warfare agents are not readily hydrolyzed in aqueous media without applying extremes of pH, heat, or bleach. Remarkably, the methods of the invention are carried out by contacting the target substance with particulate metal oxide modified with a nucleophilic group. For example, the metal oxides can be coated with a monomeric or polymeric substance comprising a nucleophilic group. In one embodiment, the modified particulate metal oxides are used in aqueous media. In another embodiment, the modified particulate metal oxides are used as air-detoxifying media by contacting the particulates with liquid droplets of organophosphate compound. For example, herein are disclosed methods of forming particulate metal oxide modified with a nucleophilic group via iron chloride co-precipitation with a stabilizing compound containing a nucleophilic group, hi certain embodiments, said nucleophilic group is an α-nucleophile. hi certain embodiments, said nucleophilic group is an oxime, hydroxamic acid, imidazole, iodozobenzoate, or a salt thereof. Importantly, in certain embodiments the modified particulate metal oxide utilized in the methods of the invention is not harmful to equipment or to humans and can easily be used directly at the site of contamination. Said metal oxide can be optionally superparamagnetic, which enables useful recovery and reuse by means of magnetic separation.

Remarkably, suspensions of magnetite (Fe₃O₄) nanoparticles modified with common antidote, 2-pralidoxime (PAM), catalyze the hydrolysis of an organophosphate-ester-containing compound at neutral pH. The oxime-modified magnetite particles function
as a nano-sized particulate carrier with a powerful α-nucleophile immobilized on its surface. It is demonstrated that the oxime-modified magnetite nanoparticles (hydrodynamic diameter of about 100 nm) are colloidal stable at neutral pH. Moreover, they are readily recovered from the aqueous milieu by high-gradient magnetic separation methods, high-gradient magnetic separation methods, high-gradient magnetic separation methods. Certain embodiments PAM can be replaced by poly(4-vinylpyridine-N-phenacyloxime-co-acrylic acid), poly(l-vinylimidazole-co-acrolein oxime-co-acrylic acid), or modified humic acid.

The immobilized metal complexes of the present invention have uses in addition to their use to decontaminate areas contaminated with nerve agents and/or pesticides. For example, the catalytic hydrolysis of nerve agents and/or pesticides using the compositions of the present invention can be employed as the operative process step in a detector system wherein the by-products of the hydrolysis reaction, such as hydrogen fluoride, may be subject to measurement to provide an indication of the presence and/or concentration of a particular phosphate ester in the environment. Additionally, the adsorbent nucleophilic particles of the instant invention may be fabricated in the form of filters, sponges, wipes, powder or any other form suitable for use in a decontamination process. For example, the particles of the invention may be used in gas masks, wearable protective garments, air filtration systems, and the like.

Definitions

For convenience, before further description of the present invention, certain terms employed in the specification, examples and appended claims are collected here. These definitions should be read in light of the remainder of the disclosure and understood as by a person of skill in the art. Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by a person of ordinary skill in the art.

The articles "a" and "an" are used herein to refer to one or to more than one (i.e., to at least one) of the grammatical object of the article. By way of example, "an element" means one element or more than one element.

The term "associated with" as used herein in such phrases as, for example, "an inorganic metal oxide associated with an stabilizing compound," refers to the presence of either weak or strong (or both) interactions between molecules. For example weak interactions may include, for example, electrostatic, van der Waals, or hydrogen-bonding interactions. Stronger interactions, also referred to as being chemically bonded, refer to, for
example, covalent, ionic, or coordinative bonds between two molecules. The term "associated with" also refers to a compound that may be physically intertwined within the foldings of another molecule, even when none of the above types of bonds are present. For example, an inorganic compound may be considered as being in association with a polymer by virtue of it existing within the interstices of the polymer.

The terms "comprise" and "comprising" are used in the inclusive, open sense, meaning that additional elements may be included.

The term "including" is used to mean "including but not limited to". "Including" and "including but not limited to" are used interchangeably.

The term "polymer" is used to mean a large molecule formed by the union of repeating units (monomers). The term polymer also encompasses copolymers.

The term "co-polymer" is used to mean a polymer of at least two or more different monomers.

The term "particle size" is used to mean a number-average or weight-average particle size as measured by conventional particle size measuring techniques well known to those skilled in the art, such as dynamic or static light-scattering, sedimentation field-flow fractionation, photon-correlation spectroscopy, or disk centrifugation. By "an effective average particle size of less than about 1000 nm" it is meant that at least about 90% of the particles have a number-average or weight-average particle size of less than about 1000 nm when measured by at least one of the above-noted techniques.

The term "interstices" is used to mean a space, especially a small or narrow one, between things or parts.

The term "chemical coprecipitation" as used herein refers to a common technique for making aqueous magnetic fluids from metal salts. This technique may be used to produce ferrite particles, such as magnetite (Fe₃O₄), maghemite (γ-Fe₂O₃), or cobalt ferrite (CoFe₂O₄).

The term "diamagnetic" as used herein means having a negative magnetic susceptibility.

The term "magnet" as used herein refers to a substance composed of ferromagnetic or ferrimagnetic material having domains that are aligned to produce a net magnetic field outside the substance or to experience a torque when placed in an external magnetic field.
The term "magnetic core" as used herein refers to a piece of magnetic material, often of iron oxide or ferrite that is within a copolymer shell, coil, transformer, or electromagnet.

The term "magnetic field" as used herein refers to a vector field occupying physical space wherein magnetic forces may be detected, typically in the presence of a permanent magnet, current-carrying conductor, or an electromagnetic wave.

The term "magnetic field strength" as used herein refers to a vector field used to describe magnetic phenomena, having the property that the curl of the field is equal to the free current density vector in the meter-kilogram-second system of units.

The term "magnetic separation" as used herein refers to a process that uses a magnetic solid and an external magnetic field to separate materials or compounds. Examples of magnetic separation include magnetocollection, magnetoflocculation, and magnetoanisotropic sorting.

The term "magnetic susceptibility" as used herein refers to the ratio of the magnetization of a substance to the applied magnetic field strength.

The term "magnetite" as used herein refers to a chemical compound represented as Fe₂O₃*FeO or Fe₃O₄ in the spinel iron oxide species with a 2:1 molar ratio of Fe ions that are present in their III and II oxidation states, respectively.

The term "magnetite nanoparticles" as used herein refers to either the magnetic core of the magnetic particles that make up a magnetic fluid, or to the magnetic particles as a whole, including both the magnetite core and the polymer shell that stabilizes them in the surrounding liquid.

The term "non-magnetic particle" as used herein refers to a particle that does not have inherent magnetic properties.

The term "superparamagnetism" as used herein refers to the tendency of fine particles to behave independently of one another in a manner similar to paramagnets, so that the particles show a net magnetization in the presence of a magnetic field, but then rapidly relax to show zero net magnetization when the applied magnetic field is removed.

The term "nucleophile" is recognized in the art, and as used herein means a chemical moiety having a reactive pair of electrons. Examples of nucleophiles include uncharged compounds, such as water, amines, mercaptans and alcohols, and charged moieties, such as alkoxides, thiolates, carbanions, oximes and a variety of organic and inorganic anions.
The term "α-nucleophile" is recognized in the art, and as used herein means a nucleophile possessing a heteroatom with an unshared electron pair adjacent to the nucleophilic center.

The term "n-nucleophile" is recognized in the art, and as used herein means a nucleophile comprising a lone pair of electronics in a non-bonding orbital.

As used herein, "fabric" preferably comprises synthetic or non-synthetic fibers or mixtures thereof. Non-synthetic fibers include, for example, cellulosic (e.g., cotton) or proteinaceous (e.g., wool or silk) fibers. Synthetic fibers include, for example, nylon and polyesters.

The term "aliphatic" is an art-recognized term and includes linear, branched, and cyclic alkanes, alkenes, or alkynes. In certain embodiments, aliphatic groups in the present invention are linear or branched and have from 1 to about 20 carbon atoms.

The term "alkyl" is art-recognized, and includes saturated aliphatic groups, including straight-chain alkyl groups, branched-chain alkyl groups, cycloalkyl (alicyclic) groups, alkyl substituted cycloalkyl groups, and cycloalkyl substituted alkyl groups. In certain embodiments, a straight chain or branched chain alkyl has about 30 or fewer carbon atoms in its backbone (e.g., C₁₋C₅₀ for straight chain, C₃₋C₃₀ for branched chain), and alternatively, about 20 or fewer. Likewise, cycloalkyls have from about 3 to about 10 carbon atoms in their ring structure, and alternatively about 5, 6 or 7 carbons in the ring structure.

Unless the number of carbons is otherwise specified, "lower alkyl" refers to an alkyl group, as defined above, but having from one to ten carbons, alternatively from one to about six carbon atoms in its backbone structure. Likewise, "lower alkenyl" and "lower alkynyl" have similar chain lengths.

The term "aralkyl" is art-recognized, and includes alkyl groups substituted with an aryl group (e.g., an aromatic or heteroaromatic group).

The terms "alkenyl" and "alkynyl" are art-recognized, and include unsaturated aliphatic groups analogous in length and possible substitution to the alkyls described above, but that contain at least one double or triple bond respectively.

The term "heteroatom" is art-recognized, and includes an atom of any element other than carbon or hydrogen. Illustrative heteroatoms include boron, nitrogen, oxygen, phosphorus, sulfur and selenium, and alternatively oxygen, nitrogen or sulfur.
The term "aryl" is art-recognized, and includes 5-, 6- and 7-membered single-ring aromatic groups that may include from zero to four heteroatoms, for example, benzene, naphthalene, anthracene, pyrene, pyrrole, furan, thiophene, imidazole, oxazole, thiazole, triazole, pyrazole, pyridine, pyrazine, pyridazine and pyrimidine, and the like. Those aryl groups having heteroatoms in the ring structure may also be referred to as "heteroaryl" or "heteroaromatics." The aromatic ring may be substituted at one or more ring positions with such substituents as described above, for example, halogen, azide, alkyl, aralkyl, alkenyl, alkynyl, cycloalkyl, hydroxyl, alkoxy, amino, nitro, sulfhydryl, imino, amido, phosphonate, phosphinate, carbonyl, carboxyl, silyl, ether, alkylthio, sulfonyl, sulfonamido, ketone, aldehyde, ester, heterocyclyl, aromatic or heteroaromatic moieties, -CF₃, -CN, or the like. The term "aryl" also includes polycyclic ring systems having two or more cyclic rings in which two or more carbons are common to two adjoining rings (the rings are "fused rings") wherein at least one of the rings is aromatic, e.g., the other cyclic rings may be cycloalkyls, cycloalkynyls, aryls and/or heterocyclyls.

The terms ortho, meta and para are art-recognized and apply to 1,2-, 1,3- and 1,4-disubstituted benzenes, respectively. For example, the names 1,2-dimethylbenzene and ortho-dimethylbenzene are synonymous.

The terms "heterocyclyl" and "heterocyclic group" are art-recognized, and include 3- to about 10-membered ring structures, such as 3- to about 7-membered rings, whose ring structures include one to four heteroatoms. Heterocycles may also be polycycles. Heterocyclyl groups include, for example, thiophene, thianthrene, furan, pyran, isobenzofuran, chromene, xanthene, phenoxathiin, pyrrole, imidazole, pyrazole, isothiazole, isoxazole, pyridine, pyrazine, pyrimidine, pyridazine, indolizine, isoindole, indole, indazole, purine, quinolizine, isoquinolizine, quinoline, phthalazine, naphthyridine, quinoxaline, quinazoline, cinnoline, pteridine, carbazole, carboline, phenanthridine, acridine, pyrimidine, phenanthrolone, phenazine, phenarsazine, phenothiazine, furazan, phenoxazine, pyrroolidine, oxolane, thiolane, oxazole, piperidine, piperazine, morpholine, lactones, lactams such as azetidinones and pyrrolidinones, sultams, sultones, and the like. The heterocyclic ring may be substituted at one or more positions with such substituents as described above, as for example, halogen, alkyl, aralkyl, alkenyl, alkynyl, cycloalkyl, hydroxyl, amino, nitro, sulfhydryl, imino, amido, phosphonate, phosphinate, carbonyl, carboxyl, silyl, ether, alkylthio, sulfonyl, ketone, aldehyde, ester, a heterocyclyl, an aromatic or heteroaromatic moiety, -CF₃, -CN, or the like.
The terms "polycyclyl" and "polycyclic group" are art-recognized, and include structures with two or more rings (e.g., cycloalkyls, cycloalkenyls, cycloalkynyls, aryls and/or lieterocycllys) in which two or more carbons are common to two adjoining rings, e.g., the rings are "fused rings". Rings that are joined through non-adjacent atoms, e.g., three or more atoms are common to both rings, are termed "bridged" rings. Each of the rings of the polycycle may be substituted with such substituents as described above, as for example, halogen, alkyl, aralkyl, alkenyl, alkynyl, cycloalkyl, hydroxyl, amino, nitro, sulfhydryl, imino, amido, phosphonate, phosphinate, carbonyl, carboxyl, silyl, ether, alkythio, sulfonyl, ketone, aldehyde, ester, a heterocyclyl, an aromatic or lieteroaromatic moiety, -CF₃, -CN, or the like.

The term "carbocycle" is art recognized and includes an aromatic or non-aromatic ring in which each atom of the ring is carbon. The following art-recognized terms have the following meanings: "nitro" means -NO₂; the term "halogen" designates -F, -Cl, -Br or -I; the term "sulfhydryl" means -SH; the term "hydroxyl" means -OH; and the term "sulfonyl" means -SO₂⁺.

The terms "amine" and "amino" are art-recognized and include both unsubstituted and substituted amines, e.g., a moiety that may be represented by the general formulas:

\[
\begin{align*}
\text{N} & \quad \text{R50} \\
\text{R51} & \\
\text{N} & \quad \text{R52} \\
\text{R53} & \\
\end{align*}
\]

wherein R50, R51 and R52 each independently represent a hydrogen, an alkyl, an alkenyl, -(CH₂)ᵅ-R61, or R50 and R51, taken together with the N atom to which they are attached complete a heterocycle having from 4 to 8 atoms in the ring structure; R61 represents an aryl, a cycloalkyl, a cycloalkenyl, a heterocycle or a polycycle; and m is zero or an integer in the range of 1 to 8. In certain embodiments, only one of R50 or R51 may be a carbonyl, e.g., R50, R51 and the nitrogen together do not form an imide. In other embodiments, R50 and R51 (and optionally R52) each independently represent a hydrogen, an alkyl, an alkenyl, or -(CH₂)ᵅ-R61. Thus, the term "alylamine" includes an amine group, as defined above, having a substituted or unsubstituted alkyl attached thereto, i.e., at least one of R50 and R51 is an alkyl group.

The term "acylamino" is art-recognized and includes a moiety that may be represented by the general formula:
wherein R50 is as defined above, and R54 represents a hydrogen, an alkyl, an alkenyl or -(CH₂)ₘ-R₆₁, where m and R₆₁ are as defined above.

The term "amido" is art recognized as an amino-substituted carbonyl and includes a moiety that may be represented by the general formula:

![Chemical structure]

wherein R50 and R51 are as defined above. Certain embodiments of the amide in the present invention will not include imides which may be unstable.

The term "alkylthio" is art recognized and includes an alkyl group, as defined above, having a sulfur radical attached thereto, hi certain embodiments, the "alkylthio" moiety is represented by one of -S-alkyl, -S-alkenyl, -S-alkynyl, and -S-(CH₂)ₘ-R₆₁, wherein m and R₆₁ are defined above. Representative alkylthio groups include methylthio, ethylthio, and the like.

The term "carbonyl" is art recognized and includes such moieties as may be represented by the general formulas:

![Chemical structure]

wherein X₅₀ is a bond or represents an oxygen or a sulfur, and R₅₅ represents a hydrogen, an alkyl, an alkenyl, -(CH₂)ₘ-R₆₁ or a pharmaceutically acceptable salt, R₅₆ represents a hydrogen, an alkyl, an alkenyl or -(CH₂)ₘ-R₆₁, where m and R₆₁ are defined above. Where X₅₀ is an oxygen and R₅₅ or R₅₆ is not hydrogen, the formula represents an "ester". Where X₅₀ is an oxygen, and R₅₅ is as defined above, the moiety is referred to herein as a carboxyl group, and particularly when R₅₅ is a hydrogen, the formula represents a "carboxylic acid". Where X₅₀ is an oxygen, and R₅₆ is hydrogen, the formula represents a "formate", hi general, where the oxygen atom of the above formula is replaced by sulfur, the formula represents a "thiocarbonyl" group. Where X₅₀ is a sulfur and R₅₅ or R₅₆ is not
hydrogen, the formula represents a "thioester." Where X50 is a sulfur and R55 is hydrogen, the formula represents a "thioester." Where X50 is a sulfur and R56 is hydrogen, the formula represents a "thioacetic acid." On the other hand, where X50 is a bond, and R55 is not hydrogen, the above formula represents a "ketone" group. Where X50 is a bond, and R55 is hydrogen, the above formula represents an "aldehyde" group.

The terms "alkoxy" or "alkoxy" are art recognized and include an alkyl group, as defined above, having an oxygen radical attached thereto. Representative alkoxy groups include methoxy, ethoxy, propyloxy, tert-butoxy and the like. An "ether" is two hydrocarbons covalently linked by an oxygen. Accordingly, the substituent of an alkyl that renders that alkyl an ether is or resembles an alkoxy, such as may be represented by one of -O-alkyl, -O-alkenyl, -O-alkynyl, -O-(CH$_2$)$_m$-R$_61$, where m and R$_61$ are described above.

The term "oxime" is an art recognized moiety that may be represented by the general formula:

\[
\begin{array}{c}
N \\
\text{OH}
\end{array}
\]

An "oximate anion" is a deprotonated oxime. Examples of useful oximes readily forming oximate anions include, but are not limited to, salicylaldoxime, 2-pyridinealdoxime, 2-hydroxy-5-nonylacetoephone oxime, 1-cetyl-3-(2-oximopropyl)imidazolium chloride, oxime methacrylate, hexadecyltrimethylammonium anti-pyruvaldehyde 1-oximate, anti-pyruvaldehyde 1-oxime (monoisonitrosoacetone), O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride, 1,1'-trimethylene bis(4-hydroxyiminomethyl) pyridinium dichloride (trimedoxime), 4-amino-4-methyl-2-pentanone oxime, and the like.

The term "hydroxamic acid" is an art recognized moiety that may be represented by the general formula:

\[
\begin{array}{c}
\text{O} \\
\text{N} \\
\text{OH}
\end{array}
\]

A "hydroxamate anion" is a deprotonated hydroxamic acid.

The term "sulfonate" is art recognized and includes a moiety that may be represented by the general formula:
in which $R_{57}$ is an electron pair, hydrogen, alkyl, cycloalkyl, or aryl.

The term "sulfate" is art recognized and includes a moiety that may be represented by the general formula:

\[
\begin{array}{c}
\text{O} \\
\text{S} \\
\text{OR}_{57} \\
\text{O}
\end{array}
\]

5

in which $R_{57}$ is as defined above.

The term "sulfonamido" is art recognized and includes a moiety that may be represented by the general formula:

\[
\begin{array}{c}
\text{O} \\
\text{N} \\
\text{S} \\
\text{OR}_{56} \\
\text{R}_{50} \\
\text{O}
\end{array}
\]

10

in which $R_{50}$ and $R_{56}$ are as defined above.

The term "sulfamoyl" is art-recognized and includes a moiety that may be represented by the general formula:

\[
\begin{array}{c}
\text{O} \\
\text{S} \\
\text{N} \\
\text{R}_{50} \\
\text{R}_{51} \\
\text{O}
\end{array}
\]

15

in which $R_{50}$ and $R_{51}$ are as defined above.

The term "sulfonyl" is art recognized and includes a moiety that may be represented by the general formula:

\[
\begin{array}{c}
\text{O} \\
\text{S} \\
\text{R}_{58}
\end{array}
\]

in which $R_{58}$ is one of the following: hydrogen, alkyl, alkenyl, alkynyl, cycloalkyl, heterocyclyl, aryl or heteroaryl.
The term "sulfoxido" is art recognized and includes a moiety that may be represented by the general formula:

![Sulfoxido Structure](image)

in which R58 is defined above.

Analogous substitutions may be made to alkenyl and alkynyl groups to produce, for example, aminoalkenyls, aminoalkynyls, amidoalkenyls, amidoalkynyls, iminoalkenyls, thioalkenyls, thioalkynyls, carbonyl-substituted alkenyls or alkynyls.

As used herein "-alkyl" or "alkyl-" refers to a radical such as -$\text{CH}_2\text{CH}_3$, while "-alkyl-" refers to a diradical such as -$\text{CH}_2\text{CH}_2$; -heteroaryl- refers to a diradical such as

![Heteroaryl Structure](image)

though it also encompasses diradicals such as , with the counterion ($Y$) being an anion, such as Br, Cl, I, OMs or OTf.

The definition of each expression, e.g. alkyl, m, n, and the like, when it occurs more than once in any structure, is intended to be independent of its definition elsewhere in the same structure.

The term "selenoalkyl" is art-recognized and refers to an alkyl group having a substituted seleno group attached thereto. Exemplary "selenoethers" which may be substituted on the alkyl are selected from one of - Se-alkyl, -Se-alkenyl, -Se-alkynyl, and -Se-(CH2)m-R61, m and R61 being defined above.

The terms triflyl, tosyl, mesyl, and nonaflyl are art-recognized and refer to trifluoromethanesulfonyl, p-toluenesulfonyl, niethanesulfonyl, and nonafluorobutanesulfonyl groups, respectively. The terms triflate, tosylate, mesylate, and nonaflate are art-recognized and refer to trifluoromethanesulfonate ester, p-toluenesulfonate ester, methanesulfonate ester, and nonafluorobutanesulfonate ester functional groups and molecules that contain said groups, respectively.

The abbreviations Me, Et, Ph, Tf, Nf, Ts, and Ms represent methyl, ethyl, phenyl, trifluoromethanesulfonyl, nonafluorobutanesulfonyl, p-toluenesulfonyl and methanesulfonyl, respectively. A more comprehensive list of the abbreviations utilized by organic chemists of ordinary skill in the art appears in the first issue of each volume of the
Journal of Organic Chemistry; this list is typically presented in a table entitled Standard List of Abbreviations.

Certain compounds contained in compositions of the present invention may exist in particular geometric or stereoisomeric forms. In addition, polymers of the present invention may also be optically active. The present invention contemplates all such compounds, including cis- and trans-isomers, R- and S-enantiomers, diastereomers, (d)-isomers, (l)-isomers, the racemic mixtures thereof, and other mixtures thereof, as falling within the scope of the invention. Additional asymmetric carbon atoms may be present in a substituent such as an alkyl group. All such isomers, as well as mixtures thereof, are intended to be included in this invention.

If, for instance, a particular enantiomer of compound of the present invention is desired, it may be prepared by asymmetric synthesis, or by derivation with a chiral auxiliary, where the resulting diastereomeric mixture is separated and the auxiliary group cleaved to provide the pure desired enantiomers. Alternatively, where the molecule contains a basic functional group, such as amino, or an acidic functional group, such as carboxyl, diastereomeric salts are formed with an appropriate optically-active acid or base, followed by resolution of the diastereomers thus formed by fractional crystallization or chromatographic means well known in the art, and subsequent recovery of the pure enantiomers.

It will be understood that "substitution" or "substituted with" includes the implicit proviso that such substitution is in accordance with permitted valence of the substituted atom and the substituent, and that the substitution results in a stable compound, e.g., which does not spontaneously undergo transformation such as by rearrangement, cyclization, elimination, or other reaction.

The term "substituted" is also contemplated to include all permissible substituents of organic compounds. In a broad aspect, the permissible substituents include acyclic and cyclic, branched and unbranched, carbocyclic and heterocyclic, aromatic and nonaromatic substituents of organic compounds. Illustrative substituents include, for example, those described herein above. The permissible substituents may be one or more and the same or different for appropriate organic compounds. For purposes of this invention, the heteroatoms such as nitrogen may have hydrogen substituents and/or any permissible substituents of organic compounds described herein which satisfy the valences of the
heteroatoms. This invention is not intended to be limited in any manner by the permissible substituents of organic compounds.

The phrase "protecting group" as used herein means temporary substituents which protect a potentially reactive functional group from undesired chemical transformations. Examples of such protecting groups include esters of carboxylic acids, silyl ethers of alcohols, and acetals and ketals of aldehydes and ketones, respectively. The field of protecting group chemistry has been reviewed (Greene, T.W.; Wuts, P.G.M. Protective Groups in Organic Synthesis, 2nd ed.; Wiley: New York, 1991). Protected forms of the inventive compounds are included within the scope of this invention.

For purposes of the invention, the chemical elements are identified in accordance with the Periodic Table of the Elements, CAS version, Handbook of Chemistry and Physics, 67th Ed., 1986-87, inside cover.

Metals

The metal in the nanoparticles of the present invention may be in the form of a cation belonging to Groups 1-15 of the Periodic Table. These metals include Li, Na, K, Mg, Ca, Sr, Ba, Sc, Y, La, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, and Hg. The term "metal" is also used to include metalloids belonging to groups 13-15. These metalloids include B, Al, Ga, In, Tl, Si, Ge, Sn, Pb, As, Sb, and Bi. In certain embodiments, the metal cations belong to Groups 8-12, which include Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, and Hg. Preferably, the metal cations of the invention are Fe, Ni, Cu or Zn. Preferably, the metal oxides are magnetic metal oxides. Magnetic metal oxides of the invention may include Fe either as Fe(II), Fe(III), or a mixture of Fe(II)/Fe(III). Non-limiting examples of such oxides include FeO, Fe₂O₃, and Fe₃O₄. The inorganic compound may also be a mixed oxide of the type M₁xM₂₃xO₄, wherein M₁ represents a divalent metal ion and M² represents a trivalent metal ion. For example, the inorganic compound may be magnetic ferrites of the formula M₁Fe₂O₄, wherein M₁ represents a divalent ion selected from the following: Mn, Co, Ni, Cu, Zn, or Ba, pure or in admixture with each other or in admixture with ferrous ions.

Particle Preparation

The inorganic compound used to prepare the compositions of the present invention can generally be any inorganic compound prepared in an aqueous or nonaqueous medium. In one embodiment, catalytic nanoparticles comprising transition metal oxides alone or
complexed with nucleophilic groups can be deposited on the surface of ion-exchange resins such as cationic or anionic cross-linked beads.

(a) Synthesis via Co-precipitation — hi one embodiment, the inorganic compound is a metal oxide prepared by dissolving a metal salt precursor in an aqueous medium. For example, iron oxides (such as Fe₃O₄ or γ-Fe₂O₃) may be synthesized through the co-precipitation of Fe²⁺ and Fe³⁺ aqueous salt solutions by addition of a base. The control of size, shape and composition of such iron nanoparticles depends on the type of salts used (e.g., chlorides, sulphates, nitrates, perchlorates, etc.), the Fe²⁺ and Fe³⁺ ratio, as well as the pH and ionic strength of the media.

hi one embodiment, to obtain catalytic magnetic particles, we employed a co-precipitation of iron (II) and (III) chlorides by ammonia. The molar stoichiometry (1:2) of the Fe²⁺ZFe³⁺ was chosen such that it results in magnetite (Fe₃O₄) under non-oxidizing conditions, with or without a stabilizing compound, as shown below. Kim, D. K. et al. "Protective Coating of Superparamagnetic Iron Oxide Nanoparticles," *Chem. Mater.* 2003, 15(8), 1617-1627. The overall reaction can be represented as:

\[
2 \text{FeCl}_3 + \text{FeCl}_2 + 8 \text{NH}_3 + 4 \text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 \downarrow + 8 \text{NH}_4\text{Cl}
\]  


(b) Synthesis via Microemulsions — hi another embodiment, metal nanoparticles may be synthesized in a microemulsion system with an internal structure consisting of small droplets. The water-in oil microemulsion is composed of nanosized compartments made up of the hydrophilic moiety of the surfactant filled with water. In the hydrophilic interior of these droplets, certain amount of water-soluble material can be dissolved; for example, transition metal salts which can then serve as precursor(s) for formation of metal nanoparticles. For example, nanoparticles may be obtained from microemulsions by the
mixing two microemulsions, one containing the precursor and the other the precipitating agent; or by addition of the precipitating agent directly to the microemulsion containing the metal precursor. The preparation of catalytic nanoparticles from mini- and microemulsions is known in the art. Eriksson, S.; Nylen, U.; Rojas, S.; Boutonnet, M. "Preparation of catalysts from microemulsions and their applications in heterogeneous catalysis," *Applied Catalysis A: General* 2004, 265(2), 207-219. As described above, prior to the precipitation the metal(s) in the aqueous mixture may be associated with a nucleophilic stabilizing compound, exemplary examples of which are outlined below.

(c) Synthesis in Water -- Furthermore, nanoparticles of the invention may be obtained as water dispersions or through reaction in water. The aqueous medium enables the required segregation at the nanometric scale and control of particle size and structure; in other words, it promotes self-assembling of amphiphilic (macro)molecules and adsorption of organic or inorganic precursors onto preformed particles or aggregates. Water can preferably participate to the hybrid construction as a reactive solvent, in a sol-gel processes known in the art. Examples of core-shell hybrid particles include, but not limited to, organic core and inorganic shell, inorganic core and organic shell, and/or more complex heterophase structures. In one embodiment the nanoparticles may be be obtained via the encapsulation of preformed particles through controlled surface-graft polymerization, heterocoaulation, sol-gel co-condensation or dispersed phase polymerization processes; or the self-assembly of amphiphilic or water-insoluble low molecular weight or polymeric molecules, conducive to a thermodynamically stable system as opposed to most colloidal dispersions where only kinetic stabilization can be achieved; or a one-pot sequential or simultaneous twofold polymerization processes (e.g., free-radical and sol-gel). Castelvetro, V.; De Vita, C. "Nanostructured hybrid materials from aqueous polymer dispersions," *Adv. Colloid Interface ScL* 2004, 108/109, 167-185.

(d) Synthesis in the Gas Phase —In another embodiment, the metal nanoparticles of the present invention may be synthesized in the gas phase. Synthesis of nanoparticles in the gas phase is based on homogeneous nucleation in the gas phase and subsequent condensation and coagulation. The ablation of a solid source with a pulsed laser can preferably yield nanoparticles. Clusters or even larger particles are ejected from the surface and may undergo coagulation. A micron-sized aerosol droplet can preferably yield nanoparticles by evaporating a solute-containing droplet. By choosing a sufficiently dilute solute, nanoparticles of the instant invention may be obtained, hi one embodiment
electrospray systems may be applied as droplet generators, as they produce very small droplets being quite monodisperse in comparison to other spray processes. Furthermore, droplet explosion due to an electrical charge which exceeds the Rayleigh limit during evaporation may yield even smaller droplets. Finally, initiating homogeneous nucleation inside aerosol droplets can result in many nanosized nuclei in the droplet, which upon drying will yield nanoparticles. Synthesis of magnetic nanoparticles is known in the art. Kruis, F. E.; Fissan, H.; Peled, A. "Synthesis of nanoparticles next term in the gas phase for electronic, optical and magnetic applications," Journal of Aerosol Science 1998, 29(5-6), 511-535.

**Exemplary Nucleophilic Stabilizing Compounds**

In certain embodiments, the inorganic compound of the invention is associated with a nucleophile-containing organic monomer or a polymer ("a stabilizing compound") which is capable of decomposing organophosphorus compounds. In certain embodiments, exemplary nucleophiles of the invention are "α-nucleophiles" (*i.e.*, nucleophiles possessing a heteroatom with an unshared electron pair adjacent to the nucleophilic center), such as oximes, hydroxamic acids, hydrazines, hydrazones, and sulfoxides. Also contemplated are heteroatom-containing resonance stabilized nucleophiles, wherein an sp²-hybridized carbon atom is the center of nucleophilicity, such as imidazoles, enamines, phenoxide ions, and iodozobenzoates. Additionally, n-nucleophiles may serve as nucleophiles of the invention.


Polymers of the invention maybe co-polymerized and cross-linked with various amounts of monomers. Such monomers include, for example, isocyanates, imidazoles, amines, epoxides, amides, triphosphates peroxides, silanes, sulfones, acids, anhydrides, alkanes, alkenes and metal oxides. Non-limiting examples of such monomers include epichlorohydrin, divinyl sulfone, acrylic acid, methacrylic acid, trifluoromethacrylic acid, 2-vinylpyridine, 4-vinylpyridine, 3(5)-vinylpyridine, p-methylbenzoic acid, itaconic acid, 1-vinylimidazole, and mixtures thereof.

In certain embodiments, the stabilizing compound comprises 2-pyridinealdoxime [PAM], poly(4-vinylpyridine-co-acrylic acid) [p(VP-AA)], or ap(VP-AA) which has undergone oximation [p(VPOx-AA)]. See Figure 2; and G. I. H. Hanania *et al.* Hanania, G. I. H.; Michailides, M. S.; Irvine, D. H. *J. Phys. Chem.* 1977, 81(14), 1382-1387; and


Studies have shown that PAM decomposes the OPE poisons via nucleophilic attack where the oximate ion is an active species.

PAM forms chelates with metal ions, such as Cu$^{2+}$ and Ni$^{2+}$, and the resulting complexes catalyze the decomposition of the OPE compounds, such as DFP and sarin, albeit less vigorously than some Cu(II)-dipyridyl and Cu(II)-imidazole complexes. Bolton, S.; Beckett, A. "Metal chelates as potential reactivators of organic phosphate poisoned acetylcholinesterase," *J. Pharm. Sci.* 1964, 53, 55-60; and Wagner-Jauregg, T. *et al.* "Model Reactions of Phosphorus-containing Enzyme Inactivators. IV. I.a The Catalytic Activity of Certain Metal Salts and Chelates in the Hydrolysis of Diisopropyl Fluorophosphate," *J. Am. Chem. Soc.* 1955, 77(4), 922-929. Copper chelates with a 1:1 molar ratio of the Cu$^{2+}$ ion to ligands, such as α-amino acids or diamines, were reported to be in a class on their own as catalysts of the DFP and sarin hydrolysis, while analogous iron (II) and (III) complexes were devoid of catalytic activity. Courtney, R. C. *et al.* "Metal Chelate Compounds as Catalysts in the Hydrolysis of Isopropyl Methylphosphonofluoridate and Diisopropylphosphorofluoridate," *J. Am. Chem. Soc.* 1957, 79(12), 3030-3036.


The PAM and a single iron ion have been described to form, in aqueous solution, a low-spin octahedral complex in which iron is bonded to six nitrogen atoms. Hanania, G. I. H. *et al.* "Reduction potentials of complex ions. The tris(pyridine-2-aldoxime)iron(III)-tris(pyridine-2-aldoxime)iron(H) system," *J. Phys. Chem.* 1968, 72(4), 1355-1361. We
reasoned that the iron-PAM complex molecule, with its three polar oxime-OH groups, would remain on the surface of a magnetite particle upon co-precipitation of PAM with iron ions. The resulting nucleophile-modified magnetite was reasoned to be active in the OPE decomposition, given that it has already been demonstrated that the complexation of transition metal ions with PAM does not lower nucleophilicity of the latter. Mancin, F.; Tecilla, P.; Tonellato, U. "Metallomicelles Made of Ni(II) and Zn(II) Complexes of 2-Pyridinealdoxime-Based Ligands as Catalyst of the Cleavage of Carboxylic Acid Esters," Langmuir 2000, 16(1), 227-233.

An analogous rationale applies to the polymeric oxime, p(VPOx-AA), which was designed to model PAM by having a quaternized pyridinium group in close proximity to the aldoxime group, which can enhance the hydrolytic properties of the latter. Aglietto, M. et al. "Synthesis and catalytic activity of optically active polymers containing oxime groups," Polymer 1980, 21, 541-544. The p(VPOx-AA) can be viewed as a polymeric analog of phenyl-2-pyridyl ketoxime, that strongly associates with iron oxides. Reiner, D.; Poe, D. P. "Removal of iron, copper, cadmium, cobalt, and nickel from sodium hydroxide by precipitation and extraction with phenyl-2-pyridyl ketoxime," Anal. Chem. 1977, 49(6), 889-891. Furthermore, desirable is the presence of numerous carboxyl moieties that may chelate with iron ions embedded in the magnetite structure and impart charge to the magnetite surface, which charge is thought to improve the stability of the particles.


In another embodiment, the stabilizing compound comprises poly(l-vinylimidazole-co-acrolein oxime-co-acrylic acid) [p(Vim-AcOx-AA)]; namely poly(l-vinylimidazole-co-acrolein-co-acrylic acid) that has undergone oximation. The presence of the oxime group in the novel copolymer was achieved by the use of acrolein that is readily converted to the acrolein oxime by oximation with hydroxylamine. However, the use of polyacrolein, per se a water-insoluble and common solvents-insoluble polymer, was impossible for the intended application. Therefore, seeded copolymerization of acrolein with an amphiphilic copolymer of 1-vinylimidazole (VIm) and acrylic acid (AA) was used to arrive at an acrolein copolymer that was subsequently oximated. An analogous free-radical polymerizations of acrolein in basic aqueous conditions initiated by persulfates and using polypyrrole as a seed agent has been reported previously. T. Basinska, D. Kowalczyk, B. Miksa, and S. Slomkowski, Polym. Adv. Technol 1995, 6, 526-533. Application of VIm has been rationalized in terms of imidazole's well-known nucleophilicity that could be weaker than the oxime's, but still sufficient to catalyze ester hydrolysis in the enzyme-like fashion. T. Kunitake, F. Shimada, and C. Aso, J Am. Chem. Soc. 1969, 91, 2716-2723. In organophosphate-hydrolytic enzymes, histidine imidazole serves as a base, deprotonating a water molecule and generating the attacking hydroxide ion that produces the hydrolysis. M. Harel, A. Aharoni, L. Gaidukov et al, Nat. Struct. Mol. Biol. 2004, 11, 412-419. Furthermore, vinylimidazole is hydrophilic even at pH above its pK_a and poly(l-vinylimidazole) has been shown to maintain colloidal stability of magnetic iron oxide particle up to pH 10. M. Takafumi, S. Ide, H. Hiara, and Z. Xu, Chem. Mater. 2004, 16, 1977-1983. Ion-exchange equilibria and complexation between the positively charged imidazole-modified particles and organophosphoric acids resulting from the OP hydrolysis can contribute to the acid metabolite recovery along with the particles, using HGMS.

Finally, AA was chosen as a minor component of the copolymer to further stabilize magnetite particle at neutral pH. The resulting copolymer was capable of stabilizing magnetite nanoparticles, which catalyzed hydrolysis of a model OP nerve agent,
diisopropyl fluorophosphate (DFP), and could be recovered from aqueous media by the HGMS, as described in the Exemplification below.

In another embodiment, the stabilizing compound comprises oximated humic acids. Humic acids are a complex mixture of partially decomposed and otherwise transformed organic materials, primarily of plant origin. There are several subclasses of humic acids such as tannins, lignins, and fulvic acids. A substantial fraction of the mass of the humic acids is in carboxylic acid functional groups, which endow these molecules with the ability to chelate positively charged multivalent ions (Mg$^{2+}$, Ca$^{2+}$, Fe$^{2+}$, most other "trace elements" of value to plants, as well as other ions such as Cd$^{2+}$ and Pb$^{2+}$). This chelation of ions is of great importance for environmental remediation. Humic acids also have a smaller fraction of phenolic functional groups, which can engage in redox reactions with various water pollutants. Humic and fulvic acids are polydisperse mixtures of natural organic polyelectrolytes with different functional groups, which can colloidal stabilize magnetite and other metal and metal oxide nanoparticles [Illes, E., Tombacz, J. Colloid Interface ScL 2006, 295, 115-123]. Because of the presence of various functional groups, humic acids contribute greatly to the removal of pollutants such as pesticides from soil. Humic sorption of polar or ionizable pesticides can involve numerous mechanisms depending on factors such as the functional group chemistry of pesticides. For such compounds, pesticide-humic substance complexation may result from ion exchange reactions, ion bridging, and hydrogen bonds, in addition to hydrophobic interactions.

Since humic acids have a strong capacity to sorb pollutant compounds from aqueous solutions, they have many environmental applications, such as liners for wastewater reservoirs, treatment of industrial wastewater, and site remediation. The major drawback of these treatment processes is that by sorbing a toxic material onto a humic acid and the like sorbent, we merely change the environmental compartment in which the toxic material exists, and a second step is still required to destroy, immobilize, or detoxify it. To overcome this problem, a novel class of humic acid carriers has been prepared herein. These compounds are humic acids in which a second functional group, and oximate group, was imparted. The second functional group is chosen so as to catalyze the decomposition of target toxic organic compounds.

It is disclosed herein that humic acid, when complexed with magnetite, can be in a form of particles, preferably nanoparticles sized less than micron in diameter. In addition, when complexed with magnetite, the humic acid-magnetite particles are strongly magnetic.
and thus are amenable to their removal from aqueous solutions by magnetic separation methods. Further, humic acids can be oximated via oximation of their ketone carbonyl groups resulting in oximated humic acids (OHA). The resulting OHA-magnetite complexes maintain their magnetic properties and thus can be separated from aqueous solutions by means of magnetic separation. Remarkably, the OHA-magnetite particles are catalytic and rapidly decompose toxic substances such as nerve agents by hydrolysis, i.e., addition, selected OHA-magnetite particles are environmentally safe, i.e., do not themselves add to the contamination of the water environment or soil to be decontaminated.

In one embodiment of the invention, a preferred method of decontamination involves application of the OHA-magnetite particles to hydrolyze toxic contaminants in water or soil, followed by the particle removal by high-gradient magnetic separation. Because of the contact between said toxins and the particles, the toxin is catalytically decomposed. Because of the absorptive properties of the OHA-magnetite particles, the products of the catalytic decomposition are removed from the said water or solid by the magnetic separation, along with the OHA-magnetite particles.

Characterization of PAM and p(VPOx-AA) Nanoparticles

Figure 3 shows the effects of pH on ζ-potential and hydrodynamic diameter of the magnetite particles modified by PAM or p(VPOx-AA) copolymer. The volume-average hydrodynamic diameter of the PAM/M and p(VPOx-AA)/M particle species was approximately 100 and 150 nm, respectively, in the pH range where the particles maintained colloidal stability. The number-average diameters of the PAM/M and p(VPOx-AA)ZM particles in the pH 6-8 were in the range 25-35 and 55-65 nm, respectively. The PAMZM particles maintained weak positive charge due to the ionization of the 1-methylpyridinium groups until pH 8, above which point the PAM became unionized and the particles aggregated. The appearance of the negative ζ-potential on the aggregates at pH greater than 8 can be attributed to the exposed magnetite surfaces, which are negatively charged at these pH. Kim, D. K. et al. "Protective Coating of Superparamagnetic Iron Oxide Nanoparticles," Chem. Mater. 2003, 15(8), 1617-1627. The observed electrokinetic mobility pattern of the PAMZM particles corresponds well with the pKa=7.8 of PAM.

Mancin, F.; Tecilla, P.; Tonellato, U.; "Metalomicelles Made of Ni(II) and Zn(II) Complexes of 2-Pyridinealdoxime-Based Ligands as Catalyst of the Cleavage of Carboxylic Acid Esters," Langmuir 2000, 16(1), 221-211.
The observed pH-dependencies of the electrokinetic mobility of the polymer-coated particles, p(VP0x-AA)/M, indicate an effect of the amphoteric nature of the copolymer, with its N-substituted 4-vinylpyridinium moieties positively charged at a pH less than or equal to about 8 and carboxyls of acrylic acid negatively charged at pH of about 4.6. That is, the particles maintained the overall negative charge at about pH 5, below which the carboxylic groups lost ionization, which lead to the particle aggregation. However, at pH less than or equal to about 8, the particles became more negatively charged overall, which can be attributed to both the loss of ionization of the 4-vinylpyridinium groups and the increased degree of ionization of the carboxyls. Electrostatic complexation between the carboxyls and 4-vinylpyridinium groups in the pH range of about 5 to about 8 is likely.

Further insight into the structure of the obtained particles was gained from the studies of their magnetization (SQUID experiments). The magnetization versus applied field curves of the oxime-modified magnetite particle suspensions were used to determine the size distribution of the Fe₃O₄ particles as described herein. The magnetic susceptibility yielded the diameter of the primary Fe₃O₄ particles to be about 7 to about 8 nm, the previously reported data on Fe₃O₄ modified by poly(acrylic acid) derivatives. Moeser, G. D.; Roach, K. A.; Green, W. H.; Laibinis, P. E.; Hatton, T. A. "Water-Based Magnetic Fluids as Extractants for Synthetic Organic Compounds," Ind. Eng. Chem. Res. 2002, 41(19), 4739-4749. When compared to the number-average diameter (see above), the obtained estimates of the size of the Fe₃O₄ clusters provide an estimate of the size of individual nanoparticles coated by the oxime-containing species. Note that the number-average distribution is less biased by the aggregate sizes than the volume average. By subtracting the median Fe₃O₄ diameter of about 8 nm from the number-average hydrodynamic diameters, we determined the thickness of the PAM and p(VPOx-AA) layers to be on the order of 10 and 25 nm, respectively. The thickness of the p(VPOx-AA) layer corresponded to the typical thicknesses of the layers of other polyelectrolytes on magnetite particles obtained via similar coprecipitation procedures. However, the estimate of the thickness layer of a low-molecular weight compound such as PAM which exceeds the size of an individual Fe₃O₄, suggests that under these conditions the primary magnetite particles form clusters.

**Characterization of p(VIm-AcOx-AA) Nanoparticles**

Figure 17 shows the effect of pH on electrokinetic mobility and particle size for magnetite particles modified by p(VIm-AcOx-AA) copolymer. As is seen, the particles
remained stable, with the number-average hydrodynamic diameter varying in the range 125-150 nm. No particle precipitation and sedimentation was observed up to pH 11.5. The ζ-potential was significant and positive at pH<8, reflecting the positive charge on imidazole moieties, and turned negative above pH 8, when the contribution from the negatively charged carboxyls of AA turned entire particle negative as the imidazole moieties were no longer charged at these pH. The pKₐ of the poly(1-vinylimidazole) is 4.9, and the pi of the VTm and AA copolymers (VTm: AA mol ratio 4:1) has been reported at 6.5. T. Roques-Carmes, F. Membrey, A. Deratani, M.R. Böhmer and A. Foissy, *J. Colloid Interface Sd*. 2002, 256, 273-283; and K. Ogawa, A. Nakayama, and E. Kokufuta, *Langmuir* 2003, 19, 3178-3184. Attachment of the poly(1-vinylimidazole) to maghemite particles resulted in the particles with pi 7.4, reflecting a shift to higher pH required for the ionization of the immobilized imidazole. Even larger shift to pH ≥ 8 is observed herein. M. Takafuji, S. Ide, H. Hiara, and Z. Xu, *Chem. Mater.* 2004, 16, 1977-1983.

Recovery of the nanoparticles from the aqueous solutions was achieved in a series of magnetic filtration experiments in each of which, following the successful catalytic hydrolysis of DFP by the oxime-coated nanoparticles, the suspension of particles was passed through the HGMS filter placed inside the magnet device. The magnetic particles were trapped in the filter and subsequently recovered by removing the steel wool-packed column from the magnetic environment and passing fresh water through the filter; these particles were then reused in the hydrolysis of a fresh batch of DFP solution (Figure 19). This cycle of the DFP hydrolysis and particle filtration and collection was repeated twice. As is seen in Figure 20, essentially complete recovery and reuse of the particles was possible. The kₐ₀s constants for DFP hydrolysis were determined in three cycles to be unchanged at (2.6±0.07)x10⁻⁵.

Hydrolysis of DFP to produce the fluoride ion was monitored by the ion-selective fluoride electrode. Typical electrode response curves are shown in Figure 18. The observed rate of DFP hydrolysis in 10 mM Tris buffer at pH 7.0 in the presence of particles was markedly higher than the kₐ₀s of the spontaneous hydrolysis, even at very small particles concentrations (Figure 20). Interestingly, the apparent second-order hydrolysis rate constant, shown in equation [8]:

\[ k'' = k [Catalyst] [Substrate] \]  

[8]
with p(VIm-AcOx-AA)-modified magnetite was 2-5 times higher than with the magnetite modified with poly(4-vinylpyridine-N-phenacyloxime-co-acrylic acid), at similar initial oxime and substrate concentrations.

**Particles of the Invention**

One aspect of the present invention relates to a particle having a diameter, comprising an inorganic metal oxide and a stabilizing compound, said stabilizing compound comprising a nucleophilic moiety; wherein said nucleophilic moiety is selected from the group consisting of alpha-nucleophiles, heteroatom-containing resonance-stabilized nucleophiles and n-nucleophiles; and said diameter is about 1 to about 1,000 nm.

Another aspect of the present invention relates to a particle having a diameter, consisting essentially of an inorganic metal oxide and a stabilizing compound, said stabilizing compound comprising a nucleophilic moiety; wherein said nucleophilic moiety is selected from the group consisting of alpha-nucleophiles, heteroatom-containing resonance-stabilized nucleophiles and n-nucleophiles; and said diameter is about 1 to about 1,000 nm.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein said nucleophilic moiety is selected from the group consisting of oximes, hydroxamic acids, enamines, aryloxides, and heteroaryloxides.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein said nucleophilic moiety is selected from the group consisting of oximes, hydroxamic acids, hydrazines, hydrazones, imidazoles, iodosoaryl compounds and sulfoxides.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein said nucleophilic moiety is an oximes.

Another aspect of the present invention relates to a particle having a diameter, comprising an inorganic metal oxide and a stabilizing compound comprising a nucleophilic moiety; wherein said diameter is about 1 to about 1,000 nm; and said stabilizing compound comprising a nucleophilic moiety is selected from a group consisting of

\[
R^1\begin{array}{c}
N^\omega\ H
\end{array}, \ R^5\ \ \ \text{and } R^5\ \ \text{I}=O;
\]

wherein, independently for each occurrence,
R is -C(O)OR\(^3\), -C(O)N(R\(^3\))\(_2\), -C(O)SR\(^3\), -C(=O)R\(^3\), -C(=NR)R\(^3\), -C(=S)R\(^3\), -C(R\(^3\))\(_2\)O(R\(^3\))\(_2\), -C≡CR\(^3\), -C≡N, -[C(R\(^3\))\(_2\)]\(_n\)-R, hydrogen, alkyi, cycloalkyl, heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl;

R\(^1\) is -OR, -NR\(^2\), -SR, -C(=O)OR, -OC(O)R, -NRC(=O)R, -C(=O)NR\(^2\), -C(=O)SR, -SC(O)R, -S(O)\(_2\)R, -C(O)R\(^3\), -C(=NR)R\(^3\), -C(=S)R\(^3\), -C(R\(^3\))=C(R\(^3\))\(_2\), -C≡CR\(^3\), -C≡N, -[C(R\(^3\))\(_2\)]\(_n\)-R, hydrogen, alkyi, cycloalkyl, heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl;

R\(^2\) is -OR, -NR\(^2\), -SR\(_2\), -C(=O)OR, -OC(O)R, -NRC(O)R, -C(=O)NR\(_2\), -C(=O)SR, -SC(O)R, -S(O)\(_2\)R, -C(O)R\(^3\), -C(=NR)R\(^3\), -C(=S)R\(^3\), -C(R\(^3\))O(R\(^3\))\(_2\), -C≡CR\(^3\), -C≡N, -[C(R\(^3\))\(_2\)]\(_n\)-R, hydrogen, halogen, alkyi, cycloalkyl, heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl;

R\(^3\) is hydrogen, halogen, alkyi, cycloalkyl, heterocycloalkyl, alkenyl, cycloalkenyl, heterocycloalkenyl, alkyi, cyano, aryl, or heteroaryl;

R\(^4\) is -OR, -NR\(^2\), -SR, -C(O)OR, -OC(O)R, -NRC(O)R, -C(O)NR\(_2\), -C(O)SR, -SC(O)R, -S(O)\(_2\)R, -C(O)R\(^3\), -C(=NR)R\(^3\), -C(=S)R\(^3\), -C(R\(^3\))O(R\(^3\))\(_2\), -C≡CR\(^3\), -C≡N, -[C(R\(^3\))\(_2\)]\(_n\)-R, hydrogen, halogen, alkyi, cycloalkyl, heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl;

R\(^5\) is aryl or heteroaryl; and

n is 0-10 inclusive.

Another aspect of the present invention relates to a particle having a diameter, consisting essentially of an inorganic metal oxide and a stabilizing compound comprising a nucleophilic moiety; wherein said diameter is about 1 to about 1,000 nm; and said stabilizing compound comprising a nucleophilic moiety is selected from a group consisting of:

\[
\begin{align*}
\text{[Diagram]} & , \text{and } R^5 = \equiv \text{O};
\end{align*}
\]

wherein, independently for each occurrence,

R is -C(O)OR\(^3\), -C(O)N(R\(^3\))\(_2\), -C(O)SR\(^3\), -C(O)R\(^3\), -C(=NR)R\(^3\), -C(=S)R\(^3\), -C(R\(^3\))=C(R\(^3\))\(_2\), -C≡CR\(^3\), -C≡N, -[C(R\(^3\))\(_2\)]\(_n\)-R, hydrogen, alkyi, cycloalkyl, heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl;

R\(^1\) is -OR, -NR\(^2\), -SR, -C(O)OR, -OC(O)R, -NRC(O)R, -C(O)NR\(_2\), -C(O)SR, -SC(O)R, -S(O)\(_2\)R, -C(O)R\(^3\), -C(=NR)R\(^3\), -C(=S)R\(^3\), -C(R\(^3\))O(R\(^3\))\(_2\), -C≡CR\(^3\),
-C≡N, -[C(R₃)]₂-R, hydrogen, alkyl, cycloalkyl, heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl;

R² is -OR, -NR₂, -SR, -C(O)OR, -OC(O)R, -NR(C(O)R)₅-C(O)NR₂, -C(O)SR, -SC(O)R, -S(O)₂R, -C(=O)R³, -C(=NR)R³, -C(=S)R³, -C(R³)=C(R³)₂, -C≡CR³, -C≡N, -[C(R₃)]₂-R, hydrogen, halogen, alkyl, cycloalkyl, heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl;

R³ is hydrogen, halogen, alkyl, cycloalkyl, heterocycloalkyl, alkenyl, cycloalkenyl, heterocycloalkenyl, alkynyl, cyano, aryl, or heteroaryl;

R⁴ is -OR, -NR₂, -SR, -C(O)OR, -OC(O)R, -NR(C(O)R)₅-C(O)NR₂, -C(O)SR, -SC(O)R, -S(O)₂R, -C(=O)R³, -C(=NR)R³, -C(=S)R³, -C(R³)=C(R³)₂, -C≡CR³, -C≡N, -[C(R₃)]₂-R, hydrogen, halogen, alkyl, cycloalkyl, heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl;

R⁵ is aryl or heteroaryl; and

n is 0-10 inclusive.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein said stabilizing compound comprising a nucleophilic moiety is

\[
\begin{align*}
\text{R}^1 & \quad \text{N}^\circ \text{H} \\
\text{R} & \quad \text{R}
\end{align*}
\]

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein said stabilizing compound comprising a nucleophilic moiety is

\[
\begin{align*}
\text{HO} & \quad \text{N} \\
\text{R}^1 & \quad \text{R}^2
\end{align*}
\]

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein said stabilizing compound comprising a nucleophilic moiety is

\[
\begin{align*}
\text{R}^3 & \quad \text{R}^4 \\
\text{R}^4 & \quad \text{R}^4
\end{align*}
\]

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein said stabilizing compound comprising a nucleophilic moiety is

\[
\begin{align*}
\text{R}^5 & \quad \text{H}=\text{O}
\end{align*}
\]

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein said stabilizing compound comprising a nucleophilic moiety is
represented by a compound selected from the group consisting of

wherein, independently for each occurrence,

\[ X_i = \text{-}[C(R_3)^2]_n; \]

\[ Y_i = \text{Br, Cl, I, OMs, or OTf;} \]

\[ R_i = \text{-}(=O)OR_3, -C(=O)N(R_3), -C(=O)SR_3, -C(=O)R_3, -C(=NR_3)R_3, -C(=S)R_3, -C(R_3)≡C(R_3)_2, -C≡C_R_3, -[C(R_3)^2]_p-R_3, \text{hydrogen, alkyl, cycloalkyl, heterocycloalkyl,} \]

cycloalkenyl, heterocycloalkenyl, ary1, or heteroaryl;

\[ R_1 = \text{hydrogen, alkyl, cycloalkyl, heterocycloalkyl, cycloalkenyl,} \]

terocycloalkenyl, ary1, or heteroaryl;

\[ R_2 = \text{-OR, -NR_2, -SR, -C(K)OR, -O(C(O))R, -NRC(K)NR, -C(K)NR_2, -C(K)SR,} \]

\[ -SC(K)NR, -S(K)R, -S(O)R_2, -C(=O)R_3, -C(=NR)R_3, -C(=S)R_3, -C(R_3)≡C(R_3)_2, -C≡CR_3, \]

\[ -C≡N, -[C(R_3)]_p-R, \text{hydrogen, halogen, alkyl, cycloalkyl, heterocycloalkyl, cycloalkenyl,} \]

heterocycloalkenyl, ary1, or heteroaryl;

\[ R_3 = \text{hydrogen, halogen, alkyl, cycloalkyl, heterocycloalkyl, alkenyl, cycloalkenyl,} \]

heterocycloalkenyl, alkynyl, cyano, ary1, or heteroaryl;

\[ n = 0-10 \text{ inclusive; and} \]

\[ P = 0-10 \text{ inclusive.} \]

In certain embodiments, the present invention relates to any of the aforementioned

particles, wherein said stabilizing compound comprising a nucleophilic moiety is
In certain embodiments, the present invention relates to any of the aforementioned particles, wherein said stabilizing compound comprising a nucleophilic moiety is

\[
\begin{align*}
\text{N} & \quad \text{R}^1 \\
\text{R}^2 & \quad \text{R}^3 \\
\text{R}^4 & \quad \text{Y} \\
\end{align*}
\]

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein said stabilizing compound comprising a nucleophilic moiety is

\[
\begin{align*}
\text{N} & \quad \text{R}^1 \\
\text{R}^2 & \quad \text{R}^3 \\
\text{R}^4 & \quad \text{Y} \\
\end{align*}
\]

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein said stabilizing compound comprising a nucleophilic moiety is

\[
\begin{align*}
\text{N} & \quad \text{R}^1 \\
\text{R}^2 & \quad \text{R}^3 \\
\text{R}^4 & \quad \text{Y} \\
\end{align*}
\]

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein \( n \) is 0.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein \( n \) is 1.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein \( n \) is 2-10 inclusive.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein \( n \) is 3-10 inclusive.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein \( n \) is 4-10 inclusive.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein \( n \) is 5-10 inclusive.
In certain embodiments, the present invention relates to any of the aforementioned particles, wherein Y is Br or I.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein R is alkyl.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein \( R^1 \) is aryl.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein \( R^2 \) is hydrogen.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein \( n \) is 0; and Y is Br or I.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein \( n \) is 0; \( Y \) is Br or I; and \( R^2 \) is hydrogen.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein \( n \) is 0; \( Y \) is Br or I; \( R^2 \) is hydrogen; and \( R \) is alkyl.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein \( n \) is 0; \( Y \) is Br or I; \( R^2 \) is hydrogen; and \( R^1 \) is aryl.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein \( n \) is 0; \( Y \) is Br or I; \( R^2 \) is hydrogen; \( R \) is alkyl; and \( R^1 \) is aryl.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein \( n \) is 0; \( X \) is Br; \( R \) is methyl; \( R^1 \) is phenyl; and \( R^2 \) is hydrogen.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein said stabilizing compound comprising a micleophilic moiety is represented by a compound selected from the group consisting of

\[
\begin{align*}
\text{X is } \{[C(R^3)]_n\}; \\
\text{Y is Br, Cl, I, OMs, or OTf;}
\end{align*}
\]
R is -C(=O)OR, -C(=O)N(R\textsubscript{3})\textsubscript{2}, -C(=O)SR, -C(=O)R\textsubscript{3}, -C(=NR\textsubscript{3})R\textsubscript{3}, -C(=S)R, -C(R\textsubscript{3})=C(R\textsubscript{3})\textsubscript{2}, \text{hydrogen, alkyl, cycloalkyl, heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl;}

R\textsubscript{1} is hydrogen, alkyl, cycloalkyl, heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl;

R\textsubscript{2} is -OR, -M\textsubscript{1}\textsubscript{2}, -SR, -C(=O)OR, -OC(=O)R, -NRC(=O)R, -C(=O)NR\textsubscript{2}, -C(=O)SR, -SC(=O)R, -S(=O)R\textsubscript{2}, -C(=O)R\textsubscript{3}, -C(=NR)R\textsubscript{3}, -C(=S)R\textsubscript{3}, -C(R\textsubscript{3})=C(R\textsubscript{3})\textsubscript{2}, -C≡CR\textsubscript{3}, -C≡N, -[C(R\textsubscript{3})\textsubscript{2}]\textsubscript{p}-R, \text{hydrogen, halogen, alkyl, cycloalkyl, heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl;}

R\textsubscript{3} is hydrogen, halogen, alkyl, cycloalkyl, heterocycloalkyl, alkenyl, cycloalkenyl, heterocycloalkenyl, alkynyl, cyano, aryl, or heteroaryl;

n is 0-10 inclusive; and

p is 0-10 inclusive.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein said stabilizing compound comprising a nucleophilic moiety is

![Diagram](image)

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein said stabilizing compound comprising a nucleophilic moiety is

![Diagram](image)

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein said stabilizing compound comprising a nucleophilic moiety is

![Diagram](image)

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein n is 0.
In certain embodiments, the present invention relates to any of the aforementioned particles, wherein \( n \) is 1.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein \( n \) is 2-10 inclusive.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein \( n \) is 3-10 inclusive.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein \( n \) is 4-10 inclusive.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein \( n \) is 5-10 inclusive.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein \( Y \) is \( \text{Br or I} \).

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein \( R \) is alkyl.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein \( R^1 \) is aryl.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein \( R^2 \) is hydrogen.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein \( n \) is 0; and \( Y \) is \( \text{Br or I} \).

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein \( n \) is 0; \( Y \) is \( \text{Br or I} \); and \( R^2 \) is hydrogen.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein \( n \) is 0; \( Y \) is \( \text{Br or I} \); and \( R^2 \) is hydrogen; and \( R \) is alkyl.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein \( n \) is 0; \( Y \) is \( \text{Br or I} \); \( R^2 \) is hydrogen; and \( R^1 \) is aryl.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein \( n \) is 0; \( Y \) is \( \text{Br or I} \); \( R^2 \) is hydrogen; \( R \) is alkyl; and \( R^1 \) is aryl.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein \( n \) is 0; \( X \) is \( \text{Br} \); \( R \) is methyl; \( R^1 \) is phenyl; and \( R^2 \) is hydrogen.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein said stabilizing compound comprising a nucleophilic moiety is
represented by a compound selected from the group consisting of $R^4$,

R

wherein, independently for each occurrence,

$R$ is $-C(=O)OR^2$, $-C(=O)N(R^3)_2$, $-C(=O)SR^3$, $-C(=O)R^3$, $-C(=NR^3)R^3$, $-C(=S)R^3$,
$-C(R^3)=C(R^3)_2$, $-C≡CR^3$, $-[C(R^3)_{2}n]_R^3$, hydrogen, alkyl, cycloalkyl, heterocycloalkenyl,
cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl;

$R^3$ is hydrogen, halogen, alkyl, cycloalkyl, heterocycloalkyl, alkenyl, cycloalkenyl,
heterocycloalkenyl, alkynyl, cyano, aryl, or heteroaryl;

$R^4$ is $-OR$, $-NR_2$, $-SR$, $-C(=O)OR$, $-OC(=O)R$, $-NRC(=O)R$, $-C(=O)NR_2$, $-C(=O)SR$,
$-SC(=O)R$, $-S(=O)R$, $-S(=O)_2R$, $-C(=O)R^3$, $-C(=NR)R^3$, $-C(=S)R^3$, $-C(R^3)=C(R^3)_2$, $-C≡CR^3$,
$-C≡N$, $-[C(R^3)_{2}n]_R$, hydrogen, halogen, acyl, cycloalkyl, heterocycloalkyl, cycloalkenyl,
heterocycloalkenyl, aryl, or heteroaryl; and

n is 0-10 inclusive.

In certain embodiments, the present invention relates to any of the aforementioned
particles, wherein $R$ is hydrogen.

In certain embodiments, the present invention relates to any of the aforementioned
particles, wherein said stabilizing compound comprising a nucleophilic moiety is

represented by a compound selected from the group consisting of

wherein, independently for each occurrence,
R is -C(=O)OR, -C(O)N(R)₂, -C(O)SR, -C(O)R, -C(=NR)R, -C(=S)R, -C≡C(R)₂, -C≡CR, -[C(R)₂]ₙ-R, hydrogen, alkyl, cycloalkyl, heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl;

R³ is hydrogen, halogen, alkyl, cycloalkyl, heterocycloalkyl, alkenyl, cycloalkenyl, heterocycloalkenyl, alkynyl, cyano, aryl, or heteroaryl; and

n is 0-10 inclusive.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein R is hydrogen or alkyl.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein R⁴ is hydrogen.

Another aspect of the present invention relates to a particle having a diameter, comprising an inorganic metal oxide and a stabilizing compound comprising a nucleophilic moiety; wherein said diameter is about 1 to about 1,000 nm; and said stabilizing compound comprising a nucleophilic moiety is a polymer or co-polymer; wherein said polymer or co-polymer comprises a plurality of monomers represented by formula I:

I

wherein, independently for each occurrence,

X is imidazolyl, -C(=N-OH)-R, -C(O)-N(R)-OH, -aryI-I(O) or -heteroaryl-I(O);

W is absent, -O-, -N(R)-, -S-, -C(O)O-, -C(O)N(R)-, -C(O)S-, -S(O)-, -S(O)₂-, -C(R)₂-, -C(O)-, -C(=NR)-, -C(=S)-, -C≡C-, -cycloalkyl-, -heterocycloalkyl-, -cycloalkenyl-, -heterocycloalkenyl-, -aryl-, or -heteroaryl-;
R is -C(=O)OR, -C(=O)N(R_3)_2, -C(=O)SR, -C(=N-K)R, -C(=NR_3)R, -C(=S)R, -C(R_3)=C(R_3)_2, -C≡C(R_3), -[C(R_3)_2]_P-R, hydrogen, alkyl, cycloalkyl, heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl;

R^1 \text{ is } -OR, -NR_2, -SR, -C(=O)OR, -OC(=O)R, -NRC(=O)R, -C(=O)SR, -SC(O)R, -S(=O)R_2, -C(=O)R, -C(=NR_3)R, -C(=S)R, -C(R_3)=C(R_3)_2, -C≡CR_3, -C≡N, -[C(R_3)_2]_p-R, hydrogen, alkyl, cycloalkyl, heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl;

R^2 \text{ is hydrogen, halogen, alkyl, cycloalkyl, heterocycloalkyl, alkenyl, cycloalkenyl, heterocycloalkenyl, alkynyl, cyano, aryl, heteroaryl or } -[C(R_3)_2]_p-R;

R^3 \text{ is hydrogen, halogen, alkyl, cycloalkyl, heterocycloalkyl, alkenyl, cycloalkenyl, heterocycloalkenyl, alkynyl, cyano, aryl, or heteroaryl; and }

n \text{ is 0-5 inclusive; }

m \text{ is 0-5 inclusive; and }

p \text{ is 0-10 inclusive. }

Another aspect of the present invention relates to a particle having a diameter, consisting essentially of an inorganic metal oxide and a stabilizing compound comprising a nucleophilic moiety; wherein said diameter is about 1 to about 1,000 nm; and said stabilizing compound comprising a nucleophilic moiety is a polymer or co-polymer; wherein said polymer or co-polymer comprises a plurality of monomers represented by formula I:

\[
\begin{align*}
\text{I} & \quad \text{wherein, independently for each occurrence,} \\
X & \text{is imidazolyl, } -\text{C(=N-OH)}\text{-R}_3, -\text{C(O)-N(R)-OH, } -\text{aryl-I(O) or } -\text{heteroaryl-I(O);} \\
W & \text{is absent, } -\text{O}, -\text{N(R)}, -\text{S}, -\text{C(O)}\text{-O}, -\text{C(O)N(R)}, -\text{C(O)S}, -\text{S(O)}, -\text{S(O)}_2, -\text{C(R}_3)_2, -\text{C(O)}, -\text{C(=NR}_3), -\text{C(=S)}, -\text{C(R}_3)(=\text{C(R}_3))_2, -\text{OC}, -\text{cycloalkyl}, -\text{heterocycloalkyl}, -\text{cycloalkenyl}, -\text{heterocycloalkenyl}, -\text{aryl}, \text{ or } -\text{heteroaryl-};
\end{align*}
\]
R is -C(=O)OR, -C(=O)N(R)₂, -C(=O)SR, -C(=O)R, -C(=NR)₃, -C(=S)R, -C(R)₂C(R)₂, -C≡C₃, -[C(R)₂]₂P-R, hydrogen, alkyl, cycloalkyl, heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl;

R¹ is -OR, -NR₂, -SR, -C(=O)OR, -OC(=O)R, -NRC(=O)R, -C(=O)NR², -C(O)SR, -SC(O)R, -S(O)R, -S(=O)₂R, -C(O)R, -C(=NR)R, -C(=S)R, -C(R)₂C(R)₂, -CsCR, -C≡N, -[C(R)₂]₂P-R, hydrogen, alkyl, cycloalkyl, heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl;

R² is hydrogen, halogen, alkyl, cycloalkyl, heterocycloalkyl, alkenyl, cycloalkenyl, heterocycloalkenyl, alkenyl, cycloalkenyl, heterocycloalkenyl, alkenyl, cyano, aryl, heteroaryl or -[C(R)₂]₂P-R;

R³ is hydrogen, halogen, alkyl, cycloalkyl, heterocycloalkyl, alkenyl, cycloalkenyl, heterocycloalkenyl, alkynyl, cyano, aryl, or heteroaryl; and

n is 0-5 inclusive;
m is 0-5 inclusive; and
p is 0-10 inclusive.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein X is imidazolyl.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein X is -C(=N-OH)-R³.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein X is -C(O)-N(R)-OH.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein X is -aryl-I(=O).

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein X is -heteroaryl-I(=O).

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein R² is hydrogen or alkyl.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein R² is hydrogen.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein n is 0.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein n is 1.
In certain embodiments, the present invention relates to any of the aforementioned particles, wherein \( n \) is 2.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein \( n \) is 3.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein \( n \) is 4.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein \( n \) is 5.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein \( m \) is 0.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein \( m \) is 1.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein \( m \) is 2.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein \( m \) is 3.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein \( m \) is 4.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein \( m \) is 5.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein \( W \) is -aryl- or -heteroaryl-.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein \( W \) is absent; \( m \) is 0; and \( X \) is imidazole.
In certain embodiments, the present invention relates to any of the aforementioned particles, wherein W is Cl, I, OMs, or OTf; and Y is Br, Cl, I, OMs, or OTf.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein W is \( R_1 \); and Y is Br.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein X is \(-C(=N-OH)-R_3\); R\( \_2 \) is hydrogen; R\( \_1 \) is hydrogen; n is 0; and m is 1.
In certain embodiments, the present invention relates to any of the aforementioned particles, wherein \( X = -\text{C} (=\text{N}-\text{OH})-\text{R}^3; \) \( \text{R}^2 \) is hydrogen; \( \text{R}^1 \) is hydrogen; \( n = 0; \) \( m = 1; \) and \( \text{R}^3 \) is phenyl.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein \( X = -\text{C} (=\text{N}-\text{OH})-\text{R}^3; \) \( \text{R}^2 \) is hydrogen; \( \text{R}^1 \) is hydrogen; \( n = 0; \) \( m = 1; \) \( \text{R}^3 \) is phenyl; \( W \) is \( \text{Br} \); and \( Y \) is Br.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein \( m = 0; \) \( W \) is absent or \(-\text{C} (=\text{O})-\); and \( X = -\text{aryl-}(=\text{O}) \) or \(-\text{heteroaryl-}(=\text{O})\).

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein \( m = 0; \) \( W \) is absent; and \( X = -\text{aryl-}(=\text{O})\).

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein \( m = 0; \) \( W \) is absent; and \( X = -\text{phenyl-}(=\text{O})\).

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein \( m = 0; \) \( W \) is \(-\text{C} (=\text{O})-\); and \( X = -\text{aryl-}(=\text{O})\).

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein \( m = 0; \) \( W \) is \(-\text{C} (=\text{O})-\); and \( X = -\text{phenyl-}(=\text{O})\).

Another aspect of the present invention relates to a particle having a diameter, comprising an inorganic metal oxide and a stabilizing compound comprising a nucleophilic moiety; wherein said diameter is about 1 to about 1,000 nm; and said stabilizing compound comprising a nucleophilic moiety is a polymer or co-polymer; wherein said polymer or co-polymer comprises one or more monomers selected from the group consisting of

\[
\begin{align*}
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{N} & \quad \text{O} \\
\text{H} & \quad \text{OH} & , & \quad \text{H} & \quad \text{H} & \quad \text{N} & \quad \text{OH} \\
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{N} & \quad \text{N} & \quad \text{Y} \\
\text{H} & \quad \text{H} & \quad \text{OH} & , & \quad \text{H} & \quad \text{H} & \quad \text{N} & \quad \text{OH} \\
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{N} & \quad \text{N} & \quad \text{Y} & \quad \text; & \quad \text{Y} & \quad \text{is} \\
\text{Br}, & \quad \text{Cl}, & \quad \text{I}, & \quad \text{OMs}, & \quad \text{or} & \quad \text{OTf}.
\end{align*}
\]

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein said polymer is a copolymer comprising at least two of the monomer
selected from the group consisting of

\[
\text{\begin{center}
\begin{array}{c}
\text{H}_2\text{O}H, \\
\text{H}_2\text{N}OH
\end{array}
\end{center}
\]

and

\[
\text{\begin{center}
\begin{array}{c}
\text{H}_2\text{O}H, \\
\text{H}_2\text{N}OH
\end{array}
\end{center}
\]

wherein \(Y\) is \(\text{Br, Cl, I, OMs, or OTf.}\)

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein said polymer is a copolymer consisting essentially of at least two of the monomer selected from the group consisting of

\[
\text{\begin{center}
\begin{array}{c}
\text{H}_2\text{O}H, \\
\text{H}_2\text{N}OH
\end{array}
\end{center}
\]

and

\[
\text{\begin{center}
\begin{array}{c}
\text{H}_2\text{O}H, \\
\text{H}_2\text{N}OH
\end{array}
\end{center}
\]

wherein \(Y\) is \(\text{Br, Cl, I, OMs, or OTf.}\)

Another aspect of the present invention relates to a particle having a diameter, comprising an inorganic metal oxide and a stabilizing compound comprising a nucleophilic moiety; wherein said diameter is about 1 to about 1,000 nm; and said stabilizing compound is oximated humic acids.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein said effective particle size is about 1 to about 500 nm.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein said effective particle size is about 1 to about 250 nm.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein said effective particle size is about 1 to about 100 nm.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein said effective particle size is about 5 to about 50 nm.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein said effective particle size is about 5 to about 25 nm.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein said inorganic metal oxide comprises at least one metal selected from the group consisting of \(\text{Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Zn and Ni.}\)
In certain embodiments, the present invention relates to any of the aforementioned particles, wherein said inorganic metal oxide comprises at least one metal selected from the group consisting of Fe, Cu, Zn and Ni.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein said inorganic metal oxide is an iron oxide.

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein said inorganic metal oxide is \( \text{Fe}_2\text{O}_3 \) or \( \text{Fe}_3\text{O}_4 \).

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein said inorganic metal oxide is \( \text{Fe}_3\text{O}_4 \).

In certain embodiments, the present invention relates to any of the aforementioned particles, wherein said composition is superparamagnetic.

**Organophosphates**

Organophosphates are rapidly absorbed by inhalation, ingestion and through the skin. The absorbed chemical as well as the active metabolite bind to the cholinesterase enzymes found in red blood cells and plasma. The binding to these enzymes leads to their inactivation and hence renders them incapable of degrading an important neurotransmitter, acetylcholine. The excessive acetylcholine then accumulates at nerve junctions in the skeletal muscle system and in the autonomic and central nervous systems. With time, typically after 24 to 36 hours, this inactivation becomes irreversible.

Organophosphate esters are used as both insecticides and chemical warfare agents. Exemplary phosphate esters which can be hydrolyzed by the compositions and methods of the present invention are phosphates, phosphorofluoridates, phosphonates, and their sulfur analogs such as phosphorothionates. Exemplary organophosphate esters include parathion, malathion, diazinon, phosmet (Imidan®), chlorpyrifos (Lorsban®), sarin, tabun (ethylphosphorodimethyl-amidocyanidate), soman (plnacolyl methylphosphonofluoridate), GF (Cyclohexyl methylphosphonofluoridate) and VX (ethyl S-2-diisopropyl aminoethyl methylphosphor-thioate). Due to the toxicity of many organophosphates, such as those listed above, hydrolysis of a model OPE nerve agent, diisopropyl fluorophosphate (DFP), was used in the exemplification disclosed herein.

**Catalytic Destruction of an Organophosphate by Compositions of the Invention**

The compositions of the present invention can be use in processes for the decontamination of chemical warfare nerve agents and pesticides. In certain embodiments, the compositions will hydrolyze materials which contain either a phosphono-group or a
phosphoro-group. One or both of the hydrolysis and adsorption properties can be employed in particular decontamination process depending upon the particular needs at the site of the decontamination.

Decontamination is accomplished simply by contacting one of the inventive compositions with the phosphate ester to adsorb and/or hydrolyze it. If a step of adsorption without hydrolysis is desired for a particular decontamination process, then a sufficient amount of said composition should be employed to adsorb substantially all of the phosphate ester. The proper amount of composition to be used in a particular cleanup can be determined by routine experimentation.

In one embodiment, hydrolysis of DFP producing fluoride ion may be monitored by the ion-selective fluoride electrode (Figure 4). Since the electrode response time is only several seconds, whereas the generation of the fluoride ion as a byproduct of the DFP decomposition is significantly slower, the inherent response time of fluoride ion-selective electrode will have no apparent influence on determination of the hydrolysis rate. Xie, Y.; Popov, B. N. "Catalyzed Hydrolysis of Nerve Gases by Metal Chelate Compounds and Potentiometric Detection of the Byproducts," Anal. Chem. 2000, 72(9), 2075-2079.

For example, in the absence of the catalytic particles in the DFP solution in 10 mM Tris buffer, at a constant pH of about 7.0, the electrode potential was stable for at least 16 h, indicating negligible accumulation of fluoride ions. Addition of DFP to the suspension of oxime-containing particles resulted in rapid appearance and accumulation of fluoride ions, as is seen from the rather dramatic response of the ion-selective electrode.

Hydrolysis of the DFP and sarin in the presence of metal chelates has been established to be of the pseudo-first-order rate with respect to the total concentration of unreacted DFP:

$$\frac{d[DFP]}{dt} = k_{obs}[DFP] \tag{2}$$


The initial slope of the $C_t$ vs $t$ kinetic curves corresponds to the initial rate of the
DFP hydrolysis ($v_0$). The observed rate constant of the DFP hydrolysis is obtained from
the integrated form of eqn [3]:

$$-W-C_r t/[DFP] = k_{obs} t$$

The observed rate of the spontaneous DFP hydrolysis in the absence of particles or PAM in
all our experiments conducted in 10 mM Tris buffer at pH 7.0 was negligibly small
($k_w = 7 \times 10^{-7} \text{ s}^{-1}$). For comparison reasons, a series of measurements was conducted under
identical conditions on the DFP hydrolysis in the presence of up to 10 mg/mL of the
particles.

Without the oxime groups present, the hydrolysis occurred with rates exceeding that
of the spontaneous hydrolysis up to 10-fold. Some hydrolytic activity of magnetite surface
toward organophosphates has been previously reported [F. Tafesse; N. C. Deppa
"Polymetallic complexes in microemulsions for the hydrolysis of 4-nitrophenyl phosphate:
a bio-mimetic model for decontamination of organophosphates in the environment,"
Ecotoxicology and Environmental Safety 2004, 58(2), 260-266]; it may be related to the
ability of the iron hydroxide groups present on the magnetite surface to participate in the
nucleophilic substitution reactions [Eisner, M.; Schwarzenbach, R. P.; Kellerhals, T.; Luzi,
S.; Zwank, L.; Angst, W.; Haderlein, S. B. "Mechanisms and Products of Surface-Mediated
Reductive Dehalogenation of Carbon Tetrachloride by Fe(II) on Goethite," Environ. ScL
Technol. 2004, 38(7), 2058-2066]. However, it can be seen from Figure 5 that the presence
of the oxime groups dramatically enhanced the nucleophilicity of the magnetite surface
with the rates of the DFP hydrolysis.

The hydrolysis of DFP or sarin by metal chelates or oximates proceeds via a
formation of complexes that are unstable and easily hydrolyzed in water [R. C. Courtney;
R. L. Gustafson; S. J. Westerback; H. Hyytiainen; S. C. Chaberek Jr.; A. E. Martell "Metal
Chelate Compounds as Catalysts in the Hydrolysis of Isopropyl Methylphosphono fluoride
and Diisopropylphosphorofluoridate," J. Am. Chem. Soc. 1957, 79(12), 3030-3036; Snow,
A.; Barger, W.R. "A chemical comparison of methanesulfonyl fluoride with
organofluorophosphorus ester anticholinesterase compounds," Chem. Res. Toxicol. 1988, 1,
379-384; and Jandorf, BJ. "Chemical Reactions of Nerve Gases in Neutral Solution. 1.
Reactions with Hydroxylamine," *J. Am. Chem. Soc.* 1956, 78(15), 3686-3691. Hence, the catalytic reaction between DFP and oxime-modified magnetite particles or PAM can be presented as is shown in Figure 6.

According to Figure 6, the rate law is given by:

\[
v = \frac{dC_L}{dt} = \frac{kJP_x[DFP]}{K_u+[DFP]}
\]  

where \( K_M = \frac{k_1 + k_{cat}}{K} \) is the Michaelis constant, \( k_{cat} \) is the catalytic rate constant, and [Ox] is the concentration of the catalytic (oxime) groups in the system.

Rearranging eqn [4] yields expressions for the \( k_{cat} \) and \( K_M \) that are convenient for treatment of the experimental data:

\[
k_{m} = A \cdot \frac{[DFP]}{K_M + [DFP]} \]  

\[
K_M = B \left( k_{cat}[Ox]_o \cdot \frac{v_o}{v} \right)
\]

where \( A = \frac{[Ox]}{v_o} \) is the slope obtained from \( V_0 \) vs [Ox] plot at constant \([DFP]_o\), whereas \( B = \frac{[DFP]}{V_0} \) is the slope obtained from \( \frac{1}{v} \) vs \( \frac{1}{[DFP]} \), that is, Lineweaver-Burk plot at constant \([Ox]_o\).

A linearity of the aforementioned plots, if observed, would lend a strong support to the mechanistic (enzyme-like) scheme (Figure 6) and ensuing eqns [5] and [6]. We thus examined corresponding dependencies of the initial rate of the DFP hydrolysis using PAM and PAM- and p(VPOX-AA)-modified magnetite and the experimental results are depicted in Figures 7 and 8.

Linear fits were obtained in all cases \((R^2 > 0.97)\), supporting relations (3) and (4) and enabling computation of the constants \( k_{cat} \) and \( K_M \). These constants, along with the second-order hydrolysis rate constant, \( k'' = V_0/[Ox]_o/[DFP]_o \), which, taken together, comprehensively characterize the observed catalytic hydrolysis of DFP, are collected in Table 1 (shown below).
Table 1. Michaelis constant (K_M), catalytic rate constant (k_{cat}) and second-order rate constant (k") found for the DFP hydrolysis in the presence of oxime-containing species, in 10 mM Tris buffer at pH 7.0.

<table>
<thead>
<tr>
<th>Species</th>
<th>K_M x 10^3 (M)</th>
<th>k_{cat} x 10^4 (s^{-1})</th>
<th>k&quot; (M^{-1}s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAM/M</td>
<td>2.5 ± 0.12</td>
<td>6.1 ± 0.37</td>
<td>0.29 ± 0.088</td>
</tr>
<tr>
<td>PAM</td>
<td>1.2 ± 0.057</td>
<td>1.2 ± 0.073</td>
<td>0.075 ± 0.051</td>
</tr>
<tr>
<td>p(VPOx-AA)/M</td>
<td>0.83 ± 0.040</td>
<td>0.12 ± 0.006</td>
<td>0.057 ± 0.018</td>
</tr>
</tbody>
</table>

Table 1 shows that the catalytic efficiency, k_{cat}/K_M, of the PAM-modified magnetite suspensions were about 2.5-fold higher than of the PAM solutions without magnetite. This interesting finding clearly points to the higher catalytic activity of the iron chelate compared to the oxime itself; an effect that has not been previously reported with magnetite-complexed PAM. Enhanced hydrolytic activity of Cu^{2+}, Ni^{2+}, or Zn^{2+} complexes with oximes compared to the oximes themselves has been described previously. R. Breslow; D. Chipman "Mixed Metal Complexes as Enzyme Models. I. Intracomplex Nucleophilic Catalysis by an Oxime Anion," J Am. Chem. Soc. 1965, 87(18), 4195-4196; and Mancin, F.; Tecilla, P.; Tonellato, U. "Metalloincentes Made of Ni(II) and Zn(II) Complexes of 2-Pyrinediadoxime-Based Ligands as Catalyst of the Cleavage of Carboxylic Acid Esters," Langmuir 2000, 16(1), 227-233. The kinetic constants measured with PAM/M were comparable to or higher than those with Cu(II)-bipyridyl complexes thus far believed to be the most catalytically active, indicating the potential utility for the nerve agent decomposition. Xie, Y.; Popov, B. N. "Catalyzed Hydrolysis of Nerve Gases by Metal Chelate Compounds and Potentiometric Detection of the Byproducts," Anal. Chem. 2000, 72(9), 2075-2079.

The hydrolysis catalyzed by the polymer-modified particles, p(VPOx-AA)/M, proceeded with 17-fold and 7-fold lesser catalytic efficiency than with PAM/M particles or PAM solutions, respectively. The DFP hydrolysis with the p(VPOx-AA)/M particles was about 2-fold faster than in the US Army report on that process catalyzed by the Cu(II) complex of poly(4-vinylpyridine), quaternized with ethyl bromide and 4-chloromethyl-4'-methyl-2,2'-bipyridine at pH 7.0 and 25°C. Hammond, P. S.; Forster, J. S. "A polymeric amine-copper (IT) complex as catalyst for the hydrolysis of 1,2,2-trimethylpropyl methylphosphonofluoridate (Soman) andbis(1-methylethyl)phosphorofluoridate (DFP)," J. Appl. Polym. ScL 1991, 43, 1925-1931. Catalytic activity of the oxime groups, which
depends on their ability to generate the oximate anion (an active species in the nucleophilic
attack on the phosphorus electrophilic centers), tends to increase with the oxime
compound's pKₐ. Buncel, E.; Cannes, C.; Chatrousse, A.-P.; Terrier, F. "Reactions of
Oximate α-Nucleophiles with Esters: Evidence from Solvation Effects for Substantial
Decoupling of Desolvation and Bond Formation," J Am. Chem. Soc. 2002, 124(30), 8766-
8767. That is, the greater the affinity of the oximate anion for a proton, the greater its
reactivity with the phosphoryl center of the OP. In this regard, the oximate activity in
p(VPOx-AA)/M particles, with their apparent pKₐ below 5, should be expected to be lower
than in PAM/M, with their pKₐ at or above 8.0. In addition, the oximate accessibility
toward the substrate (DFP), can be lower in the layers of the p(VPOx-AA) polymer
compared to the low molecular weight compound (PAM).

In another embodiments, the kinetics of the DFP decomposition of HA/magnetite
and OHA/magnetite was measured by the time-dependent response of the fluoride-selective
electrode; the results are depicted in Figure 22. As is shown, the kinetics showed various
slopes, with the OHA-modified magnetite exhibiting significantly higher slope. The
kinetics yielded kinetic parameters of the DFP hydrolysis collected in Table 2. As is seen
from Table 2, the DFP decomposition by the OHA-modified magnetite particles was
several-fold faster and more efficient than in the presence of unmodified humic acid.
Because of the larger size, over 99% of the OHA-modified particle content could be
removed by one-pass high-gradient magnetic separation using a 10-cm column packed with
steel wire.

Table 2. Kinetic constants of nerve agent decomposition in the presence of either humic
acid-modified magnetite or oximated humic acid-modified magnetite.

<table>
<thead>
<tr>
<th>Species</th>
<th>k observed, s⁻¹</th>
<th>DFP half-life, t₁/₂, h</th>
<th>Initial rate of hydrolysis, M s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA/magnetite</td>
<td>4.3 x 10⁻⁵</td>
<td>4.5</td>
<td>1.3 x 10⁻⁷</td>
</tr>
<tr>
<td>OHA/magnetite</td>
<td>1.1 x 10⁻⁴</td>
<td>1.8</td>
<td>3.2 x 10⁻⁷</td>
</tr>
</tbody>
</table>

Recycling of the Catalytic Particles

Advantage can be taken of the superparamagnetic properties of the magnetite
particles to separate the catalyst from the reaction medium following use, allowing multiple
uses.

Recovery of the nanoparticles from the aqueous solutions was achieved in a series of magnetic filtration experiments in which a suspension of the particles that had participated in the DFP hydrolysis was passed through the HGMS filter with the magnet on, and the particles trapped in the filter were recovered by removing the column from the magnet and passing fresh water through the filter; this cycle of the DFP hydrolysis, filtration and collection processes was then repeated twice as described in the exemplification section. For example, the effect of recycling on the ability of the p(VPOx-AA)/M particles to catalyze the DFP hydrolysis is depicted in Figure 8. The observed kinetic constants of the DFP hydrolysis with the PAM/M and p(VPOx-AA)/M particle species were determined in three cycles to be 
\( (19.9 \pm 1.33) \times 10^{-3} \) and 
\( (50.2 \pm 2.3) \times 10^{-6} \text{ s}^{-1} \), respectively, indicating that within less than 7% of error, no deterioration in the particle performance was observed. In addition, the SQUID measurements showed magnetization of the recovered particles identical to the original particles, within 5% of error, which suggests that the particles are stable under conditions of the DFP hydrolysis.

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**Inventive Nanoparticles as Protective Barriers in Films**

It has been reported that nanoparticles composed of metal oxides, arranged in tiny clusters, a mere 6-10-nanometers across, can be hybridized with FDA-approved antidotal drugs and used as building blocks for new materials. It was shown that thin film layers of such hybrid nanoparticles arranged on polymeric surfaces are only microns thick. Since the inventive nanoparticles described therein catalyze, in the presence of moisture, an efficient decomposition of organophosphate (OP) agents, the resulting composite films work as protective barriers against such agents.

As mentioned above, the catalytic nanoparticles of the invention are based on a unique chemistry, where a nucleophilic agent is complexed with iron oxide or other metal
oxides to form a nanostructure (-100 nm) that reacts with OP compounds, generating less toxic metabolites that are water-soluble and less prone to permeate through common polymeric films. As with the drug-containing nanoparticles described above, the inventive nanoparticles can be used to form a film. The optical properties of such films can further be optionally changed to enable a greater UV absorption, a property that could be used on windows, eyeglasses, and windshields where UV protection is important. The ability to build films from nanoparticles may provided an alternative method of producing protective barriers in the consumer products, industrial and military applications. Exemplification illustrating the performance of the novel catalytic nanoparticles as protective barriers is shown in Example 4 below.

As is seen in Figure 11, the presence of PAM/M in the buffer solution that wetted the surface of the treated film resulted in the rapid appearance and accumulation of the fluoride ions, as is seen from the significant, negative response of the ion-selective electrode. The presence of the untreated PET films did not alter the response of the electrode, which remained at less than about 10 mV/h positive drift level, which is inherent to that electrode under the experimental conditions of the present study. Varying the effective concentration of the untreated film about 5-fold did not change the mode of the electrode response. However, by varying the concentration of the treated film, and thus, the effective concentration of the PAM/M particles, the rate of the DFP decomposition varied significantly. The kinetics of the DFP decomposition was quantified via $k_{obs}$, the observed pseudo-first-order rate constant. The $k_{obs}$ was found from the experimental data using equation [7]:

$$-\ln(1-C) = \frac{[DFP]_0}{k_{obs}t}$$

[7]

where $C_i$ and $[DFP]_0$ is the time-dependent concentration of the fluoride ions and the initial concentration of the nerve agent, respectively.

The dependence of the $k_{obs}$ on the effective PAM/M concentration is depicted in Figure 12. As is seen, a proportionality between the rate of the nerve gas decomposition and the effective particle concentration was observed, illustrating the protective action of the PAM/M-treated film. Remarkably, the particle-treated film resulted in a nearly identical kinetics of the nerve gas decomposition, compared to the kinetics in aqueous milieu using the same particles that were not coated on a film. This observation indicates that the spin-coating process did not result in any deleterious effects on the particles, and the latter were accessible to the substrate (nerve gas, DFP) when soaked in the buffer solution.
**Nanoparticles as Protective Barriers in Fabrics**

As mentioned above, heightened awareness of the hazards of chemical pollutants and pesticides, coupled with a growing threat of chemical exposure due to accidental spills or terrorist action, poses a challenge to develop countermeasures. Current protection gear (e.g., gloves, masks, and clothing) is based on the removal of environmental toxins using efficient adsorption materials, and/or the use of impermeable barriers. Both approaches suffer from problems such as weight, cost, bulkiness, regeneration capabilities, and disposal safety concerns. Therefore, there is an urgent need to develop non-corrosive, environmentally benign, cost-effective, lightweight, robust, self-decontaminating, hazardous material-free systems for handling and neutralizing pesticides and toxins present in air or water. Such systems can comprise protective layers in fabrics used in wearable garments (Figure 13). To illustrate the performance of the novel catalytic nanoparticles as protective barriers, they were embedded in Polartec® fabric (Maiden Mills, Lawrence, MA) as described below and in Example 5.

As is seen in Figure 14, the presence of PAM/M particles in the fabric resulted in the appearance and accumulation of the fluoride ions, as is seen from the significant, negative response of the ion-selective electrode. The presence of the untreated fabric did not alter the response of the electrode, which remained at less than about 10 mV/h positive drift level, which is inherent to that electrode under the experimental conditions of the present study. Varying the effective concentration of the untreated fabric about 4-fold did not change the mode of the electrode response. However, by varying the concentration of the particles in the treated fabric, the rate of the DFP decomposition varied significantly. The kinetics of the DFP decomposition was quantified via $k_{obs}$, the observed pseudo-first-order rate constant. The $k_{obs}$ was found from the experimental data using equation [7] (as shown above).

The dependence of the $k_{obs}$ on the effective PAM/M concentration is depicted in Figure 15. As is shown therein, a proportionality between the rate of the nerve gas decomposition and the effective particle concentration was observed, illustrating the protective action of the PAM/M-treated fabric.

**Methods of the Invention**

One aspect of the present invention relates to a method of making a particle having a diameter, the method comprising the steps of precipitating at least one inorganic metal salt in the presence of a stabilizing compound, said stabilizing compound comprising a
nucleophilic moiety, to form a pre-particle; and oxidizing said pre-particle with an
oxidizing agent to form said particle; wherein said nucleophilic moiety is selected from the
group consisting of alpha-nucleophiles, heteroatom-containing resonance stabilized
nucleophiles and n-nucleophiles; and said diameter is about 1 to about 1,000 nm.

Another aspect of the present invention relates to a method of making a particle in a
microemulsion system with an internal structure consisting of small droplets, comprising
the steps of forming a first microemulsion comprising nanosized compartments made up of
hydrophilic moieties of the surfactant filled with water; wherein the hydrophilic interior of
these droplets contain at least one transition metal salt; adding a second microemulsion
comprising nanosized compartments made up of hydrophilic moieties of the surfactant
filled with water; wherein the hydrophilic interior of these droplets contain an amount of a
precipitating agent; or adding the precipitating agent directly to the first microemulsion
containing the metal precursor; thereby forming a particle with a diameter; and associating
with said particle a nucleophilic stabilizing compound.

Another aspect of the invention relates to the method of making a particle
comprising at least one inorganic metal salt and a stabilizing compound, said stabilizing
compound comprising a nucleophilic moiety, via controlled surface-graft polymerization;
heterocoagulation; sol-gel co-condensation or dispersed phase polymerization processes;
the self-assembly of amphiphilic or water-insoluble low molecular weight or polymeric
molecules; or a one-pot sequential or simultaneous two-fold polymerization processes (e.g.,
free-radical and sol-gel).

Another aspect of the invention relates to the method of making a particle
comprising at least one inorganic metal salt and a stabilizing compound, said stabilizing
compound comprising a nucleophilic moiety, in the gas phase based on homogeneous
nucleation in the gas phase and subsequent condensation and coagulation.

Another aspect of the present invention relates to a method for the hydrolysis of a
compound which contains at least one oxidized phosphorus group, the method comprising
the step of contacting said compound with at least one particle having a diameter for a time
period sufficient to hydrolyze at least some of the oxidized phosphorus groups in said
compound; wherein said particle comprises an inorganic metal oxide and a stabilizing
compound, said stabilizing compound comprises a nucleophilic moiety; wherein said
diameter is about 1 to about 1,000 nm; and said stabilizing compound comprising a
nucleophilic moiety is selected from the group consisting of oximes, hydroxamic acids, enamines, aryloxides, and heteroaryloxides.

Another aspect of the present invention relates to a method for the hydrolysis of a compound which contains at least one oxidized phosphorus group, the method comprising the step of contacting said compound with at least one particle having a diameter for a time period sufficient to hydrolyze at least some of the oxidized phosphorus groups in said compound; wherein said particle consists essentially of an inorganic metal oxide and a stabilizing compound, said stabilizing compound comprises a nucleophilic moiety; wherein said diameter is about 1 to about 1,000 nm; and said stabilizing compound comprising a nucleophilic moiety is selected from the group consisting of oximes, hydroxamic acids, enamines, aryloxides, and heteroaryloxides.

In certain embodiments, the present invention relates to the aforementioned method, wherein said nucleophilic moiety is selected from the group consisting of oximes, hydroxamic acids, hydrazines, hydrazones, imidazoles, iodosoaryl compounds and sulfoxides.

In certain embodiments, the present invention relates to the aforementioned method, wherein said nucleophilic moiety is an oximes.

In certain embodiments, the present invention relates to the aforementioned method, wherein said nucleophilic moiety is selected from a group consisting of

\[
R^1N=O
\]

and \( R^5=I=O \);

wherein, independently for each occurrence,

\( R \) is \(-C(O)OR, -C(=O)N(R^3)_2, -C(O)SR, -C(=O)R^3, -C(=NR)R^3, -C(S)R^3, -C(R^3)≡C(R^3)\), hydrogen, alkyl, cycloalkyl, heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl;

\( R^1 \) is \(-OR, -NR_2, -SR, -C(=O)OR, -OC(K)\), \( -NRC(O)R, -C(O)NR_2, -C(O)SR, -SC(O)R, -S(O)R, -S(O)_2R, -C(O)R^3, -C(=NR)R^3, -C(S)R^3, -C(R^3)OR, -C≡CR^3, -C≡N, -[C(R^3)]_nR^3, \) hydrogen, alkyl, cycloalkyl, heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl;

\( R^2 \) is \(-OR, -NR_2, -SR, -C(O)OR, -OC(O)R, -NRC(O)R, -C(O)NR_2, -C(O)SR, -SC(O)R, -S(O)R, -S(O)_2R, -C(O)R^3, -C(=NR)R^3, -C(S)R^3, -C(R^3)=C(R^3)_2, -C≡CR^3, \)
-C≡N, -[C(R₃)₂]ₙ-R, hydrogen, halogen, alkyl, cycloalkyl, heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl;

R³ is hydrogen, halogen, alkyl, cycloalkyl, heterocycloalkyl, alkenyl, cycloalkenyl, heterocycloalkenyl, alkynyl, cyano, aryl, or heteroaryl;

R⁴ is -OR, -NR₂, -SR, -C(=O)OR, -OC(=O)R, -C(O)NR₂, -C(O)SR, -SC(O)R, -S(O)R, -S(O)₂R, -C(=O)R³, -C(=NR)R³, -C(=S)R³, -C(R³)=C(R³)₂, -C≡CR³, -C≡N, -[C(R³)₂]ₙ-R, hydrogen, halogen, alkyl, cycloalkyl, heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl;

R⁵ is aryl or heteroaryl; and

n is 0-10 inclusive.

In certain embodiments, the present invention relates to the aforementioned method, wherein said stabilizing compound comprising a nucleophilic moiety is

\[
\text{R} \quad \text{N} \quad \text{OH}
\]

In certain embodiments, the present invention relates to the aforementioned method, wherein said stabilizing compound comprising a nucleophilic moiety is

\[
\text{HO} \quad \text{N} \quad \text{R}^1 \quad \text{R}^2
\]

In certain embodiments, the present invention relates to the aforementioned method, wherein said stabilizing compound comprising a nucleophilic moiety is

\[
\text{R}^1 \quad \text{N} \quad \text{R}^4
\]

In certain embodiments, the present invention relates to the aforementioned method, wherein said stabilizing compound comprising a nucleophilic moiety is represented by a
wherein, independently for each occurrence,

\[ X_i = \text{[C(R_3^2)]}_n^- \]

\[ Y_i = \text{Br, Cl, I, OMs, or OTf;} \]

\[ R_i = \text{-C(=O)OR}_3, \text{-C(=O)N(R_3^2), -C(=O)SR}_3, \text{-C(=O)R}_3, \text{-C(=NR)_3R}_3, \text{-C(=S)R}_3, \text{-C(R_3^2)N}=C(R_3^2), \text{-C≡CRR}_3, \text{-H, alkyl, cycloalkyl, heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl;} \]

\[ R_1 = \text{hydrogen, alkyl, cycloalkyl, heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl;} \]

\[ R_2 = \text{-OR, -NR}_2, \text{-SR, -C(=O)OR, -OC(O)R, -NRC(O)R, -C(O)NR}_2, \text{-C(O)SR, -SC(O)R, -S(O)_2R, -C(K)R}_3, -C(=NR)_3R}_3, \text{-C(=S)R}_3, \text{-C(R^3)_3} = C(R^3)_2, \text{-C≡CR}_3, \text{-C≡N, -[C(R_3^2)]p-R, hydrogen, halogen, alkyl, cycloalkyl, heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl;} \]

\[ R_3 = \text{hydrogen, halogen, alkyl, cycloalkyl, heterocycloalkyl, alkenyl, cycloalkenyl, heterocycloalkenyl, alkynyl, cyano, aryl, or heteroaryl;} \]

\[ n = 0-10 \text{ inclusive; and} \]

\[ p = 0-10 \text{ inclusive.} \]

In certain embodiments, the present invention relates to the aforementioned method.

wherein said stabilizing compound comprising a nucleophilic moiety is
In certain embodiments, the present invention relates to the aforementioned method, wherein said stabilizing compound comprising a nucleophilic moiety is

\[
\begin{array}{c}
R^2 \\
\circ \parallel \circ \parallel \circ \\
R^2 \\
X \parallel \parallel \parallel \parallel \\
Y \parallel \parallel \parallel \parallel \\
R^1 \\
\end{array}
\]

In certain embodiments, the present invention relates to the aforementioned method, wherein said stabilizing compound comprising a nucleophilic moiety is

\[
\begin{array}{c}
R^2 \\
\circ \parallel \circ \parallel \circ \\
R^2 \\
X \parallel \parallel \parallel \parallel \\
Y \parallel \parallel \parallel \parallel \\
R^1 \\
\end{array}
\]

wherein said stabilizing compound comprising a nucleophilic moiety is

\[
\begin{array}{c}
R^2 \\
\circ \parallel \circ \parallel \circ \\
R^2 \\
X \parallel \parallel \parallel \parallel \\
Y \parallel \parallel \parallel \parallel \\
R^1 \\
\end{array}
\]

wherein said stabilizing compound comprising a nucleophilic moiety is

\[
\begin{array}{c}
R^2 \\
\circ \parallel \circ \parallel \circ \\
R^2 \\
X \parallel \parallel \parallel \parallel \\
Y \parallel \parallel \parallel \parallel \\
R^1 \\
\end{array}
\]

wherein n is 0.

wherein n is 1.

wherein n is 2-10 inclusive.

wherein n is 3-10 inclusive.

wherein n is 4-10 inclusive.

wherein n is 5-10 inclusive.

wherein Y is Br or I.
In certain embodiments, the present invention relates to the aforementioned method, wherein \( R \) is alkyl.

In certain embodiments, the present invention relates to the aforementioned method, wherein \( R^1 \) is aryl.

In certain embodiments, the present invention relates to the aforementioned method, wherein \( R^2 \) is hydrogen.

In certain embodiments, the present invention relates to the aforementioned method, wherein \( n \) is 0; and \( Y \) is Br or I.

In certain embodiments, the present invention relates to the aforementioned method, wherein \( n \) is 0; \( Y \) is Br or I; and \( R^2 \) is hydrogen.

In certain embodiments, the present invention relates to the aforementioned method, wherein \( n \) is 0; \( Y \) is Br or I; \( R^2 \) is hydrogen; and \( R \) is alkyl.

In certain embodiments, the present invention relates to the aforementioned method, wherein \( n \) is 0; \( Y \) is Br or I; \( R^2 \) is hydrogen; and \( R^1 \) is aryl.

In certain embodiments, the present invention relates to the aforementioned method, wherein \( n \) is 0; \( Y \) is Br or I; \( R^2 \) is hydrogen; \( R \) is alkyl; and \( R^1 \) is aryl.

In certain embodiments, the present invention relates to the aforementioned method, wherein \( n \) is 0; \( X \) is Br; \( R \) is methyl; \( R^1 \) is phenyl; and \( R^2 \) is hydrogen.

In certain embodiments, the present invention relates to the aforementioned method, wherein said stabilizing compound comprising a nucleophilic moiety is represented by a compound selected from the group consisting of

\[
\begin{align*}
\text{and} & \quad \text{wherein, independently for each occurrence,} \\
X \text{ is } -[\text{C}(R^3)_{2}]^-; \\
Y \text{ is Br, Cl, I, OMs, or OTf;}
\end{align*}
\]
R is -C(=O)OR, -C(=O)N(R)₂, -C(=O)SR, -C(=O)R, -C(=NR)₂, -C(=S)R, -C(R)=C(R)₂, -C≡C...

R¹ is hydrogen, alkyl, cycloalkyl, heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl;


R³ is hydrogen, halogen, alkyl, cycloalkyl, heterocycloalkyl, alkenyl, cycloalkenyl, heterocycloalkenyl, alkynyl, cyano, aryl, or heteroaryl;

n is 0-10 inclusive; and

p is 0-10 inclusive.

In certain embodiments, the present invention relates to the aforementioned method,

wherein said stabilizing compound comprising a nucleophilic moiety is 

In certain embodiments, the present invention relates to the aforementioned method,

wherein said stabilizing compound comprising a nucleophilic moiety is 

hi certain embodiments, the present invention relates to the aforementioned method,

wherein said stabilizing compound comprising a nucleophilic moiety is 

hi certain embodiments, the present invention relates to the aforementioned method, wherein n is 0.

hi certain embodiments, the present invention relates to the aforementioned method, wherein n is 1.
In certain embodiments, the present invention relates to the aforementioned method, wherein n is 2-10 inclusive.

In certain embodiments, the present invention relates to the aforementioned method, wherein n is 3-10 inclusive.

5 In certain embodiments, the present invention relates to the aforementioned method, wherein n is 4-10 inclusive.

In certain embodiments, the present invention relates to the aforementioned method, wherein n is 5-10 inclusive.

In certain embodiments, the present invention relates to the aforementioned method, wherein Y is Br or I.

In certain embodiments, the present invention relates to the aforementioned method, wherein R is alkyl.

In certain embodiments, the present invention relates to the aforementioned method, wherein R^1 is aryl.

10 In certain embodiments, the present invention relates to the aforementioned method, wherein R^2 is hydrogen.

In certain embodiments, the present invention relates to the aforementioned method, wherein n is 0; and Y is Br or I.

In certain embodiments, the present invention relates to the aforementioned method, wherein n is 0; Y is Br or I; and R^2 is hydrogen.

In certain embodiments, the present invention relates to the aforementioned method, wherein n is 0; Y is Br or I; R^2 is hydrogen; and R is alkyl.

In certain embodiments, the present invention relates to the aforementioned method, wherein n is 0; Y is Br or I; R^2 is hydrogen; and R^1 is aryl.

15 In certain embodiments, the present invention relates to the aforementioned method, wherein n is 0; X is Br; R is methyl; R^1 is phenyl; and R^2 is hydrogen.

In certain embodiments, the present invention relates to the aforementioned method, wherein n is 0; X is Br; R is methyl; R^1 is phenyl; and R^2 is hydrogen.

In certain embodiments, the present invention relates to the aforementioned method, wherein said stabilizing compound comprising a nucleophilic moiety is represented by a
compound selected from the group consisting of

\[
\begin{align*}
\text{R}^4 & \quad \text{N} & \quad \text{R}^4 \\
\text{R}^4 & \quad \text{N} & \quad \text{H} \\
\text{R}^4 & \quad \text{N} & \quad \text{H} \\
\text{R}^4 & \quad \text{N} & \quad \text{H} \\
\text{R}^4 & \quad \text{N} & \quad \text{H} \\
\end{align*}
\]

wherein, independently for each occurrence,
\[
\text{R} = \text{-C(=O)OR}_3, \text{-C(=O)N(R}_3)_2, \text{-C(=O)SR}_3, \text{-C(=O)R}_3, \text{-C(=NR}_3)_2, \text{-C(=S)R}_3, \text{-C(R}_3)_2=\text{C(R}_3)_2, \text{-C≡C} \text{R}_3, \text{-[C(R}_3)_2]_n \text{-R}_3, \text{hydrogen, alkyl, cycloalkyl, heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl};
\]

\[
\text{R}_3 = \text{hydrogen, halogen, alkyl, cycloalkyl, heterocycloalkyl, alkenyl, cycloalkenyl, heterocycloalkenyl, alkynyl, cyano, aryl, or heteroaryl};
\]

\[
\text{R}_4 = \text{-OR, -NR}_2, \text{-SR}_5, \text{-C(=O)OR, -OC(=O)R, -NRC(-O)R, -C(^O)NR}_2, \text{-C(^O)SR,}
\]

\[
\text{-SC(=O)R, -S(=O)R, -S(=O)_2R, -C(=O)R}_3, -\text{C(=N)R}_3, -\text{C(=S)R}_3, -\text{C(R}_3)_2=\text{C(R}_3)_2, -\text{C≡CR}_3,
\]

\[
\text{-C=N, -[C(R}_3)_2]_n \text{-R, hydrogen, halogen, alkyl, cycloalkyl, heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl};
\]

\[
n = 0-10 \text{ inclusive.}
\]

In certain embodiments, the present invention relates to the aforementioned method, wherein \( R \) is hydrogen.

In certain embodiments, the present invention relates to the aforementioned method, wherein said stabilizing compound comprising a nucleophilic moiety is represented by a

compound selected from the group consisting of

\[
\begin{align*}
\text{R} & \quad \text{O} & \quad \text{R}_4 \\
\text{R} & \quad \text{O} & \quad \text{R}_4 \\
\text{R} & \quad \text{O} & \quad \text{R}_4 \\
\end{align*}
\]

wherein, independently for each occurrence,
\[
\text{R} = \text{-C(O)OR}_3, \text{-C(=O)N(R}_3)_2, \text{-C(=O)SR}_3, \text{-C(=O)R}_3, \text{-C(=NR}_3)_2, \text{-C(=S)R}_3, \text{-C(R}_3)_2=\text{C(R}_3)_2, \text{-C≡CR}_3,
\]

\[
\text{-[C(R}_3)_2]_n \text{-R}_3, \text{hydrogen, alkyl, cycloalkyl, heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl};
\]
R³ is hydrogen, halogen, alkyl, cycloalkyl, heterocycloalkyl, alkenyl, cycloalkenyl, heterocycloalkenyl, alkynyl, cyano, aryl, or heteroaryl;

R⁴ is -OR, -NR₂, -SR, -C(O)OR, -OC(O)R, -C(O)NR₂, -C(O)SR, -SC(O)R, -S(O)R, -S(O)₂R, -C(=O)R, -C(=S)R, -C(=NR)₃, -C(≡C)R, -C≡N, -[C(R³)₂]ₙ-R, hydrogen, halogen, alkyl, cycloalkyl, heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl; and

n is 0-10 inclusive.

In certain embodiments, the present invention relates to the aforementioned method, wherein R is hydrogen or alkyl.

In certain embodiments, the present invention relates to the aforementioned method, wherein R⁴ is hydrogen.

Another aspect of the present invention relates to a method for the hydrolysis of a compound which contains at least one oxidized phosphorus group, the method comprising the step of contacting said compound with at least one particle having a diameter for a time period sufficient to hydrolyze at least some of the oxidized phosphorus groups in said compound; wherein said particle consists essentially of an inorganic metal oxide and a stabilizing compound, said stabilizing compound comprises a nucleophilic moiety; wherein said diameter is about 1 to about 1,000 urn; and said stabilizing compound comprising a nucleophilic moiety is a polymer or co-polymer; wherein said polymer or co-polymer comprises a plurality of monomers represented by formula I:

\[
\begin{align*}
&\text{R}^2 \quad \text{C} \quad \text{R}^1 \quad \text{W} \quad \text{R}^1 \quad \text{C} \quad \text{X} \\
&\text{R}^2 \quad \text{C} \quad \text{R}^1 \quad \text{R}^1 \quad \text{R}^1 \\
\end{align*}
\]

wherein, independently for each occurrence,

X is imidazolyl, -C(=N-OH)-R³, -C(O)-N(R)-OH, -aryl-I(=O) or -heteroaryl-I(=O);

W is absent, -O-, -N(R)-, -S-, -C(O)O-, -C(O)N(R)-, -C(O)S-, -S(O)-, -S(O)₂- , -C(R³)₂- , -C(O)-, -C(=NR)₃- , -C(=S)-, -C(R³)=C(R³)-, -OC-, -cycloalkyl-, -heterocycloalkyl-, -cycloalkenyl-, -heterocycloalkenyl-, -aryl-, or -heteroaryl-.
Another aspect of the present invention relates to a method for the hydrolysis of a compound which contains at least one oxidized phosphorus group, the method comprising the step of contacting said compound with at least one particle having a diameter for a time period sufficient to hydrolyze at least some of the oxidized phosphorus groups in said compound; wherein said particle consists essentially of an inorganic metal oxide and a stabilizing compound, said stabilizing compound consists essentially of a nucleophilic moiety; wherein said diameter is about 1 to about 1,000 nm; and said stabilizing compound comprising a nucleophilic moiety is a polymer or co-polymer; wherein said polymer or co-polymer comprises a plurality of monomers represented by formula I:

\[
\begin{align*}
\text{X} & \text{ is imidazolyl, } -Q=N-OH)-R_3, -C(K))-N(R)-OH, -aryl-I(K)) \text{ or -heteroaryl-1(K)};
\end{align*}
\]

wherein, independently for each occurrence,
W is absent, \(-O-, -N(R)-, -S-, -C(O)O-, -C(O)N(R)-, -S(O)_2-, -C(R_3)_2-, -C(O)-, -C(=NR_3)-, -C(O)SR_3-, -SC(R_3)=C(R_3)_2-, -OC-, -cycloalkyl-, -heterocycloalkyl-, -cycloalkenyl-, -heterocycloalkenyl-, -aryl-, or -heteroaryl-;

\(R\) is \(-C(=O)OR_3, -C(=O)N(R_3)_2, -C(O)SR_3, -C(=O)R_3, -C(=NR_3)R_3, -C(=S)R_3, -C(R_3)_2\), \(-C(\equiv C)R_3, -[C(R_3)_2]P-R, -C(\equiv N), -[C(=O)O]R_3, -C(=O)N(R(H))-R_3, -C(=O)=C(R_3)\), hydrogen, alkyl, cycloalkyl, heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl;

\(R^1\) is \(-OR, -NR_2, -SR, -C(O)OR, -OC(O)R, -C(O)NR_2, -C(O)SR, -SC(O)R, -S(O)_2R, -C(=O)R_3, -C(=NR)R_3, -C(=S)R_3, -C(=O)S(R_3)_2, -C(=NR)R_3, -C(=S)R_3, -C(=N)S(R_3)_2, -C(=O)N(R(H))-R_3, -C(=O)O)-R, -C(=O)N(R)-R, -C(=O)=C(R_3)\), hydrogen, alkyl, cycloalkyl, heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, alkenyl, cycloalkenyl, heterocycloalkenyl, alkenyl, cycloalkenyl, heterocycloalkenyl, alkenyl, cycloalkenyl, heterocycloalkenyl, alkenyl, cycloalkenyl, or heteroaryl; and

\(R^3\) is hydrogen, halogen, alkyl, cycloalkyl, heterocycloalkyl, alkenyl, cycloalkenyl, heterocycloalkenyl, alkenyl, cycloalkenyl, heterocycloalkenyl, alkenyl, cycloalkenyl, heterocycloalkenyl, alkenyl, cycloalkenyl, heterocycloalkenyl, alkenyl, cycloalkenyl, heterocycloalkenyl, alkenyl, cycloalkenyl, heterocycloalkenyl, alkenyl, cycloalkenyl, or heteroaryl; and

\(n\) is 0-5 inclusive;

\(m\) is 0-5 inclusive; and

\(p\) is 0-10 inclusive.

In certain embodiments, the present invention relates to the aforementioned method, wherein \(X\) is imidazolyl.

In certain embodiments, the present invention relates to the aforementioned method, wherein \(X\) is \(-C(=N-OH)-R^3\).

In certain embodiments, the present invention relates to the aforementioned method, wherein \(X\) is \(-C(O)-N(R)-OH\).

In certain embodiments, the present invention relates to the aforementioned method, wherein \(X\) is \(-C(=N)=O\).

In certain embodiments, the present invention relates to the aforementioned method, wherein \(R^2\) is hydrogen.

In certain embodiments, the present invention relates to the aforementioned method, wherein \(n\) is 0.
In certain embodiments, the present invention relates to the aforementioned method, wherein \( n \) is 1.

In certain embodiments, the present invention relates to the aforementioned method, wherein \( n \) is 2.

In certain embodiments, the present invention relates to the aforementioned method, wherein \( n \) is 3.

In certain embodiments, the present invention relates to the aforementioned method, wherein \( n \) is 4.

In certain embodiments, the present invention relates to the aforementioned method, wherein \( n \) is 5.

In certain embodiments, the present invention relates to the aforementioned method, wherein \( m \) is 0.

In certain embodiments, the present invention relates to the aforementioned method, wherein \( m \) is 1.

In certain embodiments, the present invention relates to the aforementioned method, wherein \( m \) is 2.

In certain embodiments, the present invention relates to the aforementioned method, wherein \( m \) is 3.

In certain embodiments, the present invention relates to the aforementioned method, wherein \( m \) is 4.

In certain embodiments, the present invention relates to the aforementioned method, wherein \( m \) is 5.

In certain embodiments, the present invention relates to the aforementioned method, wherein \( \text{W is -aryl-, or -heteroaryl-} \).

In certain embodiments, the present invention relates to the aforementioned method, wherein \( n = 0; \text{W is absent; m is 0; and X is imidazole.} \)

In certain embodiments, the present invention relates to the aforementioned method, wherein \( n = 0; \text{W is absent; m is 0; and X is } \)
In certain embodiments, the present invention relates to the aforementioned method, wherein W is \( \) and Y is Br, Cl, I, OMs, or OTf.

In certain embodiments, the present invention relates to the aforementioned method, wherein W is \( \), and Y is Br, Cl, I, OMs, or OTf.

In certain embodiments, the present invention relates to the aforementioned method, wherein W is \( \) and Y is Br.

In certain embodiments, the present invention relates to the aforementioned method, wherein W is \( \), and Y is Br.

In certain embodiments, the present invention relates to the aforementioned method, wherein R\(^1\) is hydrogen.

In certain embodiments, the present invention relates to the aforementioned method, wherein R\(^3\) is aryl.

In certain embodiments, the present invention relates to the aforementioned method, wherein R\(^3\) is phenyl.

In certain embodiments, the present invention relates to the aforementioned method, wherein X is \(-\text{C}(=\text{N-OH})-\text{R}\(^3\); and R\(^2\) is hydrogen.

In certain embodiments, the present invention relates to the aforementioned method, wherein X is \(-\text{C}(=\text{N-OH})-\text{R}\(^3\); R\(^2\) is hydrogen; and R\(^1\) is hydrogen.

In certain embodiments, the present invention relates to the aforementioned method, wherein X is \(-\text{C}(=\text{N-OH})-\text{R}\(^3\); R\(^2\) is hydrogen; R\(^1\) is hydrogen; and n is 0.

In certain embodiments, the present invention relates to the aforementioned method, wherein X is \(-\text{C}(=\text{N-OH})-\text{R}\(^3\); R\(^2\) is hydrogen; R\(^1\) is hydrogen; n is 0; and m is 1.
In certain embodiments, the present invention relates to the aforementioned method, wherein X is -C(=N-OH)-R^3; R^2 is hydrogen; R^1 is hydrogen; n is 0; m is 1; and R^3 is phenyl.

In certain embodiments, the present invention relates to the aforementioned method, wherein X is -C(=N-OH)-R^3; R^2 is hydrogen; R^1 is hydrogen; n is 0; m is 1; R^3 is phenyl; W is absent or -C(=O)-; and X is -aryl-I(=O) or -heteroaryl-I(=O).

Another aspect of the present invention relates to a method for the hydrolysis of a compound which contains at least one oxidized phosphorus group, the method comprising the step of contacting said compound with at least one particle having a diameter for a time period sufficient to hydrolyze at least some of the oxidized phosphorus groups in said compound; wherein said particle consists essentially of an inorganic metal oxide and a stabilizing compound, said stabilizing compound comprises a nucleophilic moiety; wherein said diameter is about 1 to about 1,000 run; and said stabilizing compound comprising a nucleophilic moiety is a polymer or co-polymer; wherein said polymer or co-polymer comprises one or more monomers selected from the group consisting of
and and \( Y \) is \( \text{Br, Cl, I, OMs, or OTf} \).

In certain embodiments, the present invention relates to the aforementioned method, wherein said polymer is a copolymer comprising at least two of the monomer selected from the group consisting of

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{N} & \quad \text{O} \\
\text{H} & \quad \text{N} \\
\text{H} & \quad \text{N}
\end{align*}
\]

and

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{N} & \quad \text{O} \\
\text{H} & \quad \text{N} \\
\text{H} & \quad \text{N}
\end{align*}
\]

; wherein \( Y \) is \( \text{Br, Cl, I, OMs, or OTf} \).

In certain embodiments, the present invention relates to the aforementioned method, wherein said polymer is a copolymer consisting essentially of at least two of the monomer selected from the group consisting of

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{N} & \quad \text{O} \\
\text{H} & \quad \text{N} \\
\text{H} & \quad \text{N}
\end{align*}
\]

and

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{N} & \quad \text{O} \\
\text{H} & \quad \text{N} \\
\text{H} & \quad \text{N}
\end{align*}
\]

; wherein \( Y \) is \( \text{Br, Cl, I, OMs, or OTf} \).

Another aspect of the present invention relates to a method for the hydrolysis of a compound which contains at least one oxidized phosphorus group, the method comprising the step of contacting said compound with at least one particle having a diameter for a time period sufficient to hydrolyze at least some of the oxidized phosphorus groups in said compound; wherein said particle consists essentially of an inorganic metal oxide and a stabilizing compound, said stabilizing compound comprises a nucleophilic moiety; wherein said diameter is about 1 to about 1,000 nm; and said stabilizing compound comprising a nucleophilic moiety is a polymer or co-polymer; wherein said polymer is oximated humic acids.

In certain embodiments, the present invention relates to the aforementioned method, wherein said particle is capable of adsorbing said compound and said contacting step is
carried out for a time period sufficient to also permit adsorption of at least some of said compound onto the particle.

In certain embodiments, the present invention relates to any of the aforementioned methods, wherein said compound is selected from the group consisting of parathion, malathion, diazinon, phosmet (Imidan®), chlorpyrifos (Lorsban®), sarin, tabun (ethylphosphorodimethyl-amidocyanidate), soman (plnacolyl methylphosphonofluoridate), GF (Cyclohexyl methylphosphonofluoridate), VX (ethyl S-2-diisopropyl aminoethyl methylphosphorothioate) or diisopropyl fluorophosphate (DFP).

In certain embodiments, the present invention relates to any of the aforementioned methods, wherein said effective particle size is about 1 to about 500 nm.

In certain embodiments, the present invention relates to any of the aforementioned methods, wherein said effective particle size is about 1 to about 250 nm.

In certain embodiments, the present invention relates to any of the aforementioned methods, wherein said effective particle size is about 1 to about 100 nm.

In certain embodiments, the present invention relates to any of the aforementioned methods, wherein said effective particle size is about 5 to about 50 nm.

In certain embodiments, the present invention relates to any of the aforementioned methods, wherein said effective particle size is about 10 to about 25 nm.

In certain embodiments, the present invention relates to any of the aforementioned methods, wherein said inorganic metal oxide comprises at least one metal selected from the group consisting of Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt₃Cu, Zn and Ni.

In certain embodiments, the present invention relates to any of the aforementioned methods, wherein said inorganic metal oxide comprises at least one metal selected from the group consisting of Fe, Cu, Zn and Ni.

In certain embodiments, the present invention relates to any of the aforementioned methods, wherein said inorganic metal oxide is an iron oxide.

In certain embodiments, the present invention relates to any of the aforementioned methods, wherein said inorganic metal oxide is Fe₂O₃ or Fe₃O₄.

In certain embodiments, the present invention relates to any of the aforementioned methods, wherein said inorganic metal oxide is Fe₃O₄.

In certain embodiments, the present invention relates to any of the aforementioned methods, wherein said composition is superparamagnetic.
Selected Articles of the Invention

One aspect of the present invention relates to an article selected from the group consisting of filters, wipes, sponges, gas masks, membranes, wearable protective garments or air filtration systems; wherein said article comprises any one of the aforementioned particles.

Another aspect of the invention relates to an article, comprising a surface and a coating on said surface, wherein said coating comprises a plurality of any of the aforementioned particles.

Yet another aspect of the invention relates to an article selected from the group consisting of filters, wipes, sponges, gas masks, membranes, wearable protective garments or air filtration systems; wherein said article comprises any one of the aforementioned stabilizing compounds, monomers or polymers. In other words, some aspects of this invention are drawn to the stabilizing compounds in the absence of any metal particles.

In certain embodiments, the present invention relates to any of the aforementioned article, wherein said coating has a mass per surface area of less than about 500 µg/cm².

In certain embodiments, the present invention relates to any of the aforementioned article, wherein said coating has a mass per surface area of less than about 100 µg/cm².

In certain embodiments, the present invention relates to any of the aforementioned article, wherein said coating has a mass per surface area of less than about 50 µg/cm².

In certain embodiments, the present invention relates to any of the aforementioned article, wherein said coating has a mass per surface area of less than about 10 µg/cm².

In certain embodiments, the present invention relates to any of the aforementioned article, wherein said coating has a mass per surface area of less than about 5 µg/cm².

In certain embodiments, the present invention relates to any of the aforementioned article, wherein said surface is selected from the group consisting of non-synthetic fibers, cellulosic fibers, cotton, proteinaceous fibers, wool, silk, synthetic fibers, nylon, polyester, polyurethane, polyanhydride, polyorthoester, polyacrylonitrile, polyphenazine, latex, teflon, dacron, acrylate polymer, chlorinated rubber, fluoropolymer, polyamide resin, vinyl resin, Gore-tex®, Marlex®, expanded polytetrafluoroethylene, low density polyethylene, high density polyethylene, polypropylene, and poly(ethylene terephthalate).

Exemplification

The invention now being generally described, it will be more readily understood by reference to the following examples, which are included merely for purposes of illustration
of certain aspects and embodiments of the present invention, and are not intended to limit the invention.

Some materials used in the following exemplification, including iron (II) chloride tetrahydrate (99%), iron (III) chloride hexahydrate (98%), acrylic acid (99%), A-vinylpyridine (95%), 2-bromoacetophenone (98%), 2-pyridinealdoxime methiodide (PAM, 99%), diisopropyl fluorophosphate (DFP, 99%), and 2,2'-azobisisobutyronitrile (AIBN, 98%), were purchased from Sigma-Aldrich Chemical Co. (St. Louis, MO) and used as received. AU other chemicals, solvents, and gases were obtained from commercial sources and were of highest purity available.

Example 1 — Synthesis of a Stabilizing Polymer [p(VPOx-AA)]

Copolymer of acrylic acid (AA) and 4-vinyl pyridine (4-VP) was synthesized by free-radical copolymerization using AIBN as an initiator. A vial containing a solution of 0.1 mol (10 mL) of 4-VP, 0.1 mol (6.9 mL) of AA, and 0.2 g of AIBN in N,N-dimethylformamide (10 mL) was deaerated by nitrogen purge, sealed, and kept at 70 °C overnight. The resulting viscous copolymer [p(VP-AA)] solution was repeatedly washed by acetone and methanol and precipitated by hexane followed by drying under vacuum, dissolution in deionized water and exhaustive dialysis (membrane MWCO, 3.5 kDa) against DI water. The purified p(VP-AA) samples were lyophilized and stored dry at 2-8 °C until further use. (C_{12}H_{17}NO_{2})_X found (calc): C 69.26 (69.54); H 8.29 (8.27); N 7.74 (6.76).

1H NMR (400 MHz, CD_{3}OD): δ 1.7 (m, 2 H, CH₂ in the main chain), 2.7 (m, 1 H, CH- in the main chain), 7.2 (m, 3 H, pyridine), 8.45 (m, 2 H, pyridine). Weight average MW by GPC 63 kDa, polydispersity index 1.9.

The p(VP-AA) was further modified to yield its oximated analog, abbreviated P(VPOx-AA) (Figure 2). A solution of p(VP-AA) copolymer (3.75 g, 18 mmol) and 4.0 g (19 mmol) of 2-bromoacetophenone in 150 mL of absolute ethanol was refluxed in a round-bottom flask at 70 °C under stirring for 48 h. Then the solvent was vacuum-evaporated and the contents of the flask were resuspended in 150 mL of anhydrous methanol. After addition of hydroxylamine hydrochloride (2.5 g, 36 mmol) and sodium hydroxide (1.4 g, 36 mmol), the resulting suspension was kept at 70 °C under reflux while stirring for 48 h. Then the solvent was evaporated and the contents of the flask were repeatedly washed by diethyl ether on a filter and dried. The residual solids were dissolved in 100 mL of 15% aqueous ethanol and the solution was dialyzed against 50% aqueous ethanol followed by exhaustive dialysis against deionized water (membrane MWCO, 3.5 kDa). The resulting copolymer
was freeze-dried and stored at -20 °C. (C$_{20}$H$_{25}$N$_2$O$_3$)$_x$, found (calc): C 69.64 (70.36); H 7.17 (7.38); N 7.95 (8.20). $^1$H NMR (400 MHz, CD$_3$OD): δ 1.75 (ni, 2 H, CH$_2$- in the main chain), 2.38, 3.28 (m, 1 H, CH- in the main chain), 6.7, 7.0, 7.3 (m, 6 H, benzyl), 8.3 (m, 5H, pyridine).

Example 2 — Synthesis and Characterization of Magnetic Nanoparticles Containing Iron and a Stabilizing Compound [PAM or $p$(VP-Ox-AA)]

Magnetic nanoparticles were produced by chemical coprecipitation of UO$_2$(II) and iron(III) chlorides. Namely, 1.88 g (7.0 mmol) of FeCl$_3$·OH$_2$O and 0.69 g (3.5 mmol) of FeCl$_2$·4H$_2$O were added to 40 mL of deionized water and the solution was deaerated by nitrogen purge in a stirred 250-mL three-necked flask and temperature of the flask contents was brought to 80 °C. Then an aqueous solution of a stabilizing compound (2.6 to 2.8 g compound in 40 mL water, pH adjusted to 6) was added to the flask and the resulting mixture was equilibrated at 80 °C while stirring under nitrogen purge. Then the nitrogen purge was ceased and the contents of the flask were at once added to 80 mL of a 28% ammonium hydroxide and the mixture that rapidly turned black was vigorously stirred for 5-10 min. The resulting precipitate possessed strong magnetic properties and was thus separated from the liquid by decantation using a Franz Isodynamic Magnetic Separator (Trenton, NJ). The precipitate was then dried in an oven at 60 °C until constant weight, resuspended in deionized water by sonication for 30 s with a Branson sonifier 450 at an output of 40 %, and the suspension was dialyzed against excess deionized water (membrane MW cut-off, 3.5 kDa) and lyophilized. The contents of thus obtained oxime-containing particles were assessed by elemental analysis and are collected in Table 3.
Table 3. Elemental Analysis of Oxime-Containing Particles

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Stabilizing compound</th>
<th>Elemental analysis</th>
<th>Oxime group contents, mmol/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAM/M</td>
<td>PAM</td>
<td>([C_7H_9N_2O(Fe_2O_3)_2]_x) found (calc): C 13.43 (14.01); H 1.66 (1.51); Fe 54.80 (55.82); N 3.97 (4.67).</td>
<td>1.7</td>
</tr>
<tr>
<td>p(VPOx-AA)/M</td>
<td>P(VPOx-AA) copolymer</td>
<td>([C_{38}H_{44}N_4O_6(Fe_2O_3)_3]_x) found (calc): C 33.34 (33.87); H 3.48 (3.29); Fe 37.38 (37.30); N 5.16 (4.16).</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Dynamic light scattering (DLS) experiments were performed with a Brookhaven BI-200SM light scattering system at a measurement angle of 90°. Volume-average particle size distributions were obtained using the built-in software and the reported particle hydrodynamic diameters are the average of five measurements. All samples were filtered with a 0.45 µm syringe filter prior to the DLS tests.

Superconducting Quantum Interference Device (SQUID) experiments were conducted using a Model 32 kG Gaussmeter (Digital Measurement Systems) to determine the magnetization of the particles in an applied magnetic field. Particle suspensions weighing 40-80 mg were placed in an airtight sample cell, and the exact mass of the samples was determined following the SQUID measurement. All SQUID measurements were performed at 300 K over a -1 to +1 T range.

Kinetics of the DFP decomposition were measured at 25 °C with an Orion 96-09 combination fluoride electrode (Thermo Electron Corp., Beverly, MA) and a Model 45 Dual Display Multimeter (Fluke Corp., Everett, WA) connected to a PC with a FlukeView Forms software for data processing. The electrode potential-time output was continuously recorded and each datapoint represents an average of the voltage amplitude within one-second interval. The electrode was immersed in a 9-mL aqueous sample and the output was allowed to equilibrate for about 10 min. A known volume of DFP was added into the sample at once via a Precision Sampling syringe (Valco Instruments Co. Inc, Houston, TX) and the time commenced. Samples containing no particles were stirred by a small magnetic bar, whereas suspensions with particles sized at or above 100 nm were stirred using nitrogen bubbling. No particle sedimentation or precipitation was observed in all
experiments. The pH was measured in each sample upon completion of the kinetics measurement. No significant changes in pH set at 7.0 were observed in all cases. The electrode was calibrated in independent series of experiments using aqueous solutions of sodium fluoride with or without magnetic particles suspended at various concentrations.

Results of these studies are shown in Figures 3-8.

**Example 3 — Magnetic Separation and Reuse of Magnetic Nanoparticles Containing Iron and a Stabilizing Compound [PAM or p(VPOx-AA)]**

High-gradient magnetic separation (HGMS) experiments were performed with a permanent magnet system as follows. The HGMS system consisted of a cylindrical glass column with an internal diameter of 7 mm and a length of 22 cm (a volume of 8.46 mL) that was packed with 3.6 g of type 430 fine-grade stainless steel wool (40-66 µm diameter) supplied by S. G. Frantz Co., Inc. (Trenton, NJ). For filtration, the column was placed inside of a quadrupole magnet system comprising four nickel-plated Neodymium Iron Boron 40 MGOe permanent magnets sized 18x1.8x1.8 cm each (Dura Magnetics, Inc., Sylvania, OH). The flux density generated inside of the packed column was ca. 0.73 Tesla.

Magnetic washing of the particles was performed by passing 9 mL of a sample that initially contained 1 mg/mL particles suspended in 10 mM Tris and then allowed to equilibrate with 4.0 mM DFP solution through the column placed inside of the magnet system. The liquid was pumped through the column at 1.5 mL/min with a peristaltic pump.

Then the column was removed from the magnet, and 18 mL of deionized water (pH adjusted to 7.0) was passed through the column to collect the washed particles. Several washed samples underwent the recovery process to collect sufficient amount of particles for reuse. The particle suspension was evaporated to dryness at 50 °C and the residual solid was weighed and re-suspended in 10 mM Tris buffer by sonication to result in effective solid concentration of 1 mg/mL. The resulting suspension was subjected to the kinetic experiment using electrode detection of the fluoride ions generated by the DFL decomposition. The process of the particles recovery and reuse was repeated in two sequential cycles. Results are shown in Figure 9.

**Example 4 — Magnetic Nanoparticles Containing Iron and a Stabilizing Compound [PAM] as Protective Barriers in Films**

Catalytic particles (~100 nm) comprising magnetite (Fe₃O₄) complexed with 2-pyridinealdoxime methiodide (PAM), an FDA-approved antidote, were synthesized by coprecipitation of Fe(III) and Fe(II) chlorides with PAM as described in Example 2. The
resulting PAM/M particles contained 1.5-2 mmol of the oxime groups per gram. The particles were readily suspended in water or organic solvents such as methylethylketone (MEK) using sonication. A suspension of the particles in MEK was coated onto a polyethylene terephthalate (PET) film via spin-coating procedure using an IROCOAT CA-237 polyurethane (Huntsman Corp.) as a binder. The weight ratio of the PAM/M particles to the binder in the coating formulation was 85:15 and the total solids content was 5 wt%. The coating was conducted at 220 °F and a film speed of 10 ft/min, employing rod #3. The resulting protective film contained 1.2 mg of the PAM/M particles per cm² and was transparent with a faint yellowish color. The film was tested for its ability to decompose diisopropyl fluorophosphate (DFP) using a process described in Example 2.

Decomposition of DFP is shown in Figure 10. For decomposition, a weighed amount of the film was cut into small pieces and placed in a vial containing 9 ml of 10 mM Tris buffer (pH 7.0, ethanol content, 50 v%). At t=0, a precisely measured amount (10 µL) of DFP was injected into the film suspension and the output of an ion-selective electrode measured as a function of time. The electrode measures concentration of a product of the DFP decomposition, the fluoride ion (Figure 11).

**Example 5 — Magnetic Nanoparticles Containing Iron and a Stabilizing Compound (PAM) as Protective Barriers in Fabrics**

Catalytic particles (~100 nm) comprising magnetite (Fe₃O₄) complexed with 2-pyridinealdoxime methiodide (PAM), an FDA-approved antidote, were synthesized by coprecipitation of Fe(III) and Fe(II) chlorides with PAM as described in Example 2. The resulting PAM/M particles contained 1.5-2 mmol of the oxime groups per gram. The particles were readily suspended in water or organic solvents using sonication. Pieces of Polartec® fabric of varying size and weight were impregnated by a suspension of the particles in AVCO Binder D diluted two-fold by DI water (effective particle concentration, 16 mg/mL). After impregnation, excess liquid was removed by gently wiping the surface of the fabric by Kimwipes® wipes. Then the impregnated fabric was heat-treated at 170 °F for 2 min and the curing process was completed by drying the fabric on air at room temperature. The resulting fabric modified with nanoparticles was weighed and total content of the particles in the fabric was thus calculated. The fabric was tested for its ability to decompose diisopropyl fluorophosphate (DFP). Decomposition of DFP is shown in Figure 10. Namely, a weighed amount of the fabric was placed in a vial containing 9 ml of 10 mM Tris buffer (pH 7.0, ethanol content, 50 v%). At t=0, a precisely measured amount
(10 µL) of DFP was injected into the sample suspension and the output of an ion-selective electrode measured as a function of time under stirring. The electrode measures concentration of a product of the DFP decomposition, fluoride ion. Results are shown in Figures 14 and 15.

Example 6—Synthesis of a Stabilizing Polymer [p(TIm-AcOx-AA)]

Copolymer of N-vinylimidazole (VIm), acrolein (Ac), and acrylic acid (AA) [p(VIm-AcOx-AA)] was synthesized by seeded, free-radical copolymerization using potassium persulfate as an initiator, followed by oximation. A three-necked flask containing a deoxygenated solution of 0.1 mol (9.9 mL) of VIm, 0.025 mol (1.82 mL) of AA, and 15 mg OfK$_2$S$_2$O$_8$ in deionized water (50 mL) was deaerated by nitrogen purge and kept at 70 °C for another 0.5 h. Then 0.1 mol (5.9 mL) of Ac were added to the reaction mixture via a syringe, followed by addition of 10 mg/mL aqueous K$_2$S$_2$O$_8$ solution (10 mL) and stirring. The reaction mixture was kept under nitrogen blanket at 70 °C overnight. The resulting black, viscous copolymer [p(VIm-Ac-AA)] solution was repeatedly washed by acetone and freeze-dried. The aldehyde groups of the acrolein in the copolymer were converted to acrolein oxime by reacting the p(VIm-Ac-AA) copolymer (15 g) with 200 mL of a freshly prepared anhydrous methanol solution containing 0.15 mol (10.4 g) of hydroxylamine hydrochloride and 0.15 mol (6 g) of sodium hydroxide. The methanolic solution of the polymer and hydroxylamine was kept under reflux while stirring at 70 °C for 2 days and then methanol was evaporated and the resulting solids were repeatedly washed with excess water and acetone on a paper filter. The resulting polymer was exhaustively dialyzed against 10 mM aqueous H$_2$SO$_4$ solution using a Spectra/Por® membrane (MWCO, 3.5 kDa). The purified p(VIm-AcOx-AA) samples were lyophilized and stored dry at -20 °C until further use. C$_{37}$H$_{34}$N$_{12}$O$_e$ found (calc): C 58.14 (58.25); H 7.61 (7.13); N 22.39 (22.03). 1H NMR (400 MHz, CD$_3$OD): d 1.6 (m, 2H, CH$_2$- in the main chain), 2.2, 3.5 (m, 1H, CH- in the main chain), 7.25 (m, 2H, imidazole), 7.36 (s, IH, oxime), 7.7 (m, IH, imidazole). FTIR (KBr): 3370 (bonded N-H OH stretch), 2918, 2850 (N-H\' -N= stretch), 1695 (C=O), 1670 (aldoxime C-N), 1650 (aldoxime C=N), 1560, 1435,1371, 1266, 1094, 938, 732 cm$^{-1}$. Weight-average MW by GPC in N,N-dimethylacetamide was 128.5 kDa, polydispersity index 1.82. The structure of the p(VIm-AcOx-AA) copolymer is depicted in Figure 16.

Example 7—Synthesis and Characterization of Magnetic Nanoparticles Containing Iron and a Stabilizing Compound [P(VIm-AcOx-AA)].
Magnetic nanoparticles were produced by chemical coprecipitation of iron(II) and iron (III) chlorides. Namely, 1.88 g (7.0 mmol) of FeCl₃·6H₂O and 0.69 g (3.5 mmol) of FeCl₂·4H₂O were added to 40 mL of deionized water and the solution was deaerated with nitrogen purge in a stirred 250-mL three-necked flask and temperature of the flask contents was brought to 80 °C. An aqueous/methanol (1:1 v/v) solution of the p(VIm-AcOx-AA) copolymer (6.25 wt%, 40 mL total, pH adjusted to 6) was added to the flask and the resulting mixture was equilibrated at 80 °C while stirring under nitrogen purge. Then the nitrogen purge was ceased and the contents of the flask were at once added to 80 mL of a 28% ammonium hydroxide and the mixture was vigorously stirred for 10 min. The resulting precipitate possessed strong magnetic properties and was thus separated from the liquid by decantation using a magnetic separator. The precipitate was dried and resuspended in deionized water. L. Bromberg and T.A. Hatton, Ind. Eng. Chem. Res. 2005, 44, 7991-7998. The suspension was dialyzed against excess deionized water (membrane MW cut-off, 3.5 kDa) and lyophilized. The composition of the oxime-containing particles were assessed by elemental analysis as follows. [(C₃₇H₅₄N₁₂O₁₄(Fe₃O₄)₂]ₓ, found (calc): C 35.75 (36.25); H 4.09 (4.44); Fe 27.12 (27.33); N 13.74 (13.71), oxime group content 3.2 mmol/g.

Kinetics of the DFP decomposition were measured at 25 °C with an Orion 96-09 combination fluoride electrode (Thermo Electron Corp.) and a Model 45 Dual Display Multimeter (Fluke Corp.) connected to a PC with FlukeView Forms software for data processing. The electrode was immersed in a stirred 9-mL aqueous sample and the electrode potential-time output was recorded continuously. No significant changes in pH, set initially at 7.0, were observed in any of the runs. The electrode was calibrated in independent series of experiments using aqueous solutions of sodium fluoride. See Figures 17, 18 and 20.

Example 8 — Magnetic Separation and Reuse of Magnetic Nanoparticles Containing Iron and a Stabilizing Compound fp(VIm-AcOx-AA)

High-gradient magnetic separation (HGMS) experiments were performed using a cylindrical plastic column with an internal diameter of 7 mm and a length of 20 cm packed with 3.6 g of type 430 fine-grade stainless steel wool (40-66 mm diameter) placed inside a quadrupole magnet system comprising four nickel-plated Neodymium Iron Boron 40 MGOe permanent magnets sized 18x1.8x1.8 cm each (Dura Magnetics, Inc.). The flux density generated inside the packed column was ca. 0.73 Tesla.
Magnetic washing of the particles was performed as described previously. L. Bromberg and T.A. Hatton, *Ind. Eng. Chem. Res.* 2005, 44, 7991-7998. The resulting suspension was subjected to the kinetic experiment using electrode detection of the fluoride ions generated by the DFL decomposition. The process of particle recovery and reuse was repeated in two sequential cycles. See Figure 19.

**Example 9 — Synthesis of Oximated Humic Acid (OHA)**

Humic acid, sodium salt (Aldrich, 1.6 g) and hydroxylamine hydrochloride (Aldrich, 0.4 g) were dissolved in 100 mL of deionized water resulting in a solution of pH 5.2. The solution was refluxed at 88 °C overnight. The resulting oximated sample was freeze-dried.

**Example 10 — Synthesis and Characterization of Magnetic Nanoparticles Containing Iron and a Stabilizing Compound (FOHA)**

HA-magnetite particles. A solution of 0.94 g of FeCl$_3$-OH$_2$O and 0.335 g FeCl$_2$.4H$_2$O, both obtained from Aldrich, in 20 g water was prepared at 80 °C under nitrogen blanket. To this solution, a solution of 1.6 g of untreated humic acid (Aldrich) (100 mL total) was added and formation of black, strongly magnetic precipitate was observed. The resulting suspension was dried in the oven at 70 °C for 2 days.

OHA-magnetite particles. A solution of 0.94 g of FeCl$_3$.6Fe$_2$O and 0.335 g FeCl$_2$.4H$_2$O, both obtained from Aldrich, in 20 g water was prepared at 80 °C under nitrogen blanket. To this solution, a solution of 1.6 g of oximated humic acid in 10% NH$_4$OH (100 mL total) was added and formation of black, strongly magnetic precipitate was observed. The resulting suspension was dried in the oven at 70 °C for 2 days.

Properties of OHA-magnetite and humic acid-modified magnetite particles were assessed in aqueous (less than 0.1 wt%) dispersions at pH 7.0 using dynamic light scattering. Weigh-average diameters of the HA-modified magnetite and OHA-modified magnetite were measured in the ranges of 88-90 and 175-250 nm, respectively, which indicated significant enhancement of the complexation or clustering between the OHA-modified particles. The presence of the oximate groups in the OHA-modified magnetite particles was demonstrated by FTIR (Figure 21). The oxime stretch was seen in the OHA-modified particles.

Catalytic activity of the 10 mg/mL suspensions of the magnetite particles modified by either humic acid or oximated humic acid in 10 mM Tris buffer at pH 7.0 was assessed via the monitoring of the decomposition of the model nerve agent, diisopropyl.
fluorophosphate (DFP). The procedures of the hydrolysis monitoring have been described in detail in previous examples (Figure 22).

Incorporation by Reference

All of the U.S. patents and U.S. patent application publications cited herein are hereby incorporated by reference.

Equivalents

Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, many equivalents to the specific embodiments of the invention described herein. Such equivalents are intended to be encompassed by the following claims.
We claim:

1. A particle having a diameter, comprising an inorganic metal oxide and a stabilizing compound, said stabilizing compound comprising a nucleophilic moiety; wherein said nucleophilic moiety is selected from the group consisting of alpha-nucleophiles, heteroatom-containing resonance-stabilized nucleophiles and n-nucleophiles; and said diameter is about 1 to about 1,000 run.

2. The particle of claim 1, wherein said nucleophilic moiety is selected from the group consisting of oximes, hydroxamic acids, enamines, aryloxides, and heteroaryloxides.

3. The particle of claim 1, wherein said nucleophilic moiety is selected from the group consisting of oximes, hydroxamic acids, hydrazines, hydrazones, imidazoles, iodosoaryl compounds and sulfoxides.

4. The particle of claim 1, wherein said nucleophilic moiety is an oxime.

5. A particle having a diameter, comprising an inorganic metal oxide and a stabilizing compound comprising a nucleophilic moiety; wherein said diameter is about 1 to about 1,000 nm; and said stabilizing compound comprising a nucleophilic moiety is

selected from a group consisting of

![Chemical Structure](image-url)

and 

R\(^5\)H=O;

wherein, independently for each occurrence,

- \(R\) is \(-C=O)OR\(^3\), \(-C(=O)N(R\(^3\))\(^2\), \(-C(=SR)R\(^3\), \(-C(=O)R\(^3\), \(-C(=S)R\(^3\), \(-C(R\(^3\))=C(R\(^3\))\(^2\), \(-C\equivC\)R\(^3\), \(-C\equivN\), \(-[C(R\(^3\))\(^2\)]\(^n\)-R\(^3\), hydrogen, alkyl, cycloalkyl, heterocycloalkyl, cycloalkenyl, heterocycloalkeny, aryl, or heteroaryl;

- \(R\(^1\)) is \(-OR\), \(-NR\(^2\), \(-SR\), \(-C=C=O)OR\), \(-OC(=O)OR\), \(-C(=O)NR\(^2\), \(-C(K)=SR\), \(-SC(=O)OR\), \(-S(=O)=OR\), \(-S(=O)\)\(^2\)R\(^3\), \(-C(=O)NR\(^3\), \(-C(=S)R\(^3\), \(-C(=NR)R\(^3\), \(-C(=S)R\(^3\)=C(R\(^3\))\(^2\), \(-C\equivCR\(^3\), \(-C\equivN\), \(-[C(R\(^3\))\(^2\)]\(^n\)-R\(^3\), hydrogen, alkyl, cycloalkyl, heterocycloalkyl, cycloalkenyl, heterocycloalkeny, aryl, or heteroaryl;

- \(R\(^2\)) is \(-OR\), \(-NR\(^2\), \(-SR\), \(-CC=O)OR\), \(-OC(=O)OR\), \(-C(=O)NR\(^2\), \(-C(K)=SR\), \(-SCC=O)OR\), \(-S(=O)=OR\), \(-S(=O)\)\(^2\)R\(^3\), \(-C(=O)NR\(^3\), \(-C(=S)R\(^3\), \(-C(=NR)R\(^3\), \(-C(=S)R\(^3\)=C(R\(^3\))\(^2\), \(-C\equivCR\(^3\), \(-C\equivN\), \(-[C(R\(^3\))\(^2\)]\(^n\)-R, hydrogen, halogen, alkyl, cycloalkyl, heterocycloalkyl, cycloalkenyl, heterocycloalkeny, aryl, or heteroaryl;
R³ is hydrogen, halogen, alkyl, cycloalkyl, heterocycloalkyl, alkenyl, cycloalkeny1, heterocycloalkeny1, alkynyl, cyano, aryl, or heteroaryl;

R⁴ is -OR, -NR₂, -SR, -C(=O)OR, -OC(O)R, -NRC(O)R, -C(O)NR₂, -C(O)SR, -SC(O)R, -S(O)R, -S(O)₂R, -C(O)R³, -C(=NR)R₃, -C(=S)R₃, -C(R³)=C(R³)₂, -C≡CR³, -C≡N, -[C(R³)₂]ₙ-R, hydrogen, halogen, alkyl, cycloalkyl,

R⁵ is aryl or heteroaryl; and

nis 0-10 inclusive.

6. The particle of claim 5, wherein said stabilizing compound comprising a

\[
\text{O} \\
\text{R}^1 \text{N}^0 \text{H} \\
\text{R} 
\]

nucleophilic moiety is

7. The particle of claim 5, wherein said stabilizing compound comprising a

\[
\text{HO} \\
\text{N} \\
\text{R}^1 \text{R}^2 
\]

nucleophilic moiety is

8. The particle of claim 5, wherein said stabilizing compound comprising a

nucleophilic moiety is

9. The particle of claim 5, wherein said stabilizing compound comprising a

nucleophilic moiety is R⁵-I=O.

10. The particle of claim 5, wherein said stabilizing compound comprising a

nucleophilic moiety is represented by a compound selected from the group consisting of

\[
\text{OH} \\
\text{N} \\
\text{Y} \\
\text{R}^1 \text{R}^2 
\]

and

\[
\text{Y} \\
\text{O} \\
\text{OH} \\
\text{R}^1 
\]

wherein, independently for each occurrence,
X is \([-C(R_3)_2]_n-\);
Y is Br, Cl, I, OMs, or OTf;
R is -C(O)OR, -C(O)N(R_3)_2, -C(O)SR, -C(O)R, ...;

5

heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl;

R^1 is hydrogen, alkyl, cycloalkyl, heterocycloalkyl, cycloalkenyl,

heterocycloalkenyl, aryl, or heteroaryl;

R^2 is -OR, -NR_2, -SR, -C(O)OR, -OC(K))R, -NRC(K))R, -C(K))NR_2,

-heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl;

R^3 is hydrogen, halogen, alkyl, cycloalkyl, heterocycloalkyl, alkynyl, cyano, aryl, or heteroaryl;

n is 0-10 inclusive; and

p is 0-10 inclusive.

11. The particle of claim 10, wherein said stabilizing compound comprising a
nucleophilic moiety is

12. The particle of claim 10, wherein said stabilizing compound comprising a
nucleophilic moiety is

20 13. The particle of claim 10, wherein said stabilizing compound comprising a
nucleophilic moiety is
14. The particle of claim 10, wherein said stabilizing compound comprising a nucleophilic moiety is

![Diagram](image)

15. The particle of claim 10, wherein n is 0.

16. The particle of claim 10, wherein n is 1.

17. The particle of claim 10, wherein n is 2-10 inclusive.

18. The particle of claim 10, wherein n is 3-10 inclusive.

19. The particle of claim 10, wherein n is 4-10 inclusive.

20. The particle of claim 10, wherein n is 5-10 inclusive.

21. The particle of claim 10, wherein Y is Br or I.

22. The particle of claim 10, wherein R is alkyl.

23. The particle of claim 10, wherein R is aryl.

24. The particle of claim 10, wherein R is hydrogen.

25. The particle of claim 10, wherein n is 0; and Y is Br or I.

26. The particle of claim 10, wherein n is 0; Y is Br or I; and R is hydrogen.

27. The particle of claim 10, wherein n is 0; Y is Br or I; R is hydrogen; and R is alkyl.

28. The particle of claim 10, wherein n is 0; Y is Br or I; R is hydrogen; and R is aryl.

29. The particle of claim 10, wherein n is 0; Y is Br or I; R is hydrogen; R is alkyl; and R is aryl.

30. The particle of claim 10, wherein n is 0; X is Br; R is methyl; R is phenyl; and R is hydrogen.

31. The particle of claim 5, wherein said stabilizing compound comprising a nucleophilic moiety is represented by a compound selected from the group consisting of

![Diagram](image)

wherein, independently for each occurrence,

\[ X = \{\text{CC(BR)}\}, \]

Y is Br, Cl, I, OMs, or OTf.
R is -C(O)OR \(^3\), -C(=O)NR \(^3\) \(_2\), -C(NR \(^3\)) \(_2\), -C(R \(^3\))=C(R \(^3\)) \(_2\), -C≡C \(_3\), hydrogen, alkyl, cycloalkyl, heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl;

R \(^1\) is hydrogen, alkyl, cycloalkyl, heterocycloalkyl, cycloalkenyl,

heterocycloalkenyl, aryl, or heteroaryl;

R \(^2\) is -OR, -NR \(^2\), -SR, -C(O)OR, -CO \(_2\), -C(=O)NR \(^2\), -SC(O)R, -S(O) \(_2\), -S(O), -C(=NR) \(_3\), -C(=S) \(_3\), -C(R \(^3\))=C(R \(^3\)) \(_2\), -C≡CR \(_3\), -C≡N, -[C(R \(^3\)) \(_2\)] \(_p\)-R, hydrogen, halogen, alkyl, cycloalkyl, heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl;

R \(^3\) is hydrogen, halogen, alkyl, cycloalkyl, heterocycloalkyl, alkenyl, cycloalkenyl, heterocycloalkenyl, alkenyl, cyano, aryl, or heteroaryl;

n is 0-10 inclusive; and

p is 0-10 inclusive.

32. The particle of claim 31, wherein said stabilizing compound comprising a nucleophilic moiety is

33. The particle of claim 31, wherein said stabilizing compound comprising a nucleophilic moiety is

34. The particle of claim 31, wherein said stabilizing compound comprising a nucleophilic moiety is

35. The particle of claim 31, wherein n is 0.

36. The particle of claim 31, wherein n is 1.

37. The particle of claim 31, wherein n is 2-10 inclusive.

38. The particle of claim 31, wherein n is 3-10 inclusive.

39. The particle of claim 31, wherein n is 4-10 inclusive.

40. The particle of claim 31, wherein n is 5-10 inclusive.
41. The particle of claim 31, wherein Y is Br or I.
42. The particle of claim 31, wherein R is alkyl.
43. The particle of claim 31, wherein R\(^1\) is aryl.
44. The particle of claim 31, wherein R\(^2\) is hydrogen.

45. The particle of claim 31, wherein n is 0; and Y is Br or I.
46. The particle of claim 31, wherein n is 0; Y is Br or I; and R\(^2\) is hydrogen.
47. The particle of claim 31, wherein n is 0; Y is Br or I; R\(^2\) is hydrogen; and R is alkyl.
48. The particle of claim 31, wherein n is 0; Y is Br or I; R\(^2\) is hydrogen; and R\(^1\) is aryl.
49. The particle of claim 31, wherein n is 0; Y is Br or I; R\(^2\) is hydrogen; R is alkyl; and R\(^1\) is aryl.
50. The particle of claim 31, wherein n is 0; X is Br; R is methyl; R\(^1\) is phenyl; and R\(^2\) is hydrogen.

51. The particle of claim 5, wherein said stabilizing compound comprising a nucleophilic moiety is represented by a compound selected from the group

\[
\begin{array}{c}
\text{R}^4 \quad \text{R}^5 \\
\text{R}^6 \quad \text{R}^7 \\
\end{array}
\]

consisting of

\[
\begin{array}{c}
\text{R}^4 \quad \text{R}^5 \\
\text{R}^6 \quad \text{R}^7 \\
\end{array}
\]

and

\[
\begin{array}{c}
\text{R}^4 \quad \text{R}^5 \\
\text{R}^6 \quad \text{R}^7 \\
\end{array}
\]

wherein, independently for each occurrence,
R is -C(=O)OR\(^3\), -C(=O)N(R\(^3\))\(^2\), -C(=O)SR\(^3\), -C(=NR\(^3\))R\(^3\), -C(=S)R\(^3\),
-C(R\(^3\))=C(R\(^3\))\(^2\), -C≡CR\(^3\), -[C(R\(^3\))]\(_n\)-R\(^3\), hydrogen, alkyl, cycloalkyl,
heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl;

R\(^3\) is hydrogen, halogen, alkyl, cycloalkyl, heterocycloalkyl, alkenyl, cycloalkenyl,
heterocycloalkenyl, alkynyl, cyano, aryl, or heteroaryl;

R\(^4\) is -OR, -NR\(^2\), -SR, -C(=O)OR, -OC(=O)R, -NRC(=O)R, -C(K)NR\(^2\), -C(=O)SR,
-SC(O)R, -S(O)R, -S(O)\(^2\)R, -C(=O)R\(^3\), -C(=NR)R\(^3\), -C(=S)R\(^3\), -C(R\(^3\))=C(R\(^3\))\(^2\),
-C≡CR\(^3\), -C≡N, -[C(R\(^3\))]\(_n\)-R, hydrogen, halogen, alkyl, cycloalkyl,
heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl; and
nis 0-10 inclusive.

52. The particle of claim 51, the present invention relates to any of the aforementioned particles, wherein R is hydrogen.
53. The particle of claim 5, wherein said stabilizing compound comprising a nucleophilic moiety is represented by a compound selected from the group consisting of

\[
\begin{align*}
\text{R is } & -\text{C(O)OR}, -\text{C(O)N(R}_{3}^2), -\text{C(S)SR}, -\text{C(=O)R}_{3}^2, -\text{C(=NR}_{3}^2), -\text{C(=S)R}_{3}^2, -\text{C}(=\text{O})_{\text{R}_{3}^2}, -\text{C}=\text{CR}_{3}^2, [-\text{C}(=\text{O})_{\text{R}_{3}^2}]_{\text{n}}, -\text{hydorgen, alkyl, cycloalkyl, heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or hetroaryl;} \\
\text{R}_{3}^2 \text{ is hydrogen, halogen, alkyl, cycloalkyl, heterocycloalkyl, alkenyl, cycloalkenyl, heterocycloalkenyl, alkynyl, cyano, aryl, or hetroaryl;} \\
\text{R}_{4}^2 \text{ is } & -\text{OR}, -\text{NR}_{2}^2, -\text{SR}, -\text{C(O)OR}, -\text{OC(O)R}, -\text{NRC(O)R}, -\text{C(O)NR}_{2}^2, -\text{C(S)SR}, -\text{SC(O)R}, -\text{S(O)R}, -\text{S(O)}_{2}\text{R}, -\text{C(=O)R}_{3}^2, -\text{C(=NR)R}_{3}^2, -\text{C(=S)R}_{3}^2, -\text{C}(=\text{O})_{\text{R}_{3}^2}, -\text{C}=\text{CR}_{3}^2, -\text{C}=\text{N}, [-\text{C}(=\text{O})_{\text{R}_{3}^2}]_{\text{n}}, -\text{hydrogen, halogen, alkyl, cycloalkyl, heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or hetroaryl;} \\
\text{n}_{\text{i}} \text{ is } & 0-10 \text{ inclusive.}
\end{align*}
\]

54. The particle of claim 53, wherein R is hydrogen or alkyl.

55. The particle of claim 53, wherein R\text{\text{4}}^2 is hydrogen.

56. A particle having a diameter, comprising an inorganic metal oxide and a stabilizing compound comprising a nucleophilic moiety; wherein said diameter is about 1 to about 1,000 nm; and said stabilizing compound comprising a nucleophilic moiety is a polymer or co-polymer; wherein said polymer or co-polymer comprises a plurality of monomers represented by formula I:

\[
\begin{align*}
\text{I}
\end{align*}
\]

wherein, independently for each occurrence,

\[
\begin{align*}
\text{X is imidazolyl, -C(=N-OH)-R}_{3}^2, -\text{C(O)-N(R)-OH, -aryl-I(O) or -heteroaryl-I(O);} \\
\text{R}_{1}^1, \text{R}_{2}^2, \text{R}_{3}^3, \text{R}_{4}^4 \text{ are hydrogen, alkyl, or aryl;}
\end{align*}
\]

wherein independently for each occurrence,

\[
\begin{align*}
\text{X is imidazolyl, -C(=N-OH)-R}_{3}^2, -\text{C(O)-N(R)-OH, -aryl-I(O) or -heteroaryl-I(O);} \\
\text{R}_{1}^1, \text{R}_{2}^2, \text{R}_{3}^3, \text{R}_{4}^4 \text{ are hydrogen, alkyl, or aryl;}
\end{align*}
\]

- 88 -
W is absent, -O-, -N(R)-, -S-, -C(O)O-, -C(O)N(R)-, -C(O)S-, -S(O)-, -S(O)₂-, -C(R₃)₂-, -C(O)-, -C(=NR₃)-, -heterocycloalkyl-, -heterocycloalkenyl-, -heterocycloalkenyl-, -aryl-, or -heteroaryl-; R is -C(=O)OR, -C(=O)N(R)₂-, -C(=O)S-, -C(=S)R, -C(=NR₃)R₃-, -C(=S)R₃-, -C(=NR₃)R₃-, -C(=S)R₃-, -C(=O)N(R)-, -C(O)O-, -C(O)S-, -S(O)-, -S(O)₂-; m is 0-5 inclusive; m is 0-5 inclusive; and p is 0-10 inclusive.
73. The particle of claim 56, wherein \( m \) is 3.

74. The particle of claim 56, wherein \( m \) is 4.

75. The particle of claim 56, wherein \( m \) is 5.

76. The particle of claim 56, wherein \( W \) is -aryl-, or -heteroaryl-.

77. The particle of claim 56, wherein \( n \) is 0; \( W \) is absent; \( m \) is 0; and \( X \) is imidazole.

78. The particle of claim 56, wherein \( n \) is 0; \( W \) is absent; \( m \) is 0; and \( X \) is H.

79. The particle of claim 56, wherein \( W \) is , or ; and \( Y \) is Br, Cl, I, OMs, or OTf.

80. The particle of claim 56, wherein \( W \) is , or ; and \( Y \) is Br, Cl, I, OMs, or OTf.

81. The particle of claim 56, wherein \( W \) is ; and \( Y \) is Br.

82. The particle of claim 56, particles, wherein \( W \) is ; and \( Y \) is Br.

83. The particle of claim 56, wherein \( R^1 \) is hydrogen.

84. The particle of claim 56, wherein \( R^3 \) is aryl.

85. The particle of claim 56, wherein \( R^3 \) is phenyl.

86. The particle of claim 56, wherein \( X \) is \(-C(=N-OH)-R^3\); and \( R^2 \) is hydrogen.
87. The particle of claim 56, wherein \( X = -\text{C}(=\text{N-OH})-\text{R}^3 \); \( R^2 \) is hydrogen; and \( R^1 \) is hydrogen.

88. The particle of claim 56, wherein \( X = -\text{C}(=\text{N-OH})-\text{R}^3 \); \( R^2 \) is hydrogen; and \( n \) is 0.

89. The particle of claim 56, wherein \( X = -\text{C}(=\text{N-OH})-\text{R}^3 \); \( R^2 \) is hydrogen; \( R^1 \) is hydrogen; and \( n \) is 0; \( m \) is 1; and \( R^3 \) is phenyl.

90. The particle of claim 56, wherein \( X = -\text{C}(=\text{N-OH})-\text{R}^3 \); \( R^2 \) is hydrogen; \( R^1 \) is hydrogen; \( n \) is 0; \( m \) is 1; and \( R^3 \) is phenyl; \( W \) is \( -\text{C}(=\text{O})- \); and \( Y \) is Br.

91. The particle of claim 56, wherein \( m \) is 0; \( W \) is absent or \( -\text{C}(=\text{O})- \); and \( X \) is \( -\text{aryl-I}(=\text{O}) \) or \( -\text{heteroaryl-I}(=\text{O}) \).

92. The particle of claim 56, wherein \( m \) is 0; \( W \) is absent; and \( X \) is \( -\text{aryl-I}(=\text{O}) \).

93. The particle of claim 56, wherein \( m \) is 0; \( W \) is absent; and \( X \) is \( -\text{phenyl-I}(=\text{O}) \).

94. The particle of claim 56, wherein \( m \) is 0; \( W \) is absent; and \( X \) is \( -\text{aryl-I}(=\text{O}) \).

95. The particle of claim 56, wherein \( m \) is 0; \( W \) is \( -\text{C}(=\text{O})- \); and \( X \) is \( -\text{aryl-I}(=\text{O}) \).

96. The particle of claim 56, wherein \( m \) is 0; \( W \) is \( -\text{C}(=\text{O})- \); and \( X \) is \( -\text{phenyl-I}(=\text{O}) \).

97. A particle having a diameter, comprising an inorganic metal oxide and a stabilizing compound comprising a nucleophilic moiety; wherein said diameter is about 1 to about 1,000 
nanometers; and said stabilizing compound comprising a nucleophilic moiety is a polymer or co-polymer; wherein said polymer or co-polymer comprises one or more monomers selected from the group consisting of

\[
\begin{align*}
\text{OMs, or OTf.}
\end{align*}
\]
98. The particle of claim 97, wherein said polymer is a copolymer comprising at least two of the monomer selected from the group consisting of

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{N} \\
\text{H} & \quad \text{N} \\
\text{H} & \quad \text{OH} \\
\text{H} & \quad \text{OH} \\
\end{align*}
\]

, \quad \text{and} \quad \text{H} \quad \text{N} \quad \text{N} ; \quad \text{wherein } Y \text{ is Br, Cl, I, OMs, or OTf.}

99. The particle of claim 97, wherein said polymer is a copolymer consisting essentially of at least two of the monomer selected from the group consisting of

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{N} \\
\text{H} & \quad \text{N} \\
\text{H} & \quad \text{OH} \\
\text{H} & \quad \text{OH} \\
\end{align*}
\]

, \quad \text{and} \quad \text{H} \quad \text{N} \quad \text{N} ; \quad \text{wherein } Y \text{ is Br, Cl, I, OMs, or OTf.}

100. A particle having a diameter, comprising an inorganic metal oxide and a stabilizing compound comprising a nucleophilic moiety; wherein said diameter is about 1 to about 1,000 nm; and said stabilizing compound is oximated humic acids.

101. The particle of any one of claims 1-100, wherein said effective particle size is about 1 to about 500 nm.

102. The particle of any one of claims 1-100, wherein said effective particle size is about 1 to about 250 nm.

103. The particle of any one of claims 1-100, wherein said effective particle size is about 1 to about 100 nm.

104. The particle of any one of claims 1-100, wherein said effective particle size is about 5 to about 50 nm.

105. The particle of any one of claims 1-100, wherein said effective particle size is about 10 to about 25 nm.

106. The particle of any one of claims 1-105, wherein said inorganic metal oxide comprises at least one metal selected from the group consisting of Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Zn and Ni.
107. The particle of any one of claims 1-105, wherein said inorganic metal oxide comprises at least one metal selected from the group consisting of Fe, Cu, Zn and Ni.

108. The particle of any one of claims 1-105, wherein said inorganic metal oxide is an iron oxide.

109. The particle of any one of claims 1-105, wherein said inorganic metal oxide is Fe₂O₃ or Fe₃O₄.

110. The particle of any one of claims 1-105, wherein said inorganic metal oxide is Fe₃O₄.

111. The particle of any one of claims 1-110, wherein said composition is superparamagnetic.

112. A method for the hydrolysis of a compound which contains at least one oxidized phosphorus group, the method comprising the step of contacting said compound with at least one particle having a diameter for a time period sufficient to hydrolyze at least some of the oxidized phosphorus groups in said compound; wherein said particle comprises an inorganic metal oxide and a stabilizing compound, said stabilizing compound comprises a nucleophilic moiety; wherein said diameter is about 1 to about 1,000 nm; and said stabilizing compound comprising a nucleophilic moiety is selected from the group consisting of oximes, hydroxamic acids, enamines, aryloxides, and heteroaryloxides.

113. The method of claim 112, wherein said nucleophilic moiety is selected from the group consisting of oximes, hydroxamic acids, hydrazines, hydrazones, imidazoles, iodosoaryl compounds and sulfoxides.

114. The method of claim 112, wherein said nucleophilic moiety is an oximes.

115. The method of claim 112, wherein said nucleophilic moiety is selected from a group consisting of

wherein, independently for each occurrence,

R is \(-\text{C(O)OR}^3, \text{-C(=O)N(R}^3\text{)}_{2}, \text{-C(K)SR}^3, \text{-C(K)R}^3, \text{-C(=NR)R}^3, \text{-C(=S)R}^3, \text{-C(R}^3\text{)=C(R}^3\text{)}_{2}, \text{-C≡CR}^3, \text{-C≡N, -[C(R}^3\text{)]}_n\text{-R}^3\), hydrogen, alkyl, cycloalkyl, heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl;
R\(^1\) is -OR, -NR\(^2\), -SR, -C(=O)OR, -OCC=O)R, -CC=O)NR\(^2\), -C(=O)SR, -SCC=O)R, -SC=O)R, -S(=O)\(^2\)R, -C(=O)R\(^3\), -C(=S)R\(^3\), -C(R\(^3\))=C(R\(^3\))\(^2\), -C≡CR\(^3\), -C≡N, -[C(R\(^3\))\(^2\)]\(_n\)R, hydrogen, alkyl, cycloalkyl, heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl;

R\(^2\) is -OR\(^5\), -NR\(^2\), -SR, -CC=O)OR, -OCC=O)R, -CC=O)NR\(^2\), -CC=O)SR, -SC(=O)R, -S(=O)\(^2\)R, -C(=O)R\(^3\), -CC=NR)R\(^3\), -C(=S)R\(^3\), -C(R\(^3\))=C(R\(^3\))\(^2\), -C≡CR\(^3\), -C≡N, -[C(R\(^3\))\(^2\)]\(_n\)R, hydrogen, halogen, alkyl, cycloalkyl, heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl;

R\(^3\) is hydrogen, halogen, alkyl, cycloalkyl, heterocycloalkyl, alkenyl, cycloalkenyl, heterocycloalkenyl, alkynyl, cyano, aryl, or heteroaryl;

R\(^4\) is -OR, -NR\(^2\), -SR, -CC=O)OR, -OCC=O)R, -CC=O)NR\(^2\), -CC=O)SR, -SC(=O)R, -SC=O)R, -SC=O)\(^2\)R, -C(=O)R\(^3\), -C(=S)R\(^3\), -C(R\(^3\))=C(R\(^3\))\(^2\), -C≡CR\(^3\), -C≡N, -[CCR\(^3\)]\(_n\)R, hydrogen, halogen, alkyl, cycloalkyl, heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl;

R\(^5\) is aryl or heteroaryl; and

n is 0-10 inclusive.

116. The method of claim 112, wherein said stabilizing compound comprising a

\[
\text{N} \bigg( \begin{array}{c}
\text{R}^1 \\
\text{R}^3 \\
\text{R}^5
\end{array} \bigg)
\]

nucleophilic moiety is 

117. The method of claim 112, wherein said stabilizing compound comprising a

\[
\text{X} \bigg( \begin{array}{c}
\text{R}^1 \\
\text{R}^2
\end{array} \bigg)
\]

nucleophilic moiety is \(R^1\) \(R^2\).

118. The method of claim 112, wherein said stabilizing compound comprising a

\[
\text{R}^4 \bigg( \begin{array}{c}
\text{R}^2 \\
\text{R}^3
\end{array} \bigg)
\]

nucleophilic moiety is

119. The method of claim 112, wherein said stabilizing compound comprising a nucleophilic moiety is \(R^3\)-1=0.
120. The method of claim 112, said stabilizing compound comprising a nucleophilic moiety is represented by a compound selected from the group consisting of

wherein, independently for each occurrence,

$X$ is $-\{C(R^3)_2\}_n^-$;

$Y$ is Br, Cl, I, OMe, or OTf;

$R$ is $-C(O)OR$, $-C(=O)NR(R^3)_2$, $-C(=O)R$, $-C(=NR)R^3$, $-C(=S)R^3$, $-C(R^3)C(R^3)_2$, $-C\equiv R^3$, $-C\equiv CR^3$, $-\{C(R^3)_2\}_p$, hydrogen, alkyl, cycloalkyl, heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl;

$R^1$ is hydrogen, alkyl, cycloalkyl, heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl;

$R^2$ is $-OR$, $-NR_2$, $-SR$, $-C(K)OR$, $-OC(O)R$, $-NRC(O)R$, $-C(O)NR_2$, $-C(O)SR$, $-SC(O)R$, $-S(O)R$, $-S(O)_2R$, $-C(=O)R$, $-C(=NR)R^3$, $-C(=S)R^3$, $-C(R^3)C(R^3)_2$, $-C\equiv CR^3$, $-ON$, $-[C(R^3)_2]_p$, hydrogen, halogen, alkyl, cycloalkyl, heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl;

$n$ is 0-10 inclusive; and

$p$ is 0-10 inclusive.

121. The method of claim 120, wherein said stabilizing compound comprising a nucleophilic moiety is

122. The method of claim 120, wherein said stabilizing compound comprising a nucleophilic moiety is
123. The method of claim 120, wherein said stabilizing compound comprising a

\[
\begin{align*}
\text{HO} & \quad \text{N} \\
R^1 & \quad Y^\ominus \\
R^2 & \quad R \\
\end{align*}
\]

nucleophilic moiety is.

124. The method of claim 120, wherein said stabilizing compound comprising a

\[
\begin{align*}
\text{R}^2 & \quad \text{R}^2 \\
\text{R}^2 & \quad \text{N} \quad \text{OH} \\
\text{Y}^\ominus & \quad \text{R}^1 \\
\end{align*}
\]

nucleophilic moiety is.

5 125. The method of claim 120, wherein n is 0.

126. The method of claim 120, wherein n is 1.

127. The method of claim 120, wherein n is 2-10 inclusive.

128. The method of claim 120, wherein n is 3-10 inclusive.

129. The method of claim 120, wherein n is 4-10 inclusive.

10 130. The method of claim 120, wherein n is 5-10 inclusive.

131. The method of claim 120, wherein Y is Br or I.

132. The method of claim 120, wherein R is alkyl.

133. The method of claim 120, wherein R^1 is aryl.

134. The method of claim 120, wherein R^2 is hydrogen.

15 135. The method of claim 120, wherein n is 0; and Y is Br or I.

136. The method of claim 120, wherein n is 0; Y is Br or I; and R^2 is hydrogen.

137. The method of claim 120, wherein n is 0; Y is Br or I; R^2 is hydrogen; and R is alkyl.

138. The method of claim 120, wherein n is 0; Y is Br or I; R^2 is hydrogen; and R^1 is aryl.

140. The method of claim 120, wherein n is 0; X is Br; R is methyl; R^1 is phenyl; and R^2 is hydrogen.
141. The method of claim 112, wherein said stabilizing compound comprising a nucleophilic moiety is represented by a compound selected from the group

\[ \text{R}^1 \text{N} \equiv \text{R}^2 \text{Y}^\oplus \]

wherein, independently for each occurrence,

\[ X = -[\text{C}(\text{R}^3)_2]_n^-; \]

\[ Y = \text{Br}, \text{Cl}, \text{I}, \text{OMs}, \text{or} \text{OTf}; \]

\[ \text{R} = -\text{C}(\text{O})\text{OR}^3, -\text{C}(\text{O})\text{N}(\text{R}^3)_2, -\text{C}(\text{O})\text{SR}, -\text{C}(\text{O})\text{R}^3, -\text{C}(\text{=NR})\text{R}^3, -\text{C}(\text{=S})\text{R}^3, \]

\[ -\text{C}(\text{R}^3)\text{O}(\text{R}^3)_2, -\text{C}≡\text{C}^\text{R}^3, -[\text{C}(\text{R}^3)_2]_p^-\text{R}^3, \text{hydrogen}, \text{alkyl}, \text{cycloalkyl}, \text{heterocycloalkyl}, \text{cycloalkenyl}, \text{aryl}, \text{or heteroaryl}; \]

\[ \text{R}^1 \text{is hydrogen, alkyl, cycloalkyl, heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl;} \]

\[ \text{R}^2 \text{is -OR, -NR}_2, \text{-SR, -C}(\text{O})\text{OR, -OC}(\text{O})\text{R, -NRC}(\text{O})\text{R, -C}(\text{O})\text{NR}_2, -\text{C}(\text{O})\text{SR, -SC}(\text{O})\text{R, -S}(\text{O})\text{R, -S}(\text{O})_2\text{R, -C}(\text{O})\text{R}^3, -\text{C}(\text{=NR})\text{R}^3, -\text{C}(\text{=S})\text{R}^3, -\text{C}(\text{R}^3)\text{O}(\text{R}^3)_2, \]

\[ -\text{C}≡\text{C}^\text{R}^3, -\text{C}≡\text{N}, -[\text{C}(\text{R}^3)_2]_p^-\text{R}, \text{hydrogen}, \text{halogen}, \text{alkyl}, \text{cycloalkyl}, \text{heterocycloalkyl}, \text{cycloalkenyl}, \text{aryl}, \text{or heteroaryl}; \]

\[ \text{R}^3 \text{is hydrogen, halogen, alkyl, cycloalkyl, heterocycloalkyl, alkenyl, cycloalkenyl, heterocycloalkenyl, alkynyl, cyano, aryl, or heteroaryl;} \]

\[ n \text{is 0-10 inclusive; and} \]

\[ p \text{is 0-10 inclusive.} \]

142. The method of claim 141, wherein said stabilizing compound comprising a nucleophilic moiety is

\[ \text{R}^1 \text{N} \equiv \text{R}^2 \text{Y}^\oplus \]

143. The method of claim 141, wherein said stabilizing compound comprising a nucleophilic moiety is
144. The method of claim 141, wherein said stabilizing compound comprising a nucleophilic moiety is

\[
\begin{array}{c}
\text{HO}^- \quad \text{N} \quad \text{N} \\
\text{R} \quad \text{R} \quad \text{R} \quad \text{R} \\
\end{array}
\]

145. The method of claim 141, wherein \( n = 0 \).
146. The method of claim 141, wherein \( n = 1 \).
147. The method of claim 141, wherein \( n = 2-10 \) inclusive.
148. The method of claim 141, wherein \( n = 3-10 \) inclusive.
149. The method of claim 141, wherein \( n = 4-10 \) inclusive.
150. The method of claim 141, wherein \( n = 5-10 \) inclusive.
151. The method of claim 141, wherein \( Y = \text{Br or I} \).
152. The method of claim 141, wherein \( R = \text{alkyl} \).
153. The method of claim 141, wherein \( R^1 = \text{aryl} \).
154. The method of claim 141, wherein \( R^2 = \text{hydrogen} \).
155. The method of claim 141, wherein \( n = 0 \); and \( Y = \text{Br or I} \).
156. The method of claim 141, wherein \( n = 0 \); \( Y = \text{Br or I} \); and \( R^2 = \text{hydrogen} \).
157. The method of claim 141, wherein \( n = 0 \); \( Y = \text{Br or I} \); \( R^2 = \text{hydrogen} \); and \( R = \text{alkyl} \).
158. The method of claim 141, wherein \( n = 0 \); \( Y = \text{Br or I} \); \( R^2 = \text{hydrogen} \); and \( R^1 = \text{aryl} \).
159. The method of claim 141, wherein \( n = 0 \); \( Y = \text{Br or I} \); \( R^2 = \text{hydrogen} \); \( R = \text{alkyl} \); and \( R^1 = \text{aryl} \).
160. The method of claim 141, wherein \( n = 0 \); \( X = \text{Br} \); \( R = \text{methyl} \); \( R^1 = \text{phenyl} \); and \( R^2 = \text{hydrogen} \).
161. The method of claim 112, wherein said stabilizing compound comprising a nucleophilic moiety is represented by a compound selected from the group consisting of

\[
\begin{array}{c}
\text{R}^4 \quad \text{N} \\
\text{R}^4 \quad \text{N} \\
\end{array}
\]

wherein, independently for each occurrence,
R is -C(=O)OR 3, -C(=O)N(R 3) 2, -C(=O)SR 3, -C(=O)R 3, -C(=NR)R 3, -C(=S)R 3,
-C(R 3)=C(R 3) 2, -C≡C ... of contacting said compound
with at least one particle having a diameter for a time period sufficient to hydrolyze

162. The method of claim 161, wherein R is hydrogen.
163. The method of claim 112, wherein said stabilizing compound comprising a
nucleophilic moiety is represented by a compound selected from the group

[Diagram of chemical structures]

wherein, independently for each occurrence,
R is -CO=O)OR 3, -C(=O)N(R 3) 2, -C(=O)SR 3, -C(=O)R 3, -C(=NR 3)R 3, -C(=S)R 3,
-C(R 3)=O(R 3) 2, -C≡CR 3, -C≡N, -[C(R 3)] 2n-R, hydrogen, alkyl, cycloalkyl,
heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl;
R is hydrogen, halogen, alkyl, cycloalkyl, heterocycloalkyl, alkenyl, cycloalkenyl,
heterocycloalkenyl, alkynyl, cyano, aryl, or heteroaryl;
R 4 is -OR, -NR 2, -SR, -C(=O)OR, -OC(=O)R, -NRC(=O)R, -C(=O)NR 2, -C(K)SR,
-SR, -S(=O)R, -S(=O) 2R, -C(=O)R 3, -C(=NR)R 3, -C(=S)R 3, -C(R 3)O(R 3) 2,
-C≡CR 3, -C≡N, -[C(R 3)] 2n-R, hydrogen, halogen, alkyl, cycloalkyl,
heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl;
R 3 is hydrogen, halogen, alkyl, cycloalkyl, heterocycloalkyl, alkenyl, cycloalkenyl,
heterocycloalkenyl, alkynyl, cyano, aryl, or heteroaryl;
R 4 is -OR, -NR 2, -SR, -C(=O)OR, -OC(=O)R, -NRC(=O)R, -C(=O)NR 2, -C(K)SR,
-SR, -S(=O)R, -S(=O) 2R, -C(=O)R 3, -C(=NR)R 3, -C(=S)R 3, -C(R 3)O(R 3) 2,
-C≡CR 3, -C≡N, -[C(R 3)] 2n-R, hydrogen, halogen, alkyl, cycloalkyl,
heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl;
R 3 is hydrogen, halogen, alkyl, cycloalkyl, heterocycloalkyl, alkenyl, cycloalkenyl,
heterocycloalkenyl, alkynyl, cyano, aryl, or heteroaryl;
R 4 is -OR, -NR 2, -SR, -C(=O)OR, -OC(=O)R, -NRC(=O)R, -C(=O)NR 2, -C(K)SR,
-SR, -S(=O)R, -S(=O) 2R, -C(=O)R 3, -C(=NR)R 3, -C(=S)R 3, -C(R 3)O(R 3) 2,
-C≡CR 3, -C≡N, -[C(R 3)] 2n-R, hydrogen, halogen, alkyl, cycloalkyl,
heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl;
R 3 is hydrogen, halogen, alkyl, cycloalkyl, heterocycloalkyl, alkenyl, cycloalkenyl,
heterocycloalkenyl, alkynyl, cyano, aryl, or heteroaryl;
R 4 is -OR, -NR 2, -SR, -C(=O)OR, -OC(=O)R, -NRC(=O)R, -C(=O)NR 2, -C(K)SR,
-SR, -S(=O)R, -S(=O) 2R, -C(=O)R 3, -C(=NR)R 3, -C(=S)R 3, -C(R 3)O(R 3) 2,
-C≡CR 3, -C≡N, -[C(R 3)] 2n-R, hydrogen, halogen, alkyl, cycloalkyl,
heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl;
R 3 is hydrogen, halogen, alkyl, cycloalkyl, heterocycloalkyl, alkenyl, cycloalkenyl,
heterocycloalkenyl, alkynyl, cyano, aryl, or heteroaryl;
R 4 is -OR, -NR 2, -SR, -C(=O)OR, -OC(=O)R, -NRC(=O)R, -C(=O)NR 2, -C(K)SR,
-SR, -S(=O)R, -S(=O) 2R, -C(=O)R 3, -C(=NR)R 3, -C(=S)R 3, -C(R 3)O(R 3) 2,
-C≡CR 3, -C≡N, -[C(R 3)] 2n-R, hydrogen, halogen, alkyl, cycloalkyl,
heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl;
R 3 is hydrogen, halogen, alkyl, cycloalkyl, heterocycloalkyl, alkenyl, cycloalkenyl,
heterocycloalkenyl, alkynyl, cyano, aryl, or heteroaryl;

n is 0-10 inclusive.

164. The method of claim 163, wherein R is hydrogen or alkyl.
165. The method of claim 163, wherein R 4 is hydrogen.
166. A method for the hydrolysis of a compound which contains at least one oxidized
phosphorus group, the method comprising the step of contacting said compound
with at least one particle having a diameter for a time period sufficient to hydrolyze
at least some of the oxidized phosphorus groups in said compound; wherein said particle consists essentially of an inorganic metal oxide and a stabilizing compound, said stabilizing compound comprises a nucleophilic moiety; wherein said diameter is about 1 to about 1,000 nm; and said stabilizing compound comprising a nucleophilic moiety is a polymer or co-polymer; wherein said polymer or co-polymer comprises a plurality of monomers represented by formula I:

\[
\begin{align*}
\text{I} & \text{ where } X \text{ is imidazolyl, } -\text{C(=N-OH)}-\text{R}^3, -\text{C(=O)-N(R)-OH, } -\text{aryl-I(=O) or -heteroaryl-I(=O)}; \\
W & \text{ is absent, } -\text{O-}, -\text{N(R)-}, -\text{S-}, -\text{C(O)O-}, -\text{C(O)N(R)-}, -\text{S(O)-}, -\text{S(O)}_2^-, -\text{C(R)}^3_2-, -\text{C(=O)-}, -\text{C(=NR)}^3_3-, -\text{C(=S)-}, -\text{C(R)}^3\text{=C(R)}^3-, -\text{C≡C-}, -\text{C≡N-}, -\text{C(=O)-}, -\text{C(=NR)R}-, -\text{C(=S)-}, -\text{C(R)}^3\text{=C(R)}^3_2-, \\
R & \text{ is } -\text{C(O)OR}^3, -\text{C(=O)NR}^3_3, -\text{C(=O)SR}^3, -\text{C(=O)R}^3, -\text{C(=NR)R}^3_3, -\text{C(=S)R}^3_3, -\text{C(=O)C(R)}^3_2, -\text{C≡CR}^3, -\text{C≡N}, -\text{[C(R)}^3_2\text{P-R}^3, \text{hydrogen, alkyl, cycloalkyl, heterocycloalkyl, cycloalkenyl, heterocycloalkenyl, aryl, or heteroaryl;} \\
R^1 & \text{ is } -\text{OR}, -\text{NR}^2, -\text{SR}, -\text{C(O)OR}, -\text{OC(O)R}, -\text{NRC(O)R}, -\text{C(O)NR}^2, -\text{C(O)SR}, -\text{SC(O)R}, -\text{S(O)R}, -\text{S(O)}_2R, -\text{C(=O)R}^3, -\text{C(=NR)R}^3, -\text{C(=S)R}^3, -\text{C(R)}^3\text{=C(R)}^3_2, \\
R^2 & \text{ is hydrogen, halogen, alkyl, cycloalkyl, heterocycloalkyl, alkenyl, cycloalkenyl, heterocycloalkenyl, alkynyl, cyano, aryl, heteroaryl or } -\text{[C(R)}^3_2\text{P-R}; \\
R^3 & \text{ is hydrogen, halogen, alkyl, cycloalkyl, heterocycloalkyl, alkenyl, cycloalkenyl, heterocycloalkenyl, alkynyl, cyano, aryl, or heteroaryl; and} \\
n & \text{ is } 0-5 \text{ inclusive; } \\
m & \text{ is } 0-5 \text{ inclusive; and} \\
p & \text{ is } 0-10 \text{ inclusive.}
\end{align*}
\]

167. The method of claim 166, wherein X is imidazolyl.
168. The method of claim 166, wherein X is -C(=N-OH)-R³.
169. The method of claim 166, wherein X is -C(=O)-N(R)-OH.
170. The method of claim 166, wherein X is -aryl-I(=O).
171. The method of claim 166, wherein X is -heteroaryl-I(=O).
172. The method of claim 166, wherein R² is hydrogen or alkyl.
173. The method of claim 166, wherein R² is hydrogen.
174. The method of claim 166, wherein n is 0.
175. The method of claim 166, wherein n is 1.
176. The method of claim 166, wherein n is 2.
177. The method of claim 166, wherein n is 3.
178. The method of claim 166, wherein n is 4.
179. The method of claim 166, wherein n is 5.
180. The method of claim 166, wherein m is 0.
181. The method of claim 166, wherein m is 1.
182. The method of claim 166, wherein m is 2.
183. The method of claim 166, wherein m is 3.
184. The method of claim 166, wherein m is 4.
185. The method of claim 166, wherein m is 5.
186. The method of claim 166, wherein W is -aryl-, or -heteroaryl-.
187. The method of claim 166, wherein n is 0; W is absent; m is 0; and X is imidazole.
188. The method of claim 166, wherein n is 0; W is absent; m is 0; and X is
189. The method of claim 166, wherein W is

; and Y is Br, Cl, I, OMs, or OTf.
190. The method of claim 166, wherein W is

; and Y is Br, Cl, I, OMs, or OTf.

191. The method of claim 166, wherein W is

; and Y is Br.

192. The method of claim 166, wherein W is

; and Y is Br.

193. The method of claim 166, wherein R\(^1\) is hydrogen.

194. The method of claim 166, wherein R\(^3\) is aryl.

195. The method of claim 166, wherein R\(^3\) is phenyl.

196. The method of claim 166, wherein X is -C(=N-0H)-R\(^3\); and R\(^2\) is hydrogen.

197. The method of claim 166, wherein X is -C(=N-0H)-R\(^3\); R\(^2\) is hydrogen; and R\(^1\) is hydrogen.

198. The method of claim 166, wherein X is -C(=N-0H)-R\(^3\); R\(^2\) is hydrogen; R\(^1\) is hydrogen; and n is 0.

199. The method of claim 166, wherein X is -C(=N-0H)-R\(^3\); R\(^2\) is hydrogen; R\(^1\) is hydrogen; n is 0; and m is 1.

200. The method of claim 166, wherein X is -C(=N-0H)-R\(^3\); R\(^2\) is hydrogen; R\(^1\) is hydrogen; n is 0; m is 1; and R\(^3\) is phenyl.

201. The method of claim 166, wherein X is -C(=N-0H)-R\(^3\); R\(^2\) is hydrogen; R\(^1\) is hydrogen; n is 0; m is 1; R\(^3\) is phenyl; W is

; and Y is Br.

202. The method of claim 166, wherein m is 0; W is absent or -C(=O)s and X is -aryl-I(=O) or -heteroaryl-I(=O).

203. The method of claim 166, wherein m is 0; W is absent; and X is -aryl-I(=O).
204. The method of claim 166, wherein \( m \) is 0; \( W \) is absent; and \( X \) is -phenyl-I(=O).

205. The method of claim 166, wherein \( m \) is 0; \( W \) is -C(=O)-; and \( X \) is -aryl-I(=O).

206. The method of claim 166, wherein \( m \) is 0; \( W \) is -C(=O)-; and \( X \) is -phenyl-I(=O).

207. A method for the hydrolysis of a compound which contains at least one oxidized phosphorus group, the method comprising the step of contacting said compound with at least one particle having a diameter for a time period sufficient to hydrolyze at least some of the oxidized phosphorus groups in said compound; wherein said particle consists essentially of an inorganic metal oxide and a stabilizing compound, said stabilizing compound comprises a nucleophilic moiety; wherein said diameter is about 1 to about 1,000 nm; and said stabilizing compound comprising a nucleophilic moiety is a polymer or co-polymer; wherein said polymer or co-polymer comprises one or more monomers selected from the group consisting of

\[
\begin{align*}
\text{H} & \quad \text{H} \quad \text{O} \quad \text{H} \quad \text{N} \quad \text{OH} \\
\text{H} & \quad \text{H} \quad \text{N} \quad \text{OH} \\
\text{H} & \quad \text{H} \quad \text{N} \quad \text{OH} \\
\text{Y} & \quad \text{Y} \quad \text{N} \quad \text{OH} \\
\text{H} & \quad \text{H} \quad \text{N} \quad \text{OH} \\
\text{Y} & \quad \text{Y} \quad \text{N} \quad \text{OH} \\
\text{Y} & \quad \text{Y} \quad \text{N} \quad \text{OH} \\
\text{H} & \quad \text{H} \quad \text{N} \quad \text{OH} \\
\text{Y} & \quad \text{Y} \quad \text{N} \quad \text{OH} \\
\text{H} & \quad \text{H} \quad \text{N} \quad \text{OH} \\
\text{Y} & \quad \text{Y} \quad \text{N} \quad \text{OH} \\
\text{H} & \quad \text{H} \quad \text{N} \quad \text{OH} \\
\text{Y} & \quad \text{Y} \quad \text{N} \quad \text{OH} \\
\text{H} & \quad \text{H} \quad \text{N} \quad \text{OH} \\
\text{Y} & \quad \text{Y} \quad \text{N} \quad \text{OH} \\
\end{align*}
\]

\( Y \) is Br, Cl, I, OMs, or OTf.

208. The method of claim 207, wherein said polymer is a copolymer comprising at least

\[
\begin{align*}
\text{H} & \quad \text{H} \quad \text{O} \quad \text{H} \\
\text{H} & \quad \text{H} \quad \text{N} \quad \text{OH} \\
\text{H} & \quad \text{H} \quad \text{N} \quad \text{OH} \\
\text{Y} & \quad \text{Y} \quad \text{N} \quad \text{OH} \\
\text{H} & \quad \text{H} \quad \text{N} \quad \text{OH} \\
\text{Y} & \quad \text{Y} \quad \text{N} \quad \text{OH} \\
\text{Y} & \quad \text{Y} \quad \text{N} \quad \text{OH} \\
\text{H} & \quad \text{H} \quad \text{N} \quad \text{OH} \\
\text{Y} & \quad \text{Y} \quad \text{N} \quad \text{OH} \\
\text{H} & \quad \text{H} \quad \text{N} \quad \text{OH} \\
\text{Y} & \quad \text{Y} \quad \text{N} \quad \text{OH} \\
\text{H} & \quad \text{H} \quad \text{N} \quad \text{OH} \\
\text{Y} & \quad \text{Y} \quad \text{N} \quad \text{OH} \\
\end{align*}
\]

\( Y \) is Br, Cl, I, OMs, or OTf.

209. The method of claim 207, wherein said polymer is a copolymer consisting essentially of at least two of the monomer selected from the group consisting of

\[
\begin{align*}
\text{H} & \quad \text{H} \quad \text{O} \quad \text{H} \\
\text{H} & \quad \text{H} \quad \text{N} \quad \text{OH} \\
\text{H} & \quad \text{H} \quad \text{N} \quad \text{OH} \\
\text{Y} & \quad \text{Y} \quad \text{N} \quad \text{OH} \\
\text{H} & \quad \text{H} \quad \text{N} \quad \text{OH} \\
\text{Y} & \quad \text{Y} \quad \text{N} \quad \text{OH} \\
\text{Y} & \quad \text{Y} \quad \text{N} \quad \text{OH} \\
\text{H} & \quad \text{H} \quad \text{N} \quad \text{OH} \\
\text{Y} & \quad \text{Y} \quad \text{N} \quad \text{OH} \\
\text{H} & \quad \text{H} \quad \text{N} \quad \text{OH} \\
\text{Y} & \quad \text{Y} \quad \text{N} \quad \text{OH} \\
\text{H} & \quad \text{H} \quad \text{N} \quad \text{OH} \\
\text{Y} & \quad \text{Y} \quad \text{N} \quad \text{OH} \\
\end{align*}
\]

wherein \( Y \) is Br, Cl, I, OMs, or OTf.
210. A method for the hydrolysis of a compound which contains at least one oxidized phosphorus group, the method comprising the step of contacting said compound with at least one particle having a diameter for a time period sufficient to hydrolyze at least some of the oxidized phosphorus groups in said compound; wherein said particle consists essentially of an inorganic metal oxide and a stabilizing compound, said stabilizing compound comprises a nucleophilic moiety; wherein said diameter is about 1 to about 1,000 nm; and said stabilizing compound comprising a nucleophilic moiety is a polymer or co-polymer; wherein said polymer is oximated humic acids.

211. The method of claim 210, wherein said particle is capable of adsorbing said compound and said contacting step is carried out for a time period sufficient to also permit adsorption of at least some of said compound onto the particle.

212. The method of any one of claims 112-211, wherein said compound is selected from the group consisting of parathion, malathion, diazinon, phosmet (Imidan®), chlorpyrifos (Lorsban®), sarin, tabun (ethylphosphorodimethyl-amidocyanidate), soman (phacolyl methylphosphonofloridate), GF (Cyclohexyl methylphosphonofloridate), VX (ethyl S-2-disopropyl aminoethyl methylphosphoro-thioate) or diisopropyl fluorophosphate (DFP).

213. The method of any one of claims 112-212, wherein said effective particle size is about 1 to about 500 nm.

214. The method of any one of claims 112-212, wherein said effective particle size is about 1 to about 250 nm.

215. The method of any one of claims 112-212, wherein said effective particle size is about 1 to about 100 nm.

216. The method of any one of claims 112-212, wherein said effective particle size is about 5 to about 50 nm.

217. The method of any one of claims 112-212, wherein said effective particle size is about 10 to about 25 nm.

218. The method of any one of claims 112-217, wherein said inorganic metal oxide comprises at least one metal selected from the group consisting of Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Zn and Ni.
219. The method of any one of claims 112-217, wherein said inorganic metal oxide comprises at least one metal selected from the group consisting of Fe, Cu, Zn and Ni.

220. The method of any one of claims 112-217, wherein said inorganic metal oxide is an iron oxide.

221. The method of any one of claims 112-217, wherein said inorganic metal oxide is Fe₂O₃ or Fe₃O₄.

222. The method of any one of claims 112-217, wherein said inorganic metal oxide is Fe₃O₄.

223. The method of any one of claims 112-222, wherein said composition is superparamagnetic.

224. An article, comprising a surface and a coating on said surface, wherein said coating comprises a plurality of particles of any one of claims 1-111.

225. The article of claim 24, wherein said coating has a mass per surface area of less than about 500 µg/cm².

226. The article of claim 24, wherein said coating has a mass per surface area of less than about 100 µg/cm².

227. The article of claim 24, wherein said coating has a mass per surface area of less than about 50 µg/cm².

228. The article of claim 24, wherein said coating has a mass per surface area of less than about 10 µg/cm².

229. The article of claim 24, wherein said coating has a mass per surface area of less than about 5 µg/cm².

230. The article of claim 24, wherein said surface is selected from the group consisting of non-synthetic fibers, cellulosic fibers, cotton, proteinaceous fibers, wool, silk, synthetic fibers, nylon, polyester, polyurethane, polyanhydride, polyorthoester, polyacrylonitrile, polyphenazine, latex, teflon, dacron, acrylate polymer, chlorinatec rubber, fluoropolymer, polyamide resin, vinyl resin, Gore-tex®, Marlex®, expande* polytetrafluoroethylene, low density polyethylene, high density polyethylene, polypropylene, and poly(ethylene terephthalate).

231. The article of claim 24, wherein said article is selected from the group consisting of filters, wipes, sponges, gas masks, membranes, wearable protective garments and filtration systems.
Figure 1

[A]

[B]
Figure 2

[A]

[B]
Figure 3

The graph shows the variation of ζ-potential (mV) and diameter (nm) with pH. The curves represent different samples labeled as p(VPOx-AA)/M and PAM/M. The ζ-potential remains relatively constant across the pH range, while the diameter shows a significant change, especially at pH 9.
Figure 4

![Graph](image-url)

- **E (mV)**
- **time (s)**

Graph showing the relationship between time (s) and voltage (E) for different curves labeled 1, 2, and 3.
Figure 5

![Graph showing concentration vs. observed rate constant (k_{obs} \times 10^3 \text{ s}^{-1})](image-url)
Figure 6
Figure 7
Figure 8

Graph showing the relationship between the inverse of the initial velocity ($v_0^{-1}$) and the inverse of the [DFP] concentration ($[DFP]^{-1}$). The graph has a linear trend line with three different sets of data points (labeled 1, 2, and 3) indicating different conditions or treatments.
Figure 9

-\ln\left(1 - \frac{C_t}{C_0}\right)

Cycle #1

Cycle #2

Cycle #3

time (s)
Figure 10

\[
\text{2-pyridinealdoxime (PAM)} \overset{\text{H}_2\text{O}}{\longrightarrow} \text{DFP}
\]
Figure 12

![Graph showing concentration vs. \( k_{\text{obs}} \) with a linear scale on the y-axis and a logarithmic scale on the x-axis.]
Figure 14

[Graph showing electrode potential over time for different concentrations (2.17, 2.68, 3.36, 8.38) compared to a control. The x-axis is labeled 'time (s)' and the y-axis is labeled 'Electrode Potential, E (mV).']
Figure 15
Figure 16

\[ x : y : z = 4 : 4 : 1 \]
Figure 17

The graph shows the relationship between pH and ζ-potential (mV) and average diameter (nm). As the pH increases, the ζ-potential decreases, and the average diameter also decreases. There is a peak in the average diameter at pH 8.
Figure 18

Electrode Potential, E (mV)

0  50  100  150

0  2000  4000

time (s)

0  0.1  0.02  0.01  1.0  10
Figure 19
Figure 20

\[ k_{\text{obs}} \text{ (s}^{-1}) \]

\[ [\text{Ox}]_0 \text{ (M)} \]
Figure 21

![Graph showing absorbance vs. wavenumber for OHA-magnetite and HA-magnetite](image-url)