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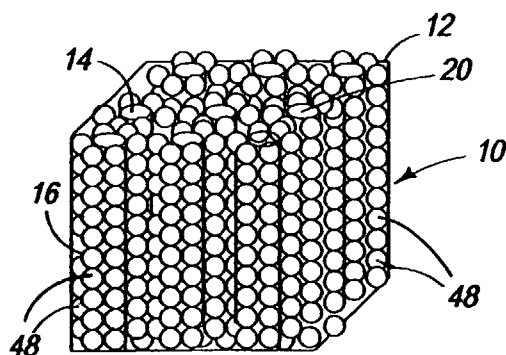
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(57) Abstract: A structured, self-assembled nanoenergetic material (10) is disclosed that includes a nanostructure comprising at least one of the group consisting of a fuel (16) and an oxidizer (14) and a plurality of substantially spherical nanoparticles (18) comprising at least the other of the group consisting of a fuel (16) and an oxidizer (14). The spherical particles (18) are arranged around the exterior surface area of a nanorod (20). This structured particle (10) assures that the oxidizer (14) and the fuel (16) have a high interfacial surface area between them. Preferably, the nanostructure is at least one of a nanorod (20), nanowire and a nanowell (24), and the second shaped nanoparticle is a nanosphere (18).

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ORDERED NANOENERGETIC COMPOSITES AND SYNTHESIS METHOD

TECHNICAL FIELD

5 This invention relates the use of nanotechnology to make metastable intermolecular composites (“MICs”) with tunable combustion characteristics. More specifically, nanoparticles of fuel and oxidizer are shaped and self-assembled to create ordered nanoenergetic composites to achieve higher burn rates resulting in creation of shock waves.

10 BACKGROUND ART

Energetic materials are those that rapidly convert chemical enthalpy to thermal enthalpy. These materials are commonly known as explosives, propulsion fuels and pyrotechnics. Thermite is a well-known subgroup of pyrotechnics. It is a combination of a fuel and an oxidizer that combusts in a self-propagating reaction producing temperatures of several thousand degrees. Either alone or in combination with other high energy materials, thermites are used for various applications that include military, mining, demolition, precision cutting, explosive welding, surface treatment and hardening of materials, pulse power applications, sintering-aid, biomedical applications, microaerospace and satellite platforms. In solid form, thermite is often a first metal and the oxide of a second metal, such as aluminum and iron oxide.

Self-propagating high temperature synthesis (“SHS”) relates to the synthesis of compounds that combust in a wave of chemical reaction that propagates over the reactants, producing a layer-by-layer heat transfer. Properties such as burn rate, reaction temperature and energy release are

very important. In powder-based SHS materials, solid fuel and oxidizer are ground into fine micron-sized particles and combined. In these systems, reactions depend strongly on the interfacial surface area between the fuel and the oxidizer which is affected by the size, impurity level and packing density of the constituent powders. Since the particle size predominates in determining particle surface area, use of smaller particles is desirable to increase the burn rate of the SHS and metastable intermolecular composites ("MIC") material.

Even if smaller particle size is achieved, mere mixing of the fuel and the oxidizer is not sufficient to guarantee an increase in the interfacial surface area. Mixing of the powders results in a random particle distribution. In such a distribution, many of the fuel particles will be surrounded by other fuel particles. There will be many places where the oxidizer has little contact with fuel particles. To significantly increase the interfacial surface area, the particles must be specifically arranged so that a large number of fuel particles contact oxidizer particles and vice versa.

The propagation rate or energy release rate is increased by homogeneous distribution of the oxidizer and the fuel in the composite. This provides high interfacial area for fuel and oxidizer as well as reduced interfacial diffusional resistance. Thus on initiating a thermite reaction, the combustion wavefront assumes maximum hot spot density resulting in a high rate of energy release. In other words, such materials would show a higher burn rate or flame propagation rates. To have homogeneous distribution of the oxidizer and fuel, a self-assembly process can be very useful. Although a similar process has been demonstrated in several different research areas, preparation of ordered nanoenergetic structures has not been shown. In the self-assembly process, fuel particles are arranged in an orderly manner around oxidizer or vice versa.

Although solid spherical nanoparticles of both the oxidizer and fuel can be assembled to create a nanoenergetic composite, the surface area

in spherical nanoparticles is generally smaller than cylindrical shaped nanoparticles. In cylindrical oxidizer nanoparticles such as nanorods, it is possible to assemble a greater number of fuel nanoparticles than spherical oxidizer nanoparticles. Such composites result in higher energy density than
5 spherical particle assembly and releases energy through conduction mechanism. In the case of porous oxidizer, such as a sol-gel oxidizer, convection generally improves the performance. Recent inventions by others provide a technique of mixing of fuel nanoparticles during gelation of oxidizers, but in these reports, the microstructures do not show homogenous
10 distribution of fuel nanoparticles inside porous oxidizers.

Manufacture of ordered nanoparticles is a technique known for the preparation of catalysts. This technique allows two different types of particles to be arranged into nanoparticles in an orderly fashion.

15 DISCLOSURE OF THE INVENTION

These and other needs in the art are met or exceeded by the present invention which generates structured particles having a high interfacial surface area between a fuel and an oxidizer. More specifically,
20 this invention relates to a MIC or SHS material that is assembled for good oxidizer-fuel contact.

In a first embodiment of the invention, a structured, self-propagating high temperature synthesis material that includes a nanostructure comprising at least one of the group consisting of a fuel and
25 an oxidizer and a plurality of substantially spherical nanoparticles comprising at least the other of the group consisting of a fuel and an oxidizer. The spherical particles are arranged around the exterior surface area of said nanorod. This structured particle assures that the oxidizer and the fuel have a high interfacial surface area between them. Preferably, the

nanostructure is at least one of a nanorod and a nanowell, and the second shaped nanoparticle is a nanosphere.

Production of fuel and oxidizer particles in the nanoparticle size range increases the potential for high interfacial surface area. Smaller particle size increases the amount of available surface area. As greater surface area is generated, more it is likely to interface with the surface of different particles, even in random mixtures of particles. Thus, reduction of particle size has the potential to increase the interfacial surface area between the fuel and the oxidizer. Creating a nanorod in place of a nanosphere for at least one particle type also leads to an increase in surface area of about 40%.

Structuring of the particles further adds to increases in the interfacial surface area. Placement of nanospheres of one material around nanorods of the other material assures at least some interfacial contact with the other material for each particle. This structure results in additional increases in interfacial surface area, leading to faster burn rates and increases in energy expended.

BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 shows a schematic diagram of a nanoenergetic material having a nanorod made of oxidizer covered fuel-containing nanospheres;

FIG. 2 shows a schematic diagram of the process of coating a nanosphere with a molecular linker;

FIG. 3 shows a schematic diagram of nanorod formation;

FIG. 4 shows a schematic diagram of a nanowell;

FIG. 5 is a graph of pressure over time during combustion of the nanoenergetic material;

FIG. 6 is a block diagram of the process for making nanoenergetic materials having nanorods; and

FIG. 7 is a block diagram of the process for making nanoenergetic materials from nanowells.

BEST MODE FOR CARRYING OUT THE INVENTION

There is, therefore, a need in the art for a composite material having a high interfacial surface area. There is also a need for a combustible material having a burn rate that exceeds the speed of sound in that material.

Turning to FIG. 1, a preferred embodiment is shown wherein a nanoenergetic particle, generally designated 10, includes a nanostructure 12 of oxidizer 14 material self-assembled with a fuel 16 in the shape of nanoparticles 18. The nanoenergetic particle 10 is preferably a thermite composition, utilizing a metal fuel 16 and an oxidizer 14 for the metal. Other preferred nanoenergetic particles include metastable intermolecular composites and SHS composites. The efficacy of the nanoenergetic particle 10 increases as the purity of the components increases, so the preferred oxidizer 14 and fuel 16 are both relatively high purity. In the discussion that follows, the fuel 16 nanoparticle 18 is described as being shaped into a nanosphere and the oxidizer 14 is shaped into a nanostructure 12, such as a nanorod 20, nanowire (not shown) or nanowell 24. These are preferred embodiments of the invention, but are not intended to be limiting in any way. Use of the fuel 16 as a nanorod 20 or nanowell 24 and spherical oxidizer 14 particles is also contemplated. The fuel 16 and the oxidizer 14 are suitably formed into any shapes that are complimentary to each other, and that increase the interfacial surface area compared to a random particle distribution.

A wide variety of fuels 16 are useful in this invention. Where the nanoenergetic material 10 is a thermite, the preferred fuel 16 is a metal. Preferred metals include aluminum, boron, beryllium, hafnium, lanthanum, lithium, magnesium, neodymium, tantalum, thorium, titanium, yttrium and

zirconium. The use of two or more metals, either physically mixed or alloyed, is contemplated. Referring to FIG. 2, the fuel 16 is formed into a shape, such as a nanosphere 18, that provides a homogeneous dispersion and a high surface area compared to the fuel volume. Sonication 26 is the preferred method for shaping the fuel 16 particles. The fuel 16 is placed in a solvent such as 2-propanol and positioned within the sonic field 30. When activated, the sound waves 30 disperse the fuel 16, creating extremely small particles that are often substantially monparticles, comprising few single atoms or molecules of fuel. The high degree of dispersion creates an extremely high fuel 16 surface area. Other shapes, or larger particles, are useful in applications where the extremely fast burn rate is not required.

The oxidizer 14 should be selected to have a high exothermic heat of reaction with the chosen fuel 16. The fuel 16 and the oxidizer 14 are chosen to assure that a self-propagating reaction takes place. As long as the fuel 16 has a higher free energy for oxide formation than the oxidizer 14, an exothermic replacement reaction will spontaneously occur. Preferred oxidizers 14 include copper oxide (CuO or Cu₂O), silver oxide (AgO or Ag₂O), boron oxide (B₂O₃) bismuth oxide (Bi₂O₃), Cobalt oxide (CoO), chromium oxide (CrO₃), iron oxide (Fe₂O₃) mercuric oxide (HgO), iodine oxide (I₂O₅), manganese oxide (MnO₂), molybdenum oxide (MoO₃), niobium oxide (Nb₂O₅), nickel oxide (NiO or Ni₂O₃), lead oxide (PbO or PbO₂), palladium oxide (PdO), silicone oxide (SiO₂), tin oxide (SnO or SnO₂), tantalum oxide (Ta₂O₅), titanium dioxide (TiO₂), uranium oxide (U₃O₈), vanadium oxide (V₂O₅) and tungsten oxide (WO₃).

Optimally, the amounts of fuel 16 and oxidizer 14 present in the thermite are in a stoichiometric ratio for combustion of the fuel with the oxidizer. Preferred equivalence ratio, $\Phi = \frac{(F/A)_{actual}}{(F/A)_{stoichiometric}}$ should be between 1.4 to 1.8.

Preferably, the oxidizer 14 is shaped into a nanorod 20, nanowire or a nanowell 24. In a preferred embodiment, the oxidizer 14 particle is shaped by providing 31 a polymeric surfactant having a micelle 32 forming of a crystalline structure inside the micelle 32 of a surfactant 34.

5 One preferred method of creating the crystals is by filling the micelle 32 with oxidizer precursors 36 that react to form the oxidizer 14 *in situ*. Synthesis of copper oxide nanorods 20, as shown in FIG. 3 for example, includes grinding copper chloride dihydrate and sodium hydroxide into fine powders, then added to a polyethylene glycol, such as PEG 400 (Alfa Aesar,

10 Ward Hill, MA).

The nanorods 20 are preferably synthesized inside and take the shape of the micelles 32 of the polymeric surfactant 34. Nanowires are long, thin nanorods 20. Diblock copolymers are known as surfactants 34 having micelles 32. Polyethylene glycol, such as PEG 400 is preferred for this task.

15 PEG 400 produces nanorods 20 of substantially uniform size. As the molecular weight of the polyethylene glycol increases, the diameter of the nanorod 20 changes, which leads to the nanowire-type structure. For example, PEG 200 produces nanospheres 18, PEG 400 produces nanorods 20, and PEG 2000 produces nanowires. The surfactant 34 is selected by the

20 size of its micelles 32 to produce nanorods 20 or nanowires of a particular diameter. Addition of water to the surfactant yields a mixture of nanorods 20 of varying length and having a longer average length.

In a preferred embodiment, the oxidizer 14 is formed by depositing 33 the reaction product of the oxidizer precursors 36 *in situ*

25 within the micelles 32 of the surfactant 34 to form the nanorods 20. In a preferred embodiment, copper chloride dihydrate and sodium hydroxide are combined to produce 35 copper oxide within the micelles of PEG 400. Other suitable precursors include copper nitrate, copper carbonate, copper acetate, copper sulfate, copper hydroxide, and copper ethoxide. The ratio of

30 copper chloride dihydrate to sodium hydroxide is from about 1.66 to about

2.1. The copper chloride dihydrate, sodium hydroxide and PEG 400 are pulverized with a mortar and pestle for 30 minutes. Preferred grinding times are from about 10 to about 45 minutes. Other methods of combining these ingredients include stirring, mixing, milling, and attrition. The copper chloride dihydrate and sodium hydroxide react to form copper oxide 14 in the PEG based template. Upon washing 39 with one or more solvents, such as water and ethanol, the polyethylene glycol is removed, yielding free-standing copper hydroxide and oxide nanorods 20. Calcination at a suitable temperature produces the finished nanorods 20 made up of the copper oxide oxidizer 14. For copper oxide, calcinations at 450°C for 4 hours is sufficient.

At least one of the oxidizer 14 and the fuel 16 is coated 41 with a molecular linking substance 40 that attracts the particles to each other. Preferably the molecular linker 40 is a polymer having two different binding sites, each of which chemically or physically bonds with either the fuel 16 or the oxidizer 14. Preferably, the binding sites are not random, but are spaced to closely fit the nanospheres 18 against the nanorods 20 for good interfacial surface area.

The presence of material other than fuel 16 and oxidizer 14 tends to slow the burn rate of the nanoenergetic material 10. Cross-linking or bonding of the molecular linker 40 with itself makes it difficult or impossible to remove excess polymer, thus reducing the burn rate. Thus, another preferred feature of the molecular linker 40 is that it does not bond with itself, allowing excess polymer to be removed until essentially a monolayer of molecular linker remains. Excess molecular linker 40 is preferably removed 43 by sonication of the particles after its application.

Suitable molecular linker polymers 40 include polyvinyl pyrrolidone, poly(4-vinyl pyridine), poly(2-vinyl pyridine), poly(ethylene imine), carboxylated poly(ethylene imine), cationic poly(ethylene glycol) grafted copolymers, polyamidine, polyether block amide, poly(acrylic acid),

cross-linked polystyrene, poly(vinyl alcohol), poly(n-isopropylacrylamide), copolymer of n-acryloxysuccinimide, poly(acrylonitrile), fluorinated polyacrylate, poly(acrylamide), polystyrene-poly(4-vinyl)pyridine and polyisoprene-poly(4-vinyl)pyridine. The use of the molecular linker 40 with
5 binding sites is a good method for self-assembly, because each polymer molecule has numerous binding sites. Therefore, when a molecular linker is adsorbed on a surface it has many more binding sites for binding other nanoparticles. Poly(4-vinyl pyridine) and its analogues are attractive to create self-assembled structures. The pyridyl group in its neutral form has a
10 lone pair of electrons which can be donated to form covalent bonds with metals, undergo hydrogen bonding with the polar species and interact with charged surfaces. The various ways in which molecular linker polymer can interact with surfaces makes it universal binding agent for nanostructural assemblies. The use of this polymer is not yet demonstrated to create self-
15 assembled ordered structure of energetic material.

Metal nanoparticles, such as aluminum nanoparticles, are sonicated in alcohol for a time sufficient to achieve homogenous dispersion. The preferred alcohol is 2-propanol, however, the use of other solvents that allow dispersion of the fuel. The ratio of fuel 16 to solvent of about 0.0875
20 to 0.75 is preferred, though other ratios are useful for other applications.

Sonication is conducted with any type of sonication equipment
44. Preferably, for synthesis purposes a sonic bath (Cole Parmer Model 8839) is used. The output sound frequency used is in the range of about 50-60 Hz. Duration of the sonication treatment is any time sufficient to remove
25 all of the molecular linker 40 except the layer that is bound to the fuel 16 or the oxidizer 14. Preferably, it is at least 3 hours, and is preferably from about 3 hours to about 16 hours. Centrifugation 47 is preferably combined with sonication to more rapidly remove the excess molecular linker 40.

The steps of sonication followed by centrifugation may be
30 repeated several times to remove excess molecular linker polymer 40 from

the fuel 16 or oxidizer 14 particles. The process is repeated as many times as needed. Polymer coated fuel particles, generally 48, result that have a very thin coating of polymer 40. Preferably the coating is so thin as to form essentially a polymer monolayer. As a result of this process, the resulting
5 coated fuel particles 48 are preferably from about 50 to about 120 nanometers in diameter. Particle diameters of about 50 to about 80 nanometers are more preferred. Reduction of coated fuel particle 48 diameter below about 18 nanometers results in a particle that has a ratio of fuel 16 to polymer 14 that is too low to burn efficiently.

10 Self-assembly of the oxidizer 14 nanorods 20 and the coated fuel particles 48 preferably takes place by sonication. Oxidizer 14 nanorods 20 are added to a solvent for several hours. The preferred solvent is 2-propanol, but other solvents for sonication as listed above are also useful. Duration for the sonication treatment is preferably from about 3 hours to
15 about 4 hours. The well-dispersed coated fuel particles 48 were then added 51 to the dispersion of the oxidizer 14 nanorods 20. An additional sonication step was carried out from about 3 hours to about 4 hours. While in the sonicator, the oxidizer 14 and the fuel 16 are thoroughly dispersed. To disperse the fuel 16 and oxidizer 14, a sonic wand with an output
20 frequency of about 55 kHz is used. The time for sonication is about 9 minutes, but longer sonication times are used depending on the specific application. During the dispersion, the fuel particles coated with the molecular linker 48 are likely to encounter and bind 53 with an oxidizer 14 nanorod 20. Since the molecular linker 40 has bonding sites specific for the
25 oxidizer 14, the oxidizer nanorods 20 will bind to the linker 40 on the coated fuel particle 48, holding them in a position to generate a product with a high interfacial surface area. The final solution is then dried to obtain the complete nanocomposite 10.

Oxidizer nanowires can also be synthesized and used to make
30 nanoparticle composite 10. The nanowires were preferably formed by

precipitation of the oxidizer 14 from a precipitate of two or more oxidizer precursors 36 from a solution that includes the surfactant 32. In one embodiment, copper oxide nanowires were synthesized using surfactant templating method. Preferably, polyethylene glycol was mixed with water
5 (2.5:1.5) under continuous stirring to make an emulsion. About 0.5g of copper chloride was dissolved in that emulsion. Another emulsion was prepared using same ratio of PEG and water and then 0.5g of NaOH was added into it under continuous stirring. The emulsion with copper chloride oxidation precursor 36 is then mixed with the emulsion with NaOH
10 oxidation precursor 36 and stirred slowly for several minutes. In the final solution, an excess amount of ethanol was added to form a grey precipitate. The grey precipitate was then sonicated for 3 hours then centrifuged at 3000 rpm for 10 minutes to collect precipitates. This cycle was repeated at least three times to remove the excess surfactant 32. The sample is then dried in
15 air at 60°C for four hours. The dried powder is then calcined at 450°C for 4 hours to get crystalline copper oxide nanowire.

Turning to FIG. 4, as another alternative to making nanorods 20, the oxidizer 14 can be formed into nanowells 24 using the technique of templating assisted nucleation. Nanowells 24 are shaped have holes or
20 openings in the oxidizer 14 structures into which the fuel 16 particles are placed. In this technique, the nanowells 24 are formed 52 around the exterior of the micelles 32 of the polymeric surfactant 34. Growth of mesopores is controlled on a length of 1-1.5 microns leading to nanowell 24 structures. This process can be used for any metal, metal oxide and metal
25 ligands. The size and shape of the nanowells 24 depends on the characteristic shape of the micelles 32 in the specific surfactant 34 selected. As with nanorods 20, the surfactant is removed 54 from the nanowell 24 prior to forming the nanoenergetic material 10.

Pluronic 123 (BASF, Mt. Olive, NJ) is a preferred block co-
30 polymer surfactant 34 for making nanowells 24. Preferably, the surfactant

34 is added to a solvent, such as ethylene glycol methyl ether (methoxyethanol)., however, other solvents such as ethoxyethanol, methoxyethanol acetate can also be used. The concentration of the surfactant 34 is in the range of 1-60 wt% based on metal alkoxide. Higher concentrations are generally limited by the solubility, which can be improved if a mild heating (up to about 40°C) with stirring is provided. To this block polymer 34 solution, copper ethoxide, in amounts of about 2-10% g/100 ml is added. Following this, a mild acid, such as 0.01 – 25 M acetic acid is added to generate a copper complex. This complex undergoes
10 olation in the presence of water and hydrochloric acid.

The fuel 16 is preferably input to the nanowells by means of impregnation. Fuel particles coated with a monolayer of the molecular linker 48 are prepared as described above. The sonicated and centrifuged particles are then dispersed in methoxyethanol and the second reaction
15 component to form the oxidizer. Fuel particles 16 are held within the nanowells 24 by the monolayer of molecular linker 40 present on the surface of the fuel.

Acetic acid and water were added to achieve the nanowell 24 gel structure. Following impregnation with the fuel 16, the gel was heat
20 processed to drive off organic impurities and templating agents. Preferably, the heat treatment occurs at temperatures of about 200°C to about 800°C. The duration of the heat treatment should be sufficient to drive off the unwanted components at the temperature selected. Pressure reduction also aids in driving off volatile components. During preparation of copper oxide
25 oxidizer 14, the gels were heat treated for 24 hours at 200°C under a vacuum. Dried gels were sonicated in n-hexane in presence of a surfactant and sonicated for few hours. After this, the gels were washed with ethanol and dried at 200°C for 2 h to obtain free flowing porous gel particles.

In addition to oxidizer 14 and fuel 16 nanoparticles, explosive
30 nanoparticles 50 are optionally added to some embodiments of the

nanoenergetic materials 10. These explosive nanoparticles 50 can be added to any of the above nanoenergetic composites 10 to improve the performance in terms of higher pressures and detonation. In synthesizing explosive nanoparticles 50, a process is used similar to that described above
5 with respect to formation of the fuel nanoparticles 18. An explosive material, such as ammonium nitrate, is formed into nanoparticles by dispersion in one or more solvents, then sonicated to obtain a homogeneous material. The solvents are removed by centrifugation and heating.

Stablization of explosive nanoparticles 50 is performed by
10 forming a core-shell structure with metal oxides. For example, a coating of copper oxide is formed on the ammonium nitrate nanoparticles 50. The process is suitable to produce the core-shell structure with several other metal oxides.

We have observed that the burn rate for $\text{Fe}_2\text{O}_3/\text{Al}$ combination
15 is significantly less compared to CuO_2/Al . The addition of nano-ammonium nitrate 50 to the iron oxide thermite increases the pressure and burn rate velocity due to gas generation. With the choice of a nanocomposite 10 of CuO/Al and nano-ammonium nitrate 50, the properties of the combined material can be tuned to achieve a green primer. However, the nanoenergetic
20 material 10 has the properties of a propellant by replacing CuO by Fe_2O_3 . FIG. 5 shows the graph of pressure over time, confirming formation of the shock wave.

Burn rates exceeding the speed of sound are attainable using the nanoenergetic materials of this invention. Table 1 shows the burn rates
25 of copper oxide and aluminum, where the materials differ only in configuration and copper oxide and aluminum added with polymer and explosive nanoparticles. As shown in this table, the copper oxide nanorods self-assembled with aluminum nanoparticles and the copper oxide nanowells impregnated with aluminum nanoparticles have the highest burn rates.

TABLE I

Serial number	Composite	Burn rate, m/s
1	Copper oxide (CuO) nanowells impregnated with Aluminum (Al)-nanoparticles	2100-2400
2	CuO nanorods mixed with Al-nanoparticles	1500-1800
3	CuO nanorods self-assembled with Al-nanoparticles	1800-2200
4	CuO nanorods mixed with 10% ammonium nitrate and Al-nanoparticles	1900-2100
5	CuO nanowire mixed with Al-nanoparticles	1900
6	CuO nanoparticles mixed with Al-nanoparticles	550-780
7	CuO nanorods mixed with Al-nanoparticles and 0.1% poly(4-vinyl pyridine)	1800-1900
8	CuO nanorods mixed with Al-nanoparticles and 0.5% poly(4-vinyl pyridine)	1400-1500
9	CuO nanorods mixed with Al-nanoparticles and 2% poly(4-vinyl pyridine)	900-1200
10	CuO nanorods mixed with Al-nanoparticles and 5% poly(4-vinyl pyridine)	400-600

Many uses are contemplated for the nanoenergetic materials described here. They may be used in applications where it is useful to generate a shock wave that is not pressure based. Such an application is in the medical field, where shock waves without detonation are used to crush stones in the kidney or gall bladder without the need for an invasive surgical procedure. Nanoenergetic materials are also useful as explosives, as detonators and other munitions applications. Because the nanoenergetic material burns so quickly, the heat from the flame can be dissipated rapidly. Thus, the nanoenergetic materials are useful in the vicinity of some materials or with some substrates without sustaining heat damage.

A particularly advantageous way of utilizing the nanoenergetic materials disclosed herein is described in copending United States Serial No. 11/xxx,xxx (Attorney Docket No. 2114.71713), entitled, "On-Chip Igniter and Method of Manufacture," previously incorporated by reference. The nanoenergetic material is patterned onto a chip having an igniter and a

detector. An electrical impulse heats the igniter, initiating combustion of the nanoenergetic material 10. When configured on the chip, the nanoenergetic material 10 is useful as an igniter for combustible materials, a detonator, a heat or power source or any apparatus that produces heat or a sonic shock
5 wave.

Example 1

Synthesis of Copper Oxide Nanorods

For the synthesis of 5.045 g of copper chloride dihydrate ($\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}$, 99.5% Sigma Aldrich) was pulverized to a fine powder by
10 grinding it in a mortar with a pestle. The finely powdered $\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}$ and 3.0 g NaOH were mixed together and 6.0 ml of PEG 400 (Polyethylene glycol 400, Alfa Aesar) was added into the mixture. This mixture was vigorously pulverized in a mortar for 45 minutes. During grinding, the copper chloride and sodium hydroxide were forced into the micelles of the
15 PEG 400. The CuCl_2 and NaOH then reacted to form CuO nanorods inside the micelles. The PEG 400 coating was removed by washing with water and ethanol.

Example 2

Synthesis of Coated Aluminum Nanospheres

20 Aluminum nanoparticles were made by sonicating 0.42 g of aluminum in 300 ml of 2-propanol for 5 hours to achieve homogenous dispersion. To this solution, 1 ml of 0.1% solution of poly (4-vinylpyridine) in 2-propanol was added and the resultant solution was sonicated for an additional 2 hours. This solution was centrifuged until a clear supernatant

was obtained. The solid recovered from the centrifuge was added to fresh 2-propanol, and the process of sonication followed by centrifugation was repeated 4-5 times to remove excess polymer. The coating that remained on the nanoparticles was substantially a monolayer.

5

Example 3

Self-Assembly of Nanoenergetics

One gram of copper oxide nanorods was sonicated in 200 ml of 2-propanol for 4 hours. The well-dispersed aluminum nanoparticles were then added into the nanorod dispersion. After sonicating for 3 hours, the final solution was dried at 120°C to obtain the self-assembled nanocomposite.

Example 4

Burn Rate Testing

The burn rate of the energetic material was evaluated using a Tektronix TDS460A 4-channel digital oscilloscope. For each experiment, a Lexan tube with 0.8 cm³ volume was filled up with energetic material and inserted into an aluminum block instrumented with fiber optic photo detectors and piezo-crystal pressure sensors to facilitate the burn rate and pressure measurement. The two pressure sensors (PCB 112A22) were installed at 2 cm spacing on one side of the block and optical fibers (Thorlabs M21L01) leading to photo-detectors (Thorlabs DET210) on the other side of the block at 1 cm interval. Each tube has two pre-drilled 1 mm ports in the tubing wall, which were aligned with the pressure sensors. As energetic reaction triggers, oscilloscope records voltage signal with respect to time for photo detectors and pressure sensors. The burn rate of energetic material was determined based on the rise time of signal for the two photo detectors and pressure was evaluated using voltage response of pressure sensors

that multiplied by the standard conversion factor. The results of burn rate testing is as follows:

5

TABLE 2

Oxidizer	Shape	Fuel	Shape	Burn Rate
CuO	Nanowell	Al	Nanoparticles	2400 m/s
CuO	Nanorods (no assembly)	Al	Nanoparticles	1480 m/s
CuO	Nanorods (self-assembled)	Al	Nanoparticles	2170 m/s
CuO	Nanorods	Al	Nanoparticles	2110 m/s
Fe ₂ O ₃	Aerogel	Al	Nanoparticles	970 m/s
CuO	Nanoparticles	Al	Nanoparticles	630 m/s
Bi ₂ O ₃	Nanoparticles	Al	Nanoparticles	340 m/s
MoO ₃	Nanoparticles	Al	Nanoparticles	171 m/s
WO ₃	Nanoparticles	Al	Nanoparticles	60 m/s

Example 5

Explosive nanoparticles were prepared by dissolving 25 gm of ammonium nitrate in 2-methoxyethanol to make 100 ml solution (25% weight/volume). The solution was then kept under vigorous stirring at 60°C for 4 hours. To this solution, 2-propanol was added as approximately 100 ml/min, under vigorous stirring. The suspension was thoroughly washed with either ethanol or 2-propanol to remove 2-methoxy ethanol. The sediment was separated by centrifugation at 2500 rpm for 10 minutes. The sediment was heated at 120°C in order to obtain ammonium nitrate nanoparticles. This process is also useful to obtain nanoparticles of traditional explosives or propellants.

Example 6

Nanoenergetic material including $\text{Fe}_2\text{O}_3/\text{Al}$ and nanoammonium nitrate was prepared. To 10 ml of a solution containing 1 g of ammonium nitrate in 2-methoxyethanol, 0.3 g of iron oxide gel was
5 added. The mixture was kept under vigorous stirring with a magnetic stirrer for 4 hours. The suspension was washed thoroughly with 2-propanol to remove excess ammonium nitrate from iron oxide. The sediment separated by centrifugation at 2500 rpm for 10 minutes was then dried in oven at 120°C for 2 hours. Ammonium nitrate infiltrated iron oxide was mixed with
10 aluminum nanoparticles to prepare a nanocomposite.

While particular embodiments of the nanoenergetic composites have been shown and described, it will be appreciated by those skilled in the art that changes and modifications may be made thereto without departing from the invention in its broader aspects and as set forth in
15 the following claims.

CLAIMS:

1. A structured, self-assembling nanoenergetic composition comprising:
 - 5 a nanostructure (20, 24) comprising at least one of the group consisting of a fuel (16) and an oxidizer (14); and
 - a plurality of substantially spherical nanoparticles (18) comprising at least the other of the group consisting of a fuel (16) and an oxidizer (14), whereby said spherical nanoparticles (18) are arranged around
 - 10 the exterior surface area of the nanostructure (20, 24).
2. The self-assembling nanoenergetic composition of claim 1 wherein the ratio of fuel (16) to oxidizer (14) is about 1.4 to about 1.8.
3. The self-assembling nanoenergetic composition of claim 1 wherein said nanorod (20) comprises said oxidizer (14).
4. The self-assembling nanoenergetic composition of claim 1 wherein said oxidizer (14) comprises at least one of the group comprising copper oxide, silver oxide, bismuth oxide, cobalt oxide, chromium oxide, iron oxide, mercuric oxide, iodine oxide, manganese oxide,
- 5 molybdenum oxide, niobium oxide, nickel oxide, lead oxide, palladium oxide, silicone oxide, tin oxide, tantalum oxide, titanium dioxide, uranium oxide, vanadium oxide and tungsten oxide.

5. The self-assembling nanoenergetic composition of claim 3 wherein said oxidizer (14) comprises copper oxide.

6. The self-assembling nanoenergetic composition of claim 1 wherein said fuel (16) comprises at least one of aluminum, boron, beryllium, hafnium, lanthanum, lithium, magnesium, neodymium, tantalum, thorium, titanium, yttrium and zirconium.

7. The self-assembling nanoenergetic composition of claim 5 wherein said fuel (16) comprises aluminum.

8. The self-assembling nanoenergetic composition of claim 1 further comprising a molecular linker (40) that bonds to each of said oxidizer (14) and said fuel (16).

9. The self-assembling nanoenergetic composition of claim 7 wherein said molecular linker (40) comprises a polymer having at least two binding sites.

10. The self-assembling nanoenergetic composition of claim 7 wherein said molecular linker (40) comprises at least one of the group consisting of polyvinyl pyrrolidone, poly(4-vinyl pyridine), poly(2-vinyl pyridine), poly(ethylene imine), carboxylated poly(ethylene imine), cationic poly(ethylene glycol) grafted copolymers, polyamine, polyether block amide, poly(acrylic acid), cross-linked polystyrene, poly(vinyl alcohol), poly(n-isopropylacrylamide), copolymer of n-acryloxysuccinimide, poly(acrylonitrile), fluorinated polyacrylate, poly(acrylamide), polystyrene-poly(4-vinyl)pyridine and polyisoprene-poly(4-vinyl)pyridine.

11. The self-assembling nanoenergetic composition of claim 1 wherein said nanostructure is one of a nanorod (20) and a nanowell (24).

12. A method of making a self-assembling structure comprising:

forming a nanostructure (20, 24) comprising at least one of a fuel (16) and an oxidizer (14);

5 creating a plurality of nanospheres (18) comprising at least the other of the fuel (16) and the oxidizer (14);

coating at least one of the group consisting of said nanostructure and said nanospheres (18) with a molecular linker (40); and

10 allowing at least the other of said nanostructure and said nanospheres (18) to bind to said molecular linker (40) forming the self-assembled structure.

13. The method of claim 12 wherein said nanostructure is at least one of the group consisting of a nanorod (20) and a nanowell (24).

14. The method of claim 13 wherein said forming step comprises forming said nanorod (20) within the micelle (32) of a polymeric surfactant (34).

15. The method of claim 14 wherein said forming step further comprises depositing a reaction product (36) within the micelle (32).

16. The method of claim 13 wherein said forming step comprises forming said nanowell (24) around the exterior of the micelle (32) of a polymeric surfactant (34).

17. The method of claim 16 wherein said forming step further comprises depositing a reaction product (36) around the micelle (34).

18. The method of claim 12 wherein said creating step further comprises dispersing the fuel (16) in a solvent to make a substantial number of fuel monoparticles.

19. The method of claim 18 wherein said dispersing step comprises sonication.

20. The method of claim 12 wherein said creating step comprises creating nanospheres (18) from fuel (16).

21. The method of claim 12 wherein said coating step further comprises removing the excess molecular linker (40).

22. The method of claim 21 wherein said coating step further comprises adding the nanospheres (18) to a fluid, sonicating the coated nanospheres (48) and separating the coated nanospheres (48) from the fluid.

23. The method of claim 22 wherein said separating step comprises centrifuging the mixture of nanospheres (48) and fluid.

24. The method of claim 12 wherein said self-assembled structure is a metastable intermolecular composite and wherein said metastable intermolecular composite produces a shock wave without detonation with propagation velocity higher than velocity of sound in the material.

25. The method of claim 12 wherein said self-assembled structure (10) is a metastable intermolecular composite with added polymers to produce a tunable pressure and propagation velocity.

26. The method of claim 12 wherein said self-assembled structure (10) is a metastable intermolecular composite with added explosive nanoparticles (50) to produce detonation.

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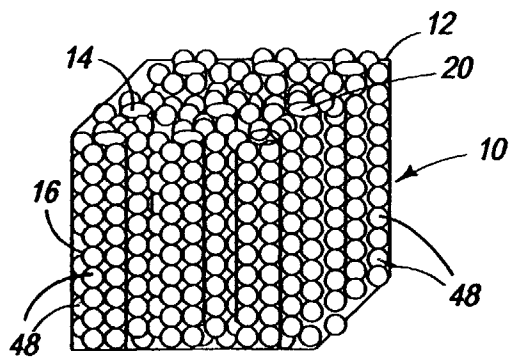


FIG. 1

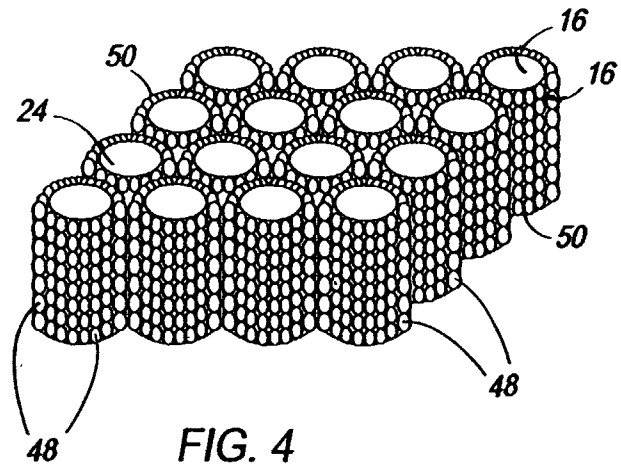


FIG. 4

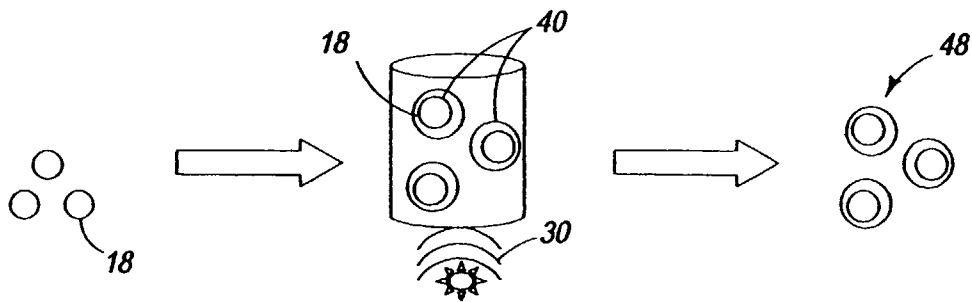


FIG. 2

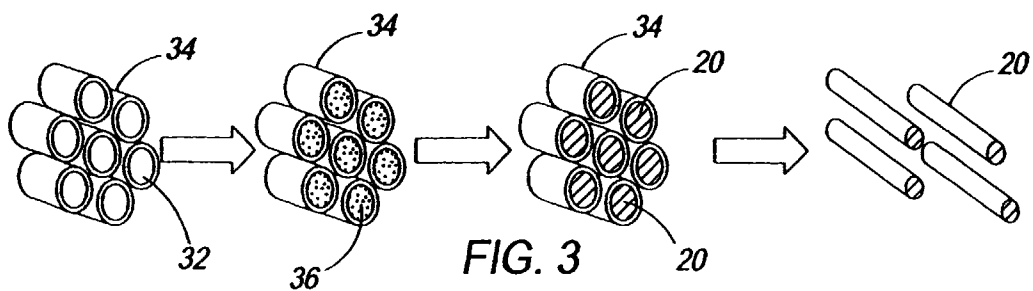


FIG. 3

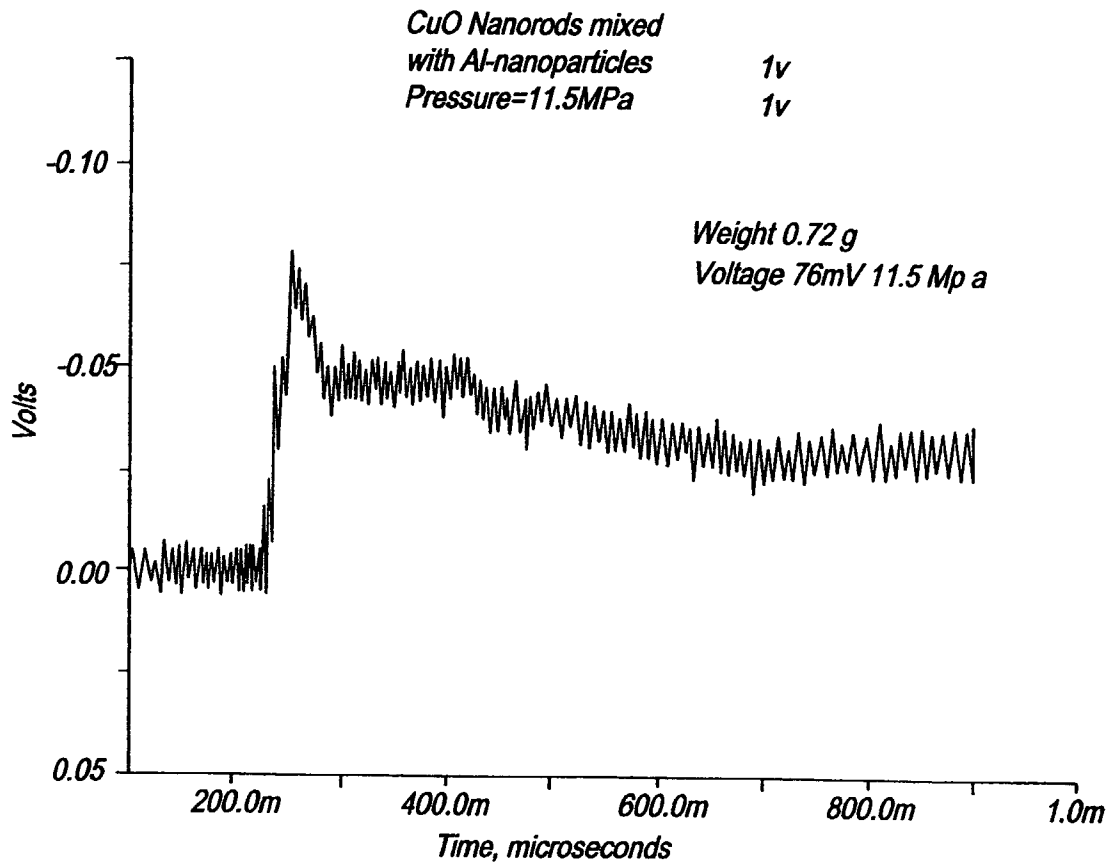


FIG. 5

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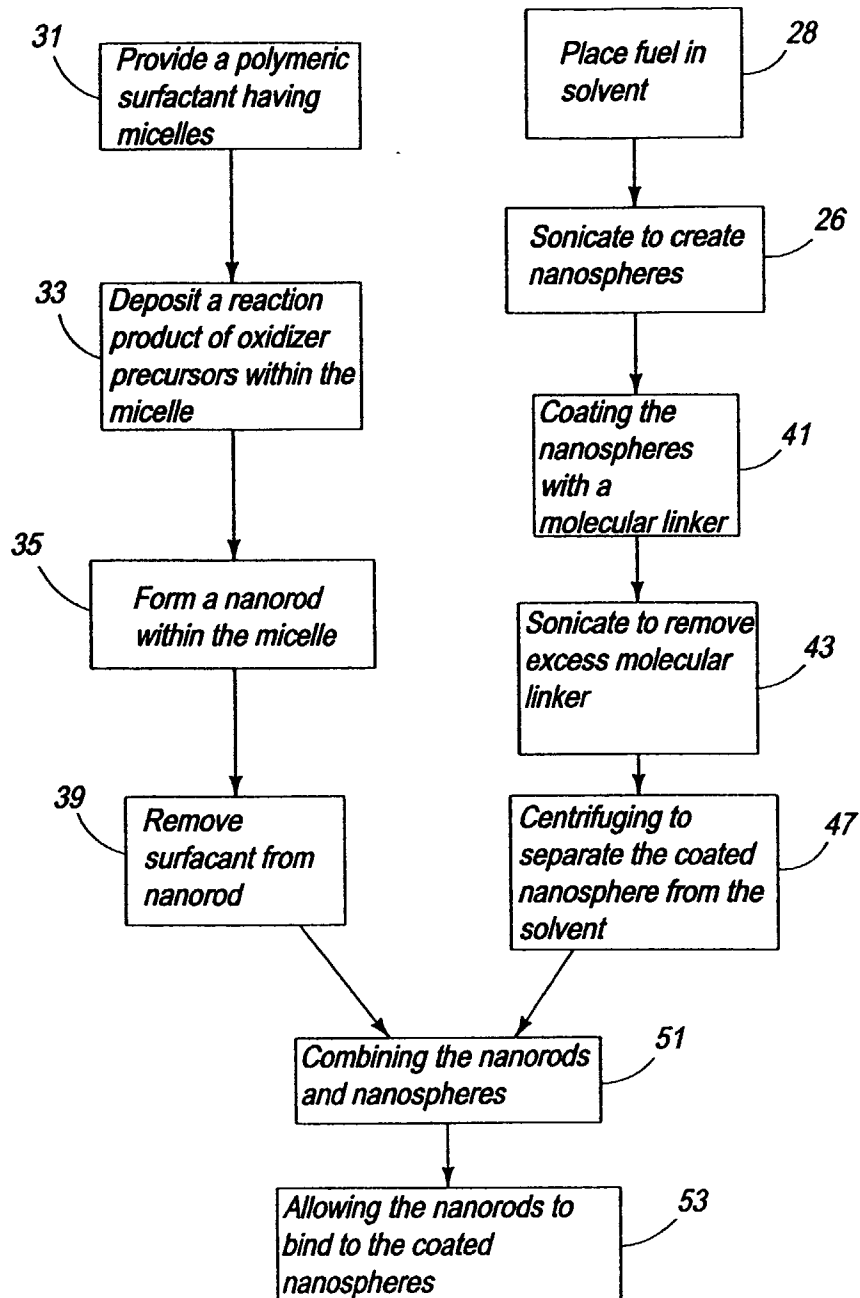


FIG. 6

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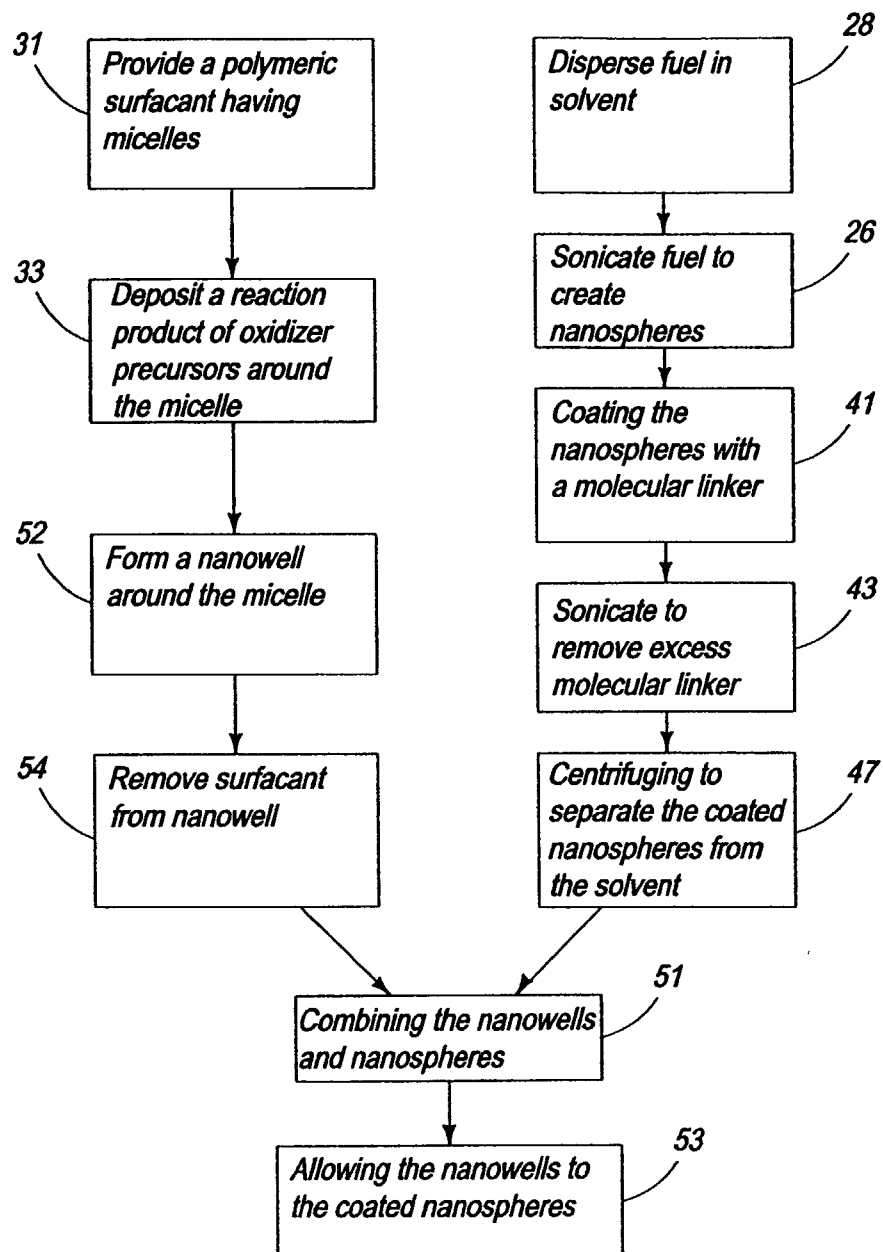


FIG. 7