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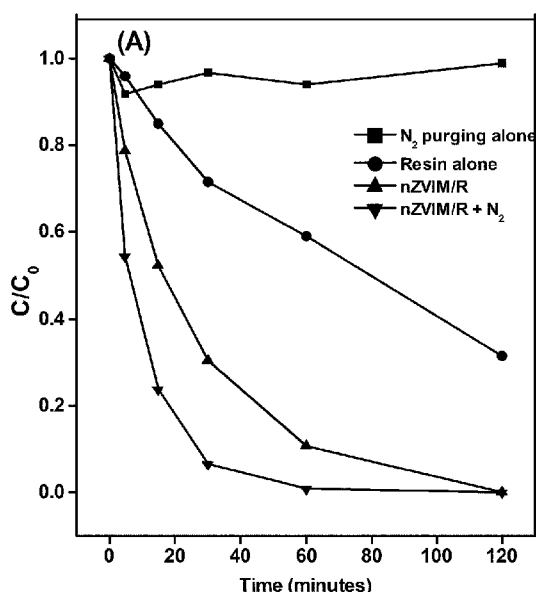


FIG. 5A

(57) Abstract: The present invention relates to a catalyst for degrading perfluorooctanoic acid (PFOA) in solution, comprising bimetallic catalytic nanoparticles immobilized on a substrate. The nanoparticles may include metals such as iron, manganese, cobalt, nickel, copper, and titanium. The substrate may be an ion exchange resin, such as an anion exchange resin. Methods for synthesizing the catalyst may include dissolving metal salts in water, titrating with a reducing agent, and immobilizing the nanoparticles on the resin. Methods of degrading PFOA include providing a plurality of bimetallic catalytic nanoparticles to a first solution comprising perfluorooctanoic acid. The method may optionally include additional steps for immobilizing the bimetallic catalytic nanoparticles, synthesizing the bimetallic catalytic nanoparticles, purging the first solution with an inert gas, and/or adjusting the pH of the first solution.

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BIMETALLIC NANOSCALE ZERO-VALENT CATALYSTS AND METHODS FOR CATALYTIC DEGRADATION OF PERFLUOROCARBOXYLIC ACIDS**CROSS-REFERENCE TO RELATED APPLICATIONS**

[0001] This application claims the benefit of the filing date of U.S. Provisional Application No. 63/524,433, filed on June 30, 2023, the disclosure of which is incorporated herein by reference in its entirety.

FIELD OF THE INVENTION

[0002] The present invention relates to bimetallic zero-valent nanoparticles and methods of using said bimetallic zero-valent nanoparticles to catalyze the degradation of perfluorocarboxylic acids (PFCAs) such as perfluorooctanoic acid (PFOA).

BACKGROUND OF THE INVENTION

[0003] This section is intended to introduce the reader to various aspects of art that may be related to various aspects of the present invention, which are described and/or claimed below. This discussion is believed to be helpful in providing the reader with background information to facilitate a better understanding of various aspects of the present invention. Accordingly, it should be understood that these statements are to be read in this light, and not as admissions of prior art.

[0004] Perfluorocarboxylic acids (PFCAs) are anthropogenic chemicals that are causing severe environmental and public health issues because they are bioaccumulative and highly water-soluble as well as due to their persistent nature. They have been widely used in making fluoropolymer coatings for heat, oil, stains, grease, and surfactants. Furthermore, PFCAs were used in clothing, furniture, adhesives, food packaging, non-stick cooking surfaces, electrical wires, insulation, and fire retardants. These compounds are reported as highly toxic and

revealing endocrine and developing effects. Many PFCAs, including perfluorooctanoic acid (PFOA), have been found in rivers, lakes, and many types of animals on land and the water. Moreover, the higher solubility of PFOA compared to many other persistent pollutants contributed to the increased PFOA migration to groundwater as well as bioaccumulation in the blood serum and liver rather than fatty tissue. Industrial wastewater and firefighters training sites are among the highest points of PFOA contamination. Proven adverse health effects, including immunotoxicity, neurotoxicity, endocrine-disrupting effects, and developmental effects, have been established from PFCAs exposure.

[0005] The high electronegativity of the fluorine atoms with the high strength of C-F bonds (C-F, 485 kJ/mol) in PFOA molecule, high redox potential to release F as F^- ($E^0 = 3.6$ V), and perfect orbitals overlap (2 s and 2p) makes it very resistant to conventional oxidation treatments. Moreover, scientists have proven the negligible reactivity of PFOA with hydroxyl radicals ($k_{OH^\bullet} \leq 10^5 \text{ M}^{-1} \text{ s}^{-1}$), thus making Advanced Oxidation Processes (AOPs) ineffective for PFOA treatment. As advanced reduction processes (ARPs) proved the ability to eliminate a wide variety of persistent contaminants and toxins, the focus increased on the role of an interesting chemical species, the hydrated electron (e_{aq}^-), due to its highly reactive intermediate in physical, chemical, and biological processes. This strong reductant proved its ability to degrade persistent contaminants, including halogenated organic compounds (HOCs) and bromate, to naturally biodegradable compounds. Since both direct ultraviolet (UV) and vacuum ultraviolet (VUV) proved only marginal removal of perfluorooctanesulfonic acid (PFOS) due to their weak absorption at 254 nm and 185 nm respectively, inorganic anions (i.e., ferrous ion, iodide, and sulfite) mediated UV photolysis were employed for the reduction of PFCAs. UV/sulfite system presented higher efficiency in reducing PFOS owing to the higher rate of generated e_{aq}^- in the system.

[0006] However, the reduction mentioned in the above methods has been unsuccessful for reducing PFOA. This may possibly be attributed to the possible cleavage of the C-C and C-F bonds in PFOS by photolysis was not sufficient to cleave the C-F bond in PFOA. Moreover, PFOS attains much higher first-order rate-constants (i.e., $6.5 \times 10^{-3} \text{ min}^{-1}$) towards hydrated electrons than PFOA (i.e., $2.9 \times 10^{-3} \text{ min}^{-1}$). Accordingly, there is a need for a catalyst that improves the reductive degradation of PFCAs, specifically PFOA.

SUMMARY OF THE INVENTION

[0007] Certain exemplary aspects of the invention are set forth below. It should be understood that these aspects are presented merely to provide the reader with a brief summary of certain forms the invention might take and that these aspects are not intended to limit the scope of the invention. Indeed, the invention may encompass a variety of aspects that may not be explicitly set forth below.

[0008] A first aspect of the invention is directed to a catalyst for degrading perfluorooctanoic acid, comprising: a plurality of bimetallic catalytic nanoparticles, wherein the bimetallic catalytic nanoparticles comprise metals selected from the group consisting of iron, manganese, cobalt, nickel, copper, and titanium; and a substrate, wherein the plurality of bimetallic catalytic nanoparticles are immobilized on the substrate; wherein the catalyst is capable of breaking carbon-fluorine bonds of perfluorooctanoic acid in solution.

[0009] In an embodiment of the first aspect of the invention, the bimetallic catalytic nanoparticles comprise manganese. In another embodiment of the first aspect of the invention, the bimetallic catalytic nanoparticles comprise iron. In another embodiment of the first aspect of the invention, the bimetallic catalytic nanoparticles comprise iron and manganese.

[0010] In an embodiment of the first aspect of the invention, the substrate comprises a resin. In another embodiment of the first aspect of the invention, the resin comprises an ion exchange resin. In another embodiment of the first aspect of the invention, the ion exchange resin is an anion exchange resin.

[0011] In an embodiment of the first aspect of the invention, the bimetallic catalytic nanoparticles have a core-shell structure. In one such embodiment, the core of the core-shell structure primarily comprises iron. In another such embodiment, the shell of the core-shell structure primarily comprises manganese. In a further embodiment, the shell of the core-shell structure primarily comprises manganese and the core of the core-shell structure primarily comprises iron.

[0012] In an embodiment of the first aspect of the invention, at least one of the metals is a zero-valent metal. In another such embodiment, both of the metals are zero valent metals. In a yet further embodiment, the zero valent metals comprise iron and manganese.

[0013] In an embodiment of the first aspect of the invention, the bimetallic catalytic nanoparticles have a substantially spherical shape.

[0014] A second aspect of the invention is directed to a method for catalyzing the degradation of perfluorooctanoic acid comprising: providing a plurality of bimetallic catalytic nanoparticles to a first solution comprising perfluorooctanoic acid, wherein the plurality of bimetallic catalytic nanoparticles comprises metals selected from the list consisting of iron, manganese, cobalt, nickel, copper, and titanium. In one such embodiment, the bimetallic catalytic nanoparticles comprise zero-valent iron. In another such embodiment, the bimetallic catalytic nanoparticles comprise zero-valent manganese. In yet another such embodiment, the bimetallic catalytic nanoparticles comprise zero-valent iron and zero-valent manganese. In a further embodiment thereof, the bimetallic catalytic nanoparticles have a core shell

structure, wherein the core primarily comprises zero-valent iron, and wherein the shell primarily comprises zero-valent manganese.

[0015] In an embodiment of the second aspect of the invention, the method further comprises immobilizing the plurality of bimetallic catalytic nanoparticles on a substrate, wherein providing the plurality of bimetallic catalytic nanoparticles comprises providing a plurality of immobilized bimetallic catalytic nanoparticles. In one such embodiment, the substrate is a resin. In a further embodiment thereof, the resin comprises an ion exchange resin. In a yet still further embodiment, the ion exchange resin is an anion exchange resin.

[0016] In an embodiment of the second aspect of the invention, immobilizing the plurality of bimetallic catalytic nanoparticles comprises mixing the bimetallic catalytic nanoparticles and the resin in water. In a further embodiment, the method further includes steps for removing the immobilized bimetallic catalytic nanoparticles from the water; washing the immobilized bimetallic catalytic nanoparticles; and drying the immobilized bimetallic catalytic nanoparticles. In one such embodiment, washing the immobilized bimetallic catalytic nanoparticles comprises washing the immobilized bimetallic catalytic nanoparticles with ethanol.

[0017] In another embodiment of the second aspect of the invention, the method further includes a step for synthesizing the bimetallic catalytic nanoparticles prior to providing the plurality of bimetallic catalytic nanoparticles to the first solution. In one such embodiment, synthesizing the bimetallic catalytic nanoparticles comprises dissolving an iron salt and a manganese salt in water to form a second solution comprising a plurality of iron cations and a plurality of manganese cations; and titrating the second solution against a reducing agent solution to produce the bimetallic catalytic nanoparticles as a precipitate. In a further embodiment thereof, the bimetallic catalytic nanoparticles comprise zero-valent iron and zero valent manganese. In one such embodiment, the reducing agent solution comprises sodium

borohydride. In one such embodiment, the iron salt comprises iron (III) chloride hexahydrate.

In one such embodiment, the manganese salt comprises manganese (II) acetate tetrahydrate.

In one such embodiment, the weight ratio of the iron salt to the manganese salt is 1:1.

[0018] In an alternate embodiment of the second aspect of the invention wherein the method comprises synthesizing immobilized bimetallic catalytic nanoparticles prior to providing the bimetallic catalytic nanoparticles to the first solution, wherein providing the plurality of bimetallic catalytic nanoparticles comprises providing a plurality of immobilized bimetallic catalytic nanoparticles. In one such embodiment, synthesizing the immobilized bimetallic catalytic nanoparticles comprises dissolving an iron salt, a manganese salt, and a resin in water to form a second solution comprising a plurality of iron cations and a plurality of manganese cations; and titrating the second solution against a reducing agent solution to produce the immobilized bimetallic catalytic nanoparticles as a precipitate. In a further embodiment thereof, the immobilized bimetallic catalytic nanoparticles comprise zero-valent iron and zero valent manganese. In one such embodiment, the reducing agent solution comprises sodium borohydride. In one such embodiment, the iron salt comprises iron (III) chloride hexahydrate. In one such embodiment, the manganese salt comprises manganese (II) acetate tetrahydrate. In one such embodiment, the weight ratio of the iron salt to the manganese salt is 1:1.

[0019] In another embodiment of the second aspect of the invention, the method further comprises purging the first solution with an inert gas. In one such embodiment, the inert gas is nitrogen gas.

[0020] In another embodiment of the second aspect of the invention, the method further comprises adjusting the pH of the first solution. In one such embodiment, adjusting the pH of the solution comprises adjusting the pH to a value greater than or equal to 6.8 and less than or equal to 9.6. In another such embodiment, adjusting the pH of the solution comprises

adjusting the pH of the solution to a value between 7.7 and 8.7. In another such embodiment, adjusting the pH of the solution comprises adjusting the pH to a value substantially equal to 8.2.

[0021] In another embodiment of the second aspect of the invention, the method comprises both purging the first solution with an inert gas and adjusting the pH of the first solution as described above.

BRIEF DESCRIPTION OF THE DRAWINGS

[0022] The accompanying drawings, which are incorporated in and constitute a part of this specification, illustrate embodiments of the invention and, together with the general description of the invention given above, and the detailed description given below, serve to explain the principles of the invention. Similar reference numerals are used to indicate similar features throughout the various figures of the drawings.

[0023] Fig. 1A shows an SEM image of amberlite IRA-402, Cl⁻ form resin taken at 100x magnification at a working distance of 12.4mm using a standard Everhart-Thornley detector (ETD).

[0024] FIG. 1B shows an SEM image of the surface morphology of bimetallic nanoscale zero-valent iron-manganese (nZVIM) immobilized on Amberlite IRA-402, Cl⁻ form ion exchange resin (nZVIM/R) taken at 50x magnification at a working distance of 12.4mm using a standard ETD.

[0025] FIG. 1C shows an SEM image of the bimetallic nZVIM/R catalyst taken at a magnification of 5000x at a working distance of 4.9 mm using a standard ETD.

[0026] Fig. 1D shows an Energy-dispersive X-ray spectroscopy (EDX) analysis of the bimetallic nZVIM/R catalyst.

[0027] Fig. 2 shows X-ray diffraction (XRD) patterns of synthesized bimetallic nZVIM/R catalyst and bare Amberlite IRA-402, Cl⁻ form ion exchange resin (R).

[0028] Fig. 3A shows a high-resolution transmission electron microscopy (HR-TEM) image of the bimetallic nZVIM/R catalyst.

[0029] Fig. 3B shows a selective area electron diffraction (SAED) pattern of the bimetallic nZVIM/R catalyst.

[0030] Fig. 3C shows an HR-TEM image of the bimetallic nZVIM/R catalyst.

[0031] Fig. 3D shows a TEM-EDX mapping image of the bimetallic nZVIM/R catalyst showing the distribution of manganese (Mn).

[0032] Fig. 3E shows a TEM-EDX mapping image of the bimetallic nZVIM/R catalyst showing the distribution of iron (Fe).

[0033] Fig. 3F shows a TEM-EDX mapping image of the bimetallic nZVIM/R catalyst showing the distribution of oxygen (O).

[0034] Fig. 4A shows the X-ray photoelectron spectroscopy (XPS) survey spectrum of the nZVIM/R catalyst.

[0035] Fig. 4B shows the XPS survey spectrum of the nZVIM/R catalyst for the Mn 2p orbitals before catalytic degradation of PFOA.

[0036] Fig. 4C shows the XPS survey spectrum of the nZVIM/R catalyst for the Mn 2p orbitals after catalytic degradation of PFOA.

[0037] Fig. 4D shows the XPS survey spectrum of the nZVIM/R catalyst for the Fe 2p orbitals after catalytic degradation of PFOA.

[0038] Fig. 4E shows the XPS survey spectrum of the nZVIM/R catalyst for the Fe 2p orbitals after catalytic degradation of PFOA.

[0039] Fig. 5A shows a line graph representing the catalytic degradation of PFOA as normalized concentration over time for systems using only nitrogen (N₂) gas purging alone, systems using only the Amberlite IRA-402, Cl⁻ form ion exchange resin (R), systems using only the nZVIM/R catalyst, and systems using the nZVIM/R catalyst with N₂ gas purging.

[0040] Fig. 5B shows a bar graph representing the corresponding apparent rate constant (k_{app}) values for catalytic degradation of PFOA using only N₂ gas purging alone, systems using only the Amberlite IRA-402, Cl⁻ form ion exchange resin (R), systems using only the nZVIM/R catalyst, and systems using the nZVIM/R catalyst with N₂ gas purging.

[0041] Fig. 6A shows a line graph representing the catalytic degradation of PFOA as normalized concentration over time for the nZVIM with N₂ gas purging at various pH values.

[0042] Fig. 6B shows a bar graph representing the corresponding apparent rate constant (k_{app}) values for catalytic degradation of PFOA for the nZVIM with N₂ gas purging at various pH values.

[0043] Fig. 7A shows the mass spectra of degradation products resulting from the catalyzed PFOA degradation at five (5) minutes.

[0044] Fig. 7B shows the mass spectra of degradation products resulting from the catalyzed PFOA degradation at fifteen (15) minutes.

[0045] Fig. 7C shows the mass spectra of degradation products resulting from the catalyzed PFOA degradation at thirty (30) minutes.

[0046] Fig. 7D shows the mass spectra of degradation products resulting from the catalyzed PFOA degradation at one (1) hour.

[0047] Fig. 7E shows the mass spectra of degradation products resulting from the catalyzed PFOA degradation at two (2) hours.

[0048] Fig. 7F shows the mass spectra of degradation products resulting from the catalyzed PFOA degradation at four (4) hours.

[0049] Fig. 8 shows a line graph representing the evolution profile of PFOA degradation products using the nZVIM/R catalyst having m/z values of 293.176, 375.179, 221.155, and 236.106.

DETAILED DESCRIPTION OF EMBODIMENTS OF THE INVENTION

[0050] One or more specific embodiments of the present invention will be described below. In an effort to provide a concise description of these embodiments, all features of an actual implementation may not be described in the specification. It should be appreciated that in the development of any such actual implementation, as in any engineering or design project, numerous implementation-specific decisions must be made to achieve the developers' specific goals, such as compliance with system-related and business-related constraints, which may vary from one implementation to another. Moreover, it should be appreciated that such a development effort might be complex and time consuming, but would nevertheless be a routine undertaking of design, fabrication, and manufacture for those of ordinary skill having the benefit of this disclosure.

[0051] Bimetallic, nanoscale metal catalysts have been identified as useful in catalyzing the reductive degradation of PFCAs, including PFOA. These bimetallic, nanoscale metal catalysts can be represented using " $n(M_1)(M_2)$ " wherein M_1 corresponds to a first metal and

M₂ corresponds to a second metal. In one embodiment, the first and second metals are selected from the list consisting of iron (Fe), manganese (Mn), cobalt (Co), nickel (Ni), copper (Cu), and titanium (Ti). In an alternate embodiment, the first metal is selected from a list consisting of iron, cobalt, nickel, and copper. In an alternate embodiment, the second metal is selected from a list consisting of manganese and titanium. In one embodiment, the first metal is iron and the second metal is manganese.

[0052] In one embodiment, at least one of the first metal and the second metal is in a zero-valent state. In one such example, the first metal is in a zero-valent state. In another such example, the second metal is in a zero-valent state. In yet another such example, both the first and second metal are in a zero-valent state. In such an embodiment, these bimetallic, nanoscale catalysts can be represented using “nZV(M₁)(M₂)”, wherein M₁ corresponds to a first zero-valent metal and M₂ corresponds to a second zero-valent metal. In one embodiment, the first and second metals are selected from the list consisting of iron (Fe), manganese (Mn), cobalt (Co), nickel (Ni), copper (Cu), and titanium (Ti). In one further embodiment, the first zero-valent metal is selected from a list consisting of iron, cobalt, nickel, and copper. In an alternate further embodiment, the second zero-valent metal is selected from a list consisting of manganese and titanium. In one embodiment, the catalyst is a nanoscale zero-valent iron-manganese catalyst (nZVIM).

[0053] The bimetallic, nanoscale catalyst may have a core-shell structure wherein the shell substantially comprises the first metal and the core substantially comprises the second metal. In one such embodiment, the first metal is iron. In another such embodiment, the second metal comprises manganese. In a further embodiment, the core-shell structure forms a substantially spherical shape.

[0054] In one embodiment, a plurality of the bimetallic, nanoscale catalysts described above are immobilized on a substrate (nZVIM/S). In one embodiment, the bimetallic,

nanoscale catalysts are immobilized on a substrate to reduce the agglomeration of catalyst particles. In another embodiment, the bimetallic, nanoscale catalysts are immobilized on a substrate to increase surface area of the catalyst. In another embodiment, the bimetallic, nanoscale catalysts are immobilized on a substrate to facilitate collection of the catalyst after degrading the PFCA compound to limit environmental toxicity caused by the catalyst.

[0055] The substrate on which the catalyst is immobilized on may be selected from the list consisting of clays, a resin (e.g., an ion exchange resin), and biochar. In one embodiment, the substrate on which the catalyst is immobilized is a resin, which can be represented using “ $nZV(M_1)(M_2)/R$ ”. In a further embodiment, the resin is an ion exchange resin. In a yet further embodiment, the ion exchange resin is an anion exchange resin. In an alternate further embodiment, the ion exchange resin is a cation exchange resin.

[0056] The $n(M_1)(M_2)$, $nZV(M_1)(M_2)$, and/or the $nZV(M_1)(M_2)/R$ may be used in a method for catalytic degradation of a PFCA such as, for example, PFOA. In one such embodiment, the $n(M_1)(M_2)$ is used as a catalyst for the catalytic degradation of PFOA. In another such embodiment, the $nZV(M_1)(M_2)$ is used as a catalyst for the catalytic degradation of PFOA. In yet another embodiment, the $nZV(M_1)(M_2)/R$ is used as a catalyst for the catalytic degradation of PFOA.

[0057] The method for catalyzing the degradation of PFOA includes a step for providing a plurality of at least one of the bimetallic, nanoscale catalysts described above—such as the $n(M_1)(M_2)$, $nZV(M_1)(M_2)$, or the $nZV(M_1)(M_2)/R$ —to a solution comprising PFOA.

[0058] In one embodiment, the method includes a step for immobilizing one of the $n(M_1)(M_2)$ or the $nZV(M_1)(M_2)$ on a substrate, such that providing the $n(M_1)(M_2)$ or the $nZV(M_1)(M_2)$ to the PFOA solution involves providing the $n(M_1)(M_2)/S$ or the $nZV(M_1)(M_2)/S$ to the PFOA solution. In a further embodiment, the method involves a step for immobilizing one of the $n(M_1)(M_2)$ or the $nZV(M_1)(M_2)$ on a resin, then providing the

$n(M_1)(M_2)/R$ or the $nZV(M_1)(M_2)/R$ to the PFOA solution. In a yet further embodiment, the method involves immobilizing one of the $n(M_1)(M_2)$ or the $nZV(M_1)(M_2)$ on an ion exchange resin. In a still further embodiment, the method involves immobilizing one of the $n(M_1)(M_2)$ or the $nZV(M_1)(M_2)$ on an anion exchange resin, such as the Amberlite IRA-402, Cl^- form, ion exchange resin.

[0059] In one embodiment, the method step for immobilizing the plurality of bimetallic catalytic nanoparticles on the substrate involves mixing the plurality of bimetallic catalytic nanoparticles and the substrate (e.g., the resin, the ion exchange resin, or the anion exchange resin) together in water. In a further embodiment, the method further includes one or more step selected from the following list: removing the immobilized bimetallic catalytic nanoparticles from the water; washing the immobilized bimetallic catalytic nanoparticles; and drying the immobilized bimetallic catalytic nanoparticles. In a yet further embodiment, the method includes separate steps for removing, washing, and drying the immobilized bimetallic catalytic nanoparticles described above. In embodiments including a step for washing the bimetallic catalytic nanoparticles, washing the bimetallic catalytic nanoparticles involves using an organic solvent such as, for example, ethanol.

[0060] In one embodiment of the method for catalytically degrading PFOA, the method includes a step for synthesizing the bimetallic catalytic nanoparticles prior to providing the plurality. In one such embodiment, synthesizing the bimetallic catalytic nanoparticles includes dissolving a first metal salt and a second metal salt in water to form a synthesis solution, wherein the synthesis solution contains a plurality of first metal cations and second metal cations; and titrating the synthesis solution against a reducing agent solution to produce the bimetallic nanoparticles as a precipitate. For example, the method may include a step for dissolving an iron salt (e.g., iron (III) chloride hexahydrate) and a manganese salt (e.g., manganese (II) acetate tetrahydrate) in water to form a synthesis solution containing iron and

manganese cations, then titrating that synthesis solution against a reducing agent solution (e.g., a borohydride solution) to produce the nZVM bimetallic catalytic nanoparticles. In a yet further embodiment, the weight ratio of the first metal salt to the second metal salt in the synthesis solution is approximately 1:1, or alternatively is 1:1.

[0061] In alternate embodiments of the method including the step for synthesizing the bimetallic catalytic nanoparticles, the above step can be modified to synthesize the immobilized bimetallic catalytic nanoparticle in a single step. In one such embodiment, forming the synthesis solution involves adding the substrate to the synthesis solution including the first metal cations and the second metal cations such that, when the synthesis solution is titrated against the reducing agent solution, the immobilized bimetallic catalytic nanoparticles are produced in a single step.

[0062] The method for catalytically degrading PFOA using the bimetallic catalytic nanoparticles may further comprise purging the PFOA solution with an inert gas. This may improve the catalytic degradation of PFOA by removing dissolved oxygen from the solution. In one such embodiment, the inert gas used to purge the PFOA solution is selected from the list consisting of nitrogen (N₂) gas, argon gas, helium gas, neon gas, krypton gas, Xenon gas, and radon gas. In a further such embodiment, the inert gas is nitrogen gas.

[0063] The method for catalytically degrading PFOA may further include a step for adjusting the pH of the solution. The pH of the solution can impact the final concentration of PFOA in solution and/or the speed of the reaction. In one such embodiment, the pH is adjusted to a value greater than or equal to 6.8, alternatively greater than or equal to 7.2, or alternatively greater than or equal to 8.2. In another such embodiment, the pH is adjusted to a value less than or equal to 9.6, alternatively less than or equal to 8.7, or alternatively less than or equal to 8.2. In yet another such embodiment, the pH is adjusted to a value greater than or equal to 6.8 and less than or equal to 9.6, alternatively greater than or equal to 7.7 and less

than or equal to 8.7, or alternatively approximately equal to 8.2. In a yet still alternate embodiment, the pH is adjusted to a value equal to 8.2.

[0064] In one embodiment, adjusting the pH of the PFOA solution involves adding an acid salt to the PFOA solution. In another embodiment, adjusting the pH of the PFOA solution involves adding a basic salt to the PFOA solution. In yet another embodiment, adjusting the pH of the PFOA solution involves adding a buffer to the PFOA solution. In one such embodiment, the buffer may be configured to maintain the pH of the PFOA within a certain range. Exemplary buffers include, by way of example and not limitation, tricine, bicine, HEPBS, and TAPS.

[0065] In one embodiment, greater than or equal to 80% of the PFOA in the PFOA solution may be catalytically degraded in less than or equal to 4 hours, alternatively less than or equal to 2 hours, alternatively less than or equal to 1 hour, or alternatively less than or equal to 30 minutes. In another embodiment, greater than or equal to 90% of the PFOA in the PFOA solution may be catalytically degraded in less than or equal to 4 hours, alternatively less than or equal to 2 hours, or alternatively less than or equal to 1 hour. In yet another alternate embodiment, greater than or equal to 95% of the PFOA in the PFOA solution may be catalytically degraded in less than or equal to 4 hours, alternatively less than or equal to 2 hours, or alternatively less than or equal to 1 hour.

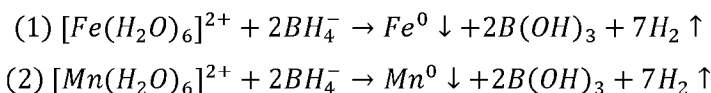
[0066] EXAMPLE 1

[0067] *Materials*

[0068] Sodium borohydride (99%) and iron (III) chloride hexahydrate (ACS reagent 97%) were supplied by Sigma-Aldrich. Amberlite IRA-402, Cl⁻ form, ion exchange resin, Manganese (II) acetate tetrahydrate (99+ %), and ethanol (99.5%, ACS reagent) were supplied by Across.

[0069] *Catalyst Synthesis Method*

[0070] A one-pot borohydride reduction method was used according to the following reactions:



[0071] The nZVIM immobilized on ion exchange resin (R) to produce the nZVIM/R as follows: 1 g of Manganese (II) acetate tetrahydrate was dissolved in 2 mL water and then mixed with 1 g of iron (III) chloride hexahydrate, and the solution was diluted up to 100 mL water milli-Q water. To this solution, 0.6 g of Amberlite IRA-402, Cl⁻ form, ion exchange resin was added. The mixture was stirred overnight on a magnetic stirrer. The prepared solution was then titrated against sodium borohydride (2g/100mL) in a dropwise manner. Subsequently, the black color precipitate of nZVIM immobilized on ion exchange resin was obtained, which was collected after centrifugation at 4000 rpm for 25 mins and washed with ethanol three times. The obtained catalyst was then dried in a vacuum drying oven at 60 °C for 2hrs before use.

[0072] *Catalyst Characterization*

[0073] The crystallographic investigations of the as-synthesized catalyst were performed by X-ray diffraction analysis (a PAN-analytical-Xpert Pro diffractometer was used at $\lambda=1.5406 \text{ \AA}$ of copper K α radiation). The morphology and material properties were investigated by energy-dispersive X-ray spectroscopy (EDS or EDX) installed in the scanning electron microscopy (SEM). The detailed material structure and particle crystallinity were examined by JEOL (JEM-2010 F) high resolution-transmission electron microscope (HR-TEM, 200 kV field transmission). The surface properties of the nZVIM immobilized on ion exchange resin were characterized by x-ray photoelectron spectroscopy (XPS) equipped with a monochromated (Al) X-Ray source with 12 kV and 10 mA.

[0074] *Discussion*

[0075] FIG. 1A represents the SEM image of bare resin, which depicts the clean and smooth surface. The SEM image of nZVIM loaded over ion exchange resin (nZVIM/R) is shown in FIG. 1B. With reference to FIG. 1C, it can be seen that the nZVIM particles are mostly spherical and are well dispersed over the ion exchange resin. The main elements of the as-synthesized nZVIM immobilized on ion exchange resin were Fe, Mn, O, S, Cl, Na as indicated by SEM-EDX graph shown in FIG. 1D. This EDX image confirmed the successful synthesis of Mn^0 and Fe^0 over the surface of ion-exchange resin and relative inclusion of each element in the sample as shown below.

Element	Weight (%)	Atomic (%)	Error (%)
Oxygen (O)	49.84	73.14	6.52
Sodium (Na)	8.03	8.20	18.50
Sulfur (S)	1.98	1.45	13.64
Chloride (Cl)	0.72	0.47	29.86
Manganese (Mn)	23.30	9.96	2.43
Iron (Fe)	16.14	6.79	3.32

Table 1: Table 1 shows the relative weight and atomic percent inclusions for each element detected in the synthesized nZVIM/R catalyst and the errors for each.

[0076] The successful synthesis of nZVIM/R has also been confirmed by the XRD analysis as shown in FIG. 2 which contains line 10 showing the XRD diffraction of the nZVIM/R sample and line 20 which shows the XRD diffraction of the resin (R) by itself. The diffraction peaks at $2\theta = 45.5^\circ$ and 50.4° corresponds to Mn^0 (JCPDS No. 88-2327) and are in accordance with the previous findings in the field, while the appearance of peaks at $2\theta = 44.7^\circ$ and 65.2° reveals the existence of Fe^0 (JCPDS No.87-0721). Moreover, there is an additional peak at $2\theta = 33.58^\circ$ in the XRD pattern of nZVIM/R and is comparable to the XRD peak in case of bare resin ($2\theta = 31.39^\circ$) could be attributed to the chlorides in the resin (R).

[0077] With reference to FIG. 3A, the TEM image of nZVIM particles depicts the well-dispersed spherical and a characteristic core-shell structure for the as-synthesized nZVIM catalysts. The outer shell is due to Mn^0 , while the metallic Fe^0 is present in the core. The formation of manganese oxides from Mn^0 could also be advantageous in the catalytic oxidation of PFOA. With reference to FIG. 3B, the selective area electron diffraction (SAED) image shows circular rings, which suggests that the as synthesized nZVIM/R has a semi-crystalline nature. This finding is consistent with the XRD results discussed above. With reference to FIG. 3C, the high-resolution transmission electron microscope (HRTEM) image of nZVIM/R indicates crystal lattice distances of 0.210 nm and 0.205 nm in the sample, which corresponds to the (033) plane of Mn^0 and the (011) plane of Fe^0 , respectively.

[0078] With reference to FIGS. 3D-F, the TEM-EDX mapping of nZVIM/R for elemental Mn, Fe, and O, respectively, are shown. The TEM-EDX mapping indicates that both Mn and Fe are homogeneously distributed. The brighter contrast suggests that Mn forms the outer layer/shell (FIG. 3D) and Fe is in the core/attached to the resin's surface (FIG. 3E). FIG. 3F suggests that the evenly distributed presence of O indicates the oxides of Mn and/or Fe.

[0079] With reference to FIGS. 4A-E, the XPS surveys of the nZVIM/R samples are shown. FIG. 4A depicts the full XPS survey of nZVIM immobilized on ion exchange resin. It can be seen that the as-synthesized catalyst mainly consists of Cl 2p, C 1s, O 1s, Mn 2p, Fe 2p, and Na 1s. The peaks of Cl 2p and Na 1s probably come from the NaBH_4 , applied as a reducing agent during the synthesis procedures.

[0080] FIGS. 4B and 4C respectively show the XPS spectra for Mn before and after the nZVIM/R catalyst is used for catalytic degradation of PFOA (discussed further below in Example 2). With reference to FIG. 4B, it can be seen that Mn 2p shows peaks at binding energy (BE) values of 639.47 eV, 640.57 eV, and 641.03 eV ($\text{Mn } 2p_{3/2}$), corresponding to

Mn⁰, Mn (II), and Mn (III), respectively. The peak at 644.21 eV is a satellite peak, and the peaks at 648.98 eV, 650.44 eV, and 651.83 eV (Mn 2p_{1/2}) are attributed to Mn⁰, Mn (III) and Mn (IV), respectively. With reference to FIG. 4C, after the catalyst has been applied for degradation of PFOA, not only are the BE values of Mn 2p are slightly shifted towards higher values, but also the peak intensity of Mn⁰ also decreased. This suggests the partial oxidation of Mn⁰ and Mn (II).

[0081] FIGS. 4D and 4E respectively show the XPS spectra for Fe before and after the nZVIM/R catalyst is used for catalytic degradation of PFOA (discussed further below in Example 2). With reference to FIG. 4D, the high-resolution XPS spectra of Fe 2p clearly shown the existence of Fe⁰ at 706.5 eV in the nZVIM/R before use in catalytic degradation. With reference to FIG. 4E, after applying the catalyst for degradation of PFOA, the Fe 2p shifted to higher binding energy values, and the corresponding peak for Fe⁰ disappeared and suggesting the oxidation of Fe⁰ to Fe (II) and Fe (III) states. Moreover, it can be seen that the peak intensity of Fe 2p is lower compared to Mn 2p, which is due to the shielding effect of Mn on the outer surface and thus confirms the core-shell structure of the as-synthesized catalyst with Fe in the core.

[0082] EXAMPLE 2

[0083] *Materials*

[0084] Perfluorooctanoic acid (96%), sodium borohydride (99%), and iron (III) chloride hexahydrate (ACS reagent 97%) were supplied by Sigma-Aldrich. Amberlite IRA-402, Cl⁻ form, ion exchange resin, Manganese (II) acetate tetrahydrate (99+ %), and ethanol (99.5%, ACS reagent) were supplied by Across.

[0085] *Catalytic Degradation Analysis*

[0086] A nZVIM/R catalyst was prepared according to the Catalyst Synthesis Method described above in Example 1.

[0087] A stock solution of PFOA (100 mg L^{-1}) was prepared in Milli-Q water and stored at 4°C before use. The catalytic degradation experiments were conducted in 60 mL glass tubes with a PFOA initial concentration of 1 mg L^{-1} . The amount of catalyst being added was 0.08g. The samples were taken out from the reactor at time intervals of 0, 5, 15, 30, 60, 120, and 240 mins and were filtered by $0.45 \mu\text{m}$ polypropylene filters to remove the catalyst particles before analysis.

[0088] In embodiments where the PFOA solution was subjected to nitrogen (N_2) gas purging, N_2 gas was bubbled through the system for the duration of the catalytic degradation reaction.

[0089] In embodiments where the PFOA solution was subjected to pH adjustment, HClO_4 was added to the solution to lower to pH and/or NaOH was added to the solution to raise the pH.

[0090] *Characterization Methods*

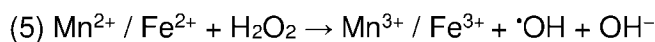
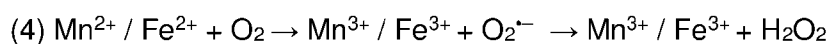
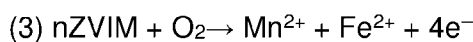
[0091] The quantitative and qualitative analysis of PFOA and its degradation products (DPs) was performed by liquid chromatography/Quadrupole TOF-tandem electron spray ionization mass spectrometry (LC/Q-TOF-ESI-MS) in negative ionization mode. The mobile phase composition was composed of water and methanol, and the flow rate was controlled at 0.4 mL min^{-1} . The gradient elution was applied at 5% B that was increased up to 95% 10 min, and then finally to 5% at 12 min. The column used for analysis was Agilent Zorbax Eclipse XDB-C18, narrow bore $2.1 \times 100 \text{ mm}$, 3.5 microns.

[0092] *Discussion*

[0093] FIG. 5A compares the degradation of PFOA as a function of normalized concentration of PFOA after being subjected to the following conditions: nitrogen (N_2) gas purging only; the Amberlite IRA-402, Cl^- form, ion exchange resin only; the nZVIM/R catalyst without N_2 purging; and the nZVIM/R catalyst with N_2 purging. The results depict

that for the reaction time of 60 minutes, PFOA degradation (1 mg L^{-1}) was 6.1% under N_2 -purging alone, 40.9% with resin-alone, 89.0% for the nZVIM/R without N_2 purging, and 98.5% for the nZVIM/R with N_2 purging. Thus, nZVIM/R showed efficient catalytic performance, and the catalytic degradation of PFOA was accelerated when the reaction mixture was purged with N_2 -gas. With reference to FIG. 5B, the k_{app} values were calculated as 0.0002, 0.0094, 0.0382, and 0.0634 for N_2 -purging alone, resin-alone, nZVIM/R without N_2 purging, and nZVIM/R with N_2 purging, respectively.

[0094] At the first stage, electrons are generated due to the oxidation of nZVIM (*see* Reaction 3 below). Under neutral conditions, the corrosion products of nZVIM (Mn^{2+} and Fe^{2+}) reduces O_2 to H_2O_2 via a series of one-electron transfer (*see* Reaction 4 below). The produced H_2O_2 may then be converted to $\cdot\text{OH}$ (*see* Reaction 5 below). These generated reductive and oxidative species ($4\text{e}^- + \cdot\text{OH}/\text{O}_2^{\cdot-}$) are responsible for the efficient degradation of PFOA molecule via the nZVIM/R catalyst (*see* Reaction 6 below). Moreover, the accelerated degradation of PFOA in the case of the nZVIM/R with N_2 purging is due to the favored reductive environment by eliminating dissolved oxygen from the reaction. Since it has been documented that the reductive pathways are generally more preferable for PFOA degradation. Thus, it can be concluded that both reductive and oxidative species are involved in the degradation of PFOA by nZVIM/R.



[0095] FIGS. 6A and 6B represent the comparative removal of PFOA at pH levels of 4.4, 6.8, 8.2 and 9.6 by nZVIM/R with N_2 purging. With reference to FIG. 4A, it can be seen that

catalytic degradation of PFOA was appreciable at all pH values except at pH = 4.4. The % degradation of PFOA by nZVIM/R with N₂ purging at pH = 4.4, 6.8, 8.2 and 9.6 was 27, 76.2, 76.8 and 78.5%, respectively after one hour. With reference to FIG. 6B, the k_{app} values for catalytic degradation of PFOA by nZVIM/R with N₂ purging at pH = 4.4, 6.8, 8.2 and 9.6 were 0.01, 0.0634, 0.0836 and 0.042 min⁻¹, respectively. This suggests that the highest catalytic degradation of PFOA by nZVIM/R + N₂-purging process was achieved at pH = 8.2 and lowest degradation at pH = 4.4. The higher degradation of PFOA by N₂-purging process at pH = 8.2 could be associated with the formation of aqueous electrons e_{aq}^- , which is responsible for reductive degradation of PFOA.

With reference to FIGS. 7A-7F and 8, degradation byproducts (DPs) of PFOA were analyzed over time, indicating the mass spectra of PFOA DPs at a reaction times of 5, 15, 30, 60, 120, and 240 minutes to confirm the degradation of PFOA, respectively. Four DPs, having m/z values of 375.179 (DP1), 293.176 (DP2), and 236.106 (DP3), 221.155 (DP4) were found. With reference to FIG. 8, the appearance and disappearance of these DPs are shown. It can be seen that DP2 evolved rapidly and reached its maximum concentration at a reaction time of 15 minutes, and then started to decrease until it reached 28% to its maximum detected concentration at a reaction time of 240 minutes. The DP3 and DP4 both appeared at identical patterns with maximum concentration at a reaction time of 4 minutes, followed by a gradual decrease. The DP1 had evolved at relatively slow kinetics.

[0096] With reference to FIG. 9, the molecular structures of the detected DPs and their degradation pathways A and B are presented. With reference to degradation pathway A, the DP1 is suggested to be formed due to substitution at C3 of PFOA followed by defluorination at C7 of PFOA. The DP2 could be formed due to the substitution of F by OH group (C3 atom of DP2) and then decarbonylation at C1 of DP2. Pathway B suggests the elimination reactions. The DP3 could be formed by elimination at C7 of PFOA by the attack of oxidative

species (*OH). Similarly, the subsequent elimination of the -CH₃ group results in the formation of DP4.

[0097] While the present invention has been illustrated by the description of one or more embodiments thereof, and while the embodiments have been described in considerable detail, they are not intended to restrict or in any way limit the scope of the appended claims to such detail. The various features shown and described herein may be used alone or in any combination. Additional advantages and modifications will readily appear to those skilled in the art. The invention in its broader aspects is therefore not limited to the specific details, representative apparatus and methods and illustrative examples shown and described. Accordingly, departures may be made from such details without departing from the scope or spirit of Applicants' general inventive concept.

WHAT IS CLAIMED IS:

1. A catalyst for degrading perfluorooctanoic acid, comprising:
a plurality of bimetallic catalytic nanoparticles, wherein the bimetallic catalytic nanoparticles comprise metals selected from the group consisting of iron, manganese, cobalt, nickel, copper, and titanium; and
a substrate, wherein the plurality of bimetallic catalytic nanoparticles is immobilized on the substrate;
wherein the catalyst is capable of breaking carbon-fluorine bonds of perfluorooctanoic acid in solution.
2. The catalyst of claim 1, wherein the bimetallic catalytic nanoparticles comprise manganese.
3. The catalyst of claim 1, wherein the bimetallic catalytic nanoparticles comprise iron.
4. The catalyst of claim 1, wherein the bimetallic catalytic nanoparticles comprise manganese and iron.
5. The catalyst of claim 1, wherein the substrate material comprises a resin.
6. The catalyst of claim 5, wherein the resin comprises an ion exchange resin.
7. The catalyst of claim 6, wherein the ion exchange resin is an anion exchange resin.

8. The catalyst of claim 1, wherein the bimetallic catalytic nanoparticles have a core-shell structure.
9. The catalyst of claim 8, wherein the core of the core-shell structure primarily comprises iron.
10. The catalyst of claim 8, wherein the shell of the core-shell structure primarily comprises manganese.
11. The catalyst of claim 10, wherein the shell of the core-shell structure primarily comprises iron.
12. The catalyst of claim 1, wherein at least one of the metals is a zero-valent metal.
13. The catalyst of claim 1, wherein both metals are zero-valent metals.
14. The catalyst of claim 13, wherein the two zero-valent metals comprise iron and manganese.
15. The catalyst of claim 1, wherein the bimetallic catalytic nanoparticles have a substantially spherical shape.
16. A method for catalyzing the degradation of perfluorooctanoic acid comprising:

providing a plurality of bimetallic catalytic nanoparticles to a first solution comprising perfluorooctanoic acid, wherein the plurality of bimetallic catalytic nanoparticles comprises metals selected from the list consisting of iron, manganese, cobalt, nickel, copper, and titanium.

17. The method of claim 16, wherein the bimetallic catalytic nanoparticles comprise zero-valent iron.

18. The method of claim 17, wherein the bimetallic catalytic nanoparticles further comprise zero-valent manganese.

19. The method of claim 18, wherein the bimetallic catalytic nanoparticles have a core-shell structure, wherein the core primarily comprises zero-valent iron, and wherein the shell primarily comprises zero-valent manganese.

20. The method of claim 16 further comprising:
immobilizing the plurality of bimetallic catalytic nanoparticles on a resin;
wherein providing the plurality of bimetallic catalytic nanoparticles comprises providing a plurality of immobilized bimetallic catalytic nanoparticles.

21. The method of claim 20, wherein the resin comprises an ion exchange resin.

22. The method of claim 21, wherein the ion exchange resin is an anion exchange resin.

23. The method of claim 20, wherein immobilizing the plurality of bimetallic catalytic nanoparticles comprises:

mixing the bimetallic catalytic nanoparticles and the resin in water.

24. The method of claim 23, further comprising:

removing the immobilized bimetallic catalytic nanoparticles from the water;

washing the immobilized bimetallic catalytic nanoparticles; and

drying the immobilized bimetallic catalytic nanoparticles.

25. The method of claim 24, wherein washing the immobilized bimetallic catalytic nanoparticles comprises washing the immobilized bimetallic catalytic nanoparticles with ethanol.

26. The method of claim 16, further comprising:

synthesizing the bimetallic catalytic nanoparticles prior to providing the plurality of bimetallic catalytic nanoparticles to the first solution.

27. The method of claim 26, wherein synthesizing the bimetallic catalytic nanoparticles comprises:

dissolving an iron salt and a manganese salt in water to form a second solution comprising a plurality of iron cations and a plurality of manganese cations; and

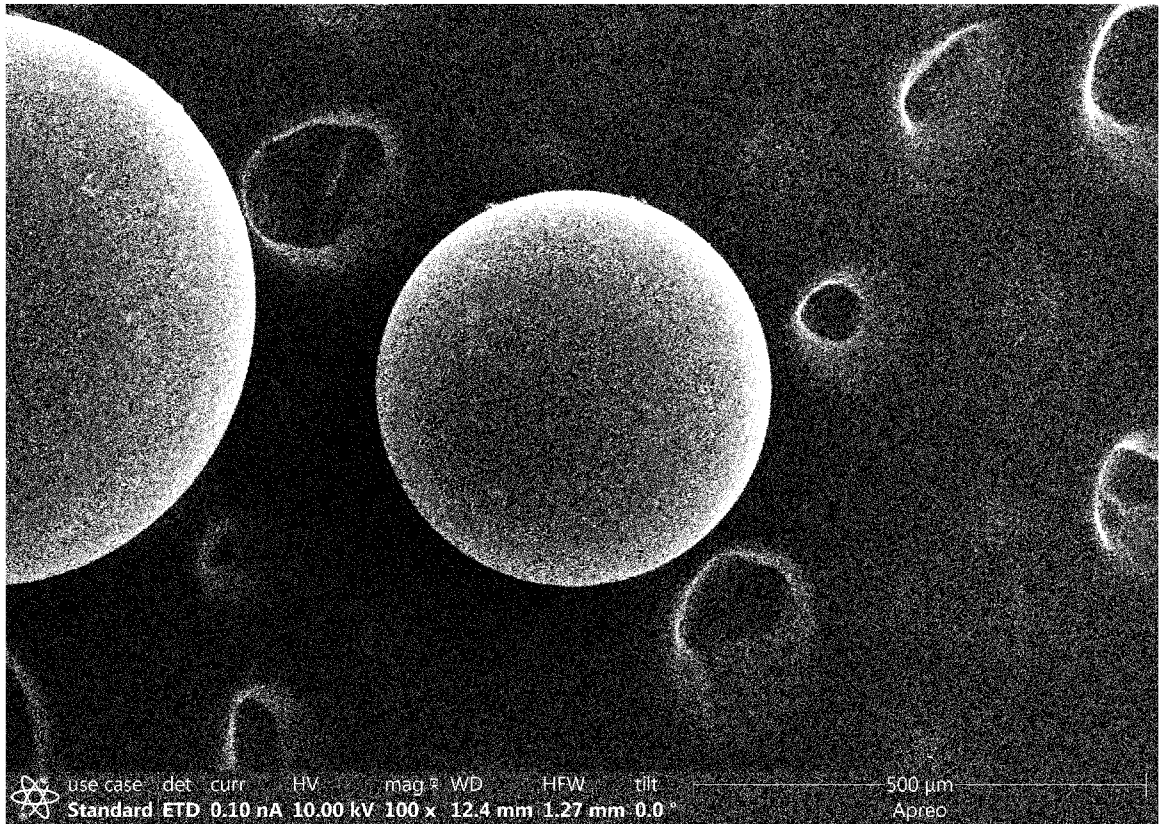
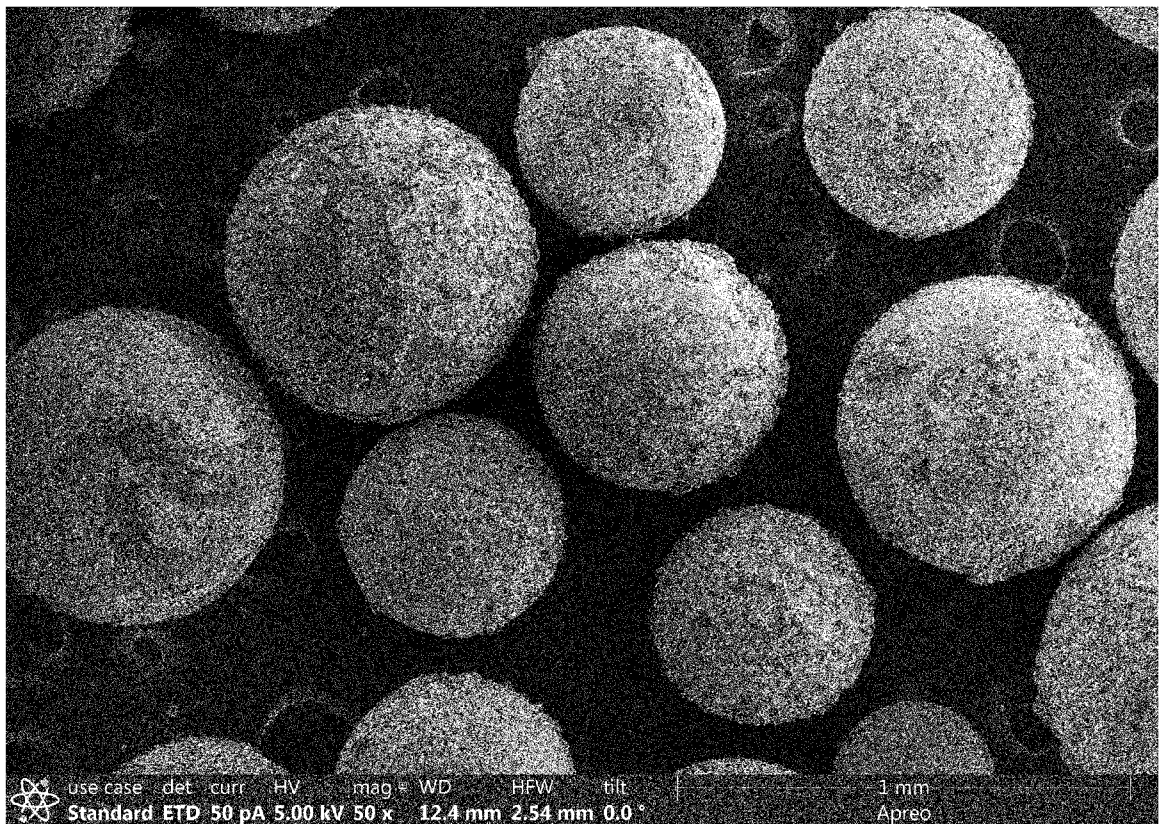
titrating the second solution against a reducing agent solution to produce the bimetallic catalytic nanoparticles as a precipitate.

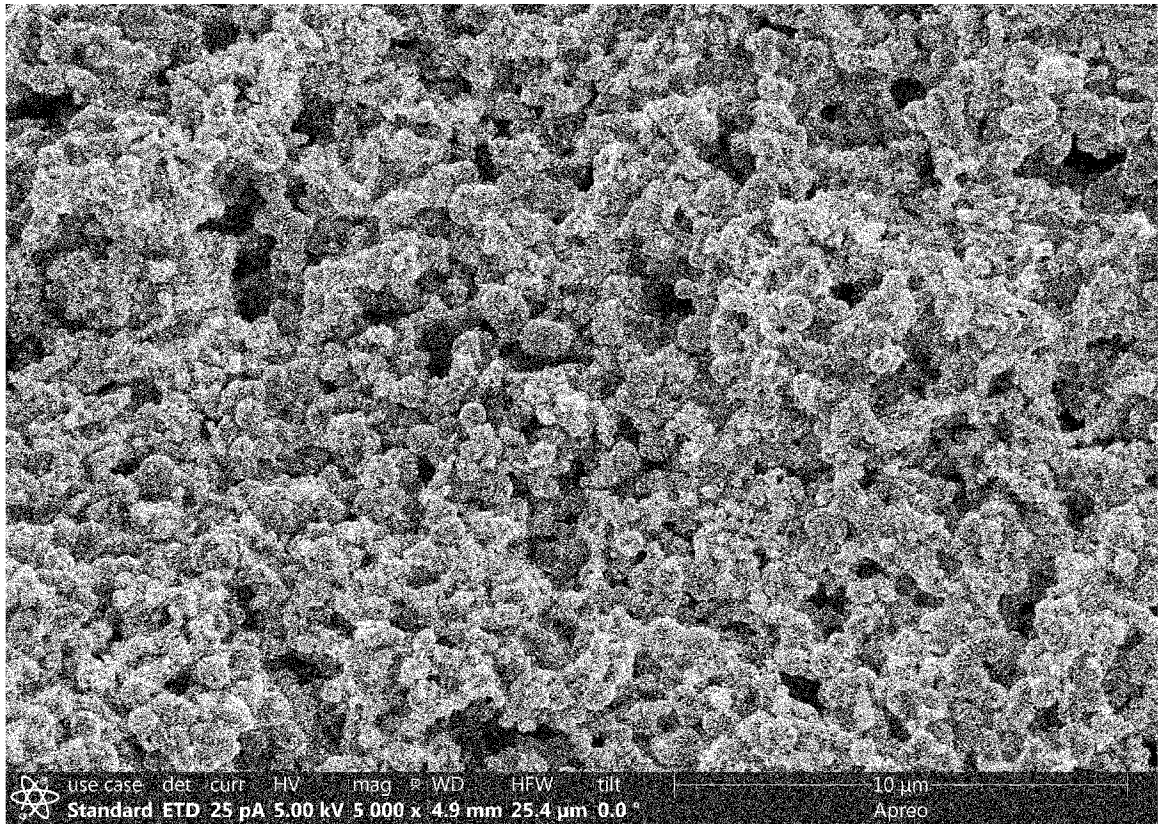
28. The method of claim 27, wherein the bimetallic catalytic nanoparticles comprise zero-valent iron and zero valent manganese.

29. The method of claim 27, wherein the reducing agent solution comprises sodium borohydride.
30. The method of claim 27, wherein the iron salt comprises iron (III) chloride hexahydrate.
31. The method of claim 30, wherein the manganese salt comprises manganese (II) acetate tetrahydrate.
32. The method of claim 30, wherein the weight ratio of the iron salt to the manganese salt is 1:1.
33. The method of claim 16 further comprising synthesizing immobilized bimetallic catalytic nanoparticles prior to providing the bimetallic catalytic nanoparticles to the first solution, wherein providing the plurality of bimetallic catalytic nanoparticles comprises providing a plurality of immobilized bimetallic catalytic nanoparticles.
34. The method of claim 33, wherein synthesizing immobilized bimetallic catalytic nanoparticles comprises:
- dissolving an iron salt, a manganese salt, and a resin in water to form a second solution comprising a plurality of iron cations and a plurality of manganese cations; and
 - titrating the second solution against a reducing agent solution to produce the immobilized bimetallic catalytic nanoparticles as a precipitate.
35. The method of claim 34, wherein the immobilized bimetallic catalytic nanoparticles comprise zero-valent iron and zero valent manganese.

36. The method of claim 34, wherein the reducing agent solution comprises sodium borohydride.
37. The method of claim 34, wherein the iron salt comprises iron (III) chloride hexahydrate.
38. The method of claim 37, wherein the manganese salt comprises manganese (II) acetate tetrahydrate.
39. The method of claim 38, wherein the weight ratio of the iron salt to the manganese salt is 1:1.
40. The method of claim 16 further comprising:
purging the first solution with an inert gas.
41. The method of claim 40, wherein the inert gas comprises nitrogen (N₂) gas.
42. The method of claim 40 further comprising:
adjusting the pH of the first solution to a value greater than or equal to 6.8 and less than or equal to 9.6.
43. The method of claim 40 further comprising:
adjusting the pH of the first solution to a value greater than or equal to 7.7 and less than or equal to 8.7.

44. The method of claim 40 further comprising:
adjusting the pH of the first solution to a value substantially equal to 8.2.
45. The method of claim 16 further comprising:
adjusting the pH of the first solution to a value greater than or equal to 6.8.
46. The method of claim 45, wherein adjusting the pH of the first solution further comprises
adjusting the pH of the first solution to a value less than or equal to 9.6.
47. The method of claim 16 further comprising:
adjusting the pH of the first solution to a value greater than or equal to 7.7 and less than
or equal to 8.7.
48. The method of claim 16 further comprising:
adjusting the pH of the first solution to a value substantially equal to 8.2.

**FIG. 1A****FIG. 1B**

**FIG. 1C**

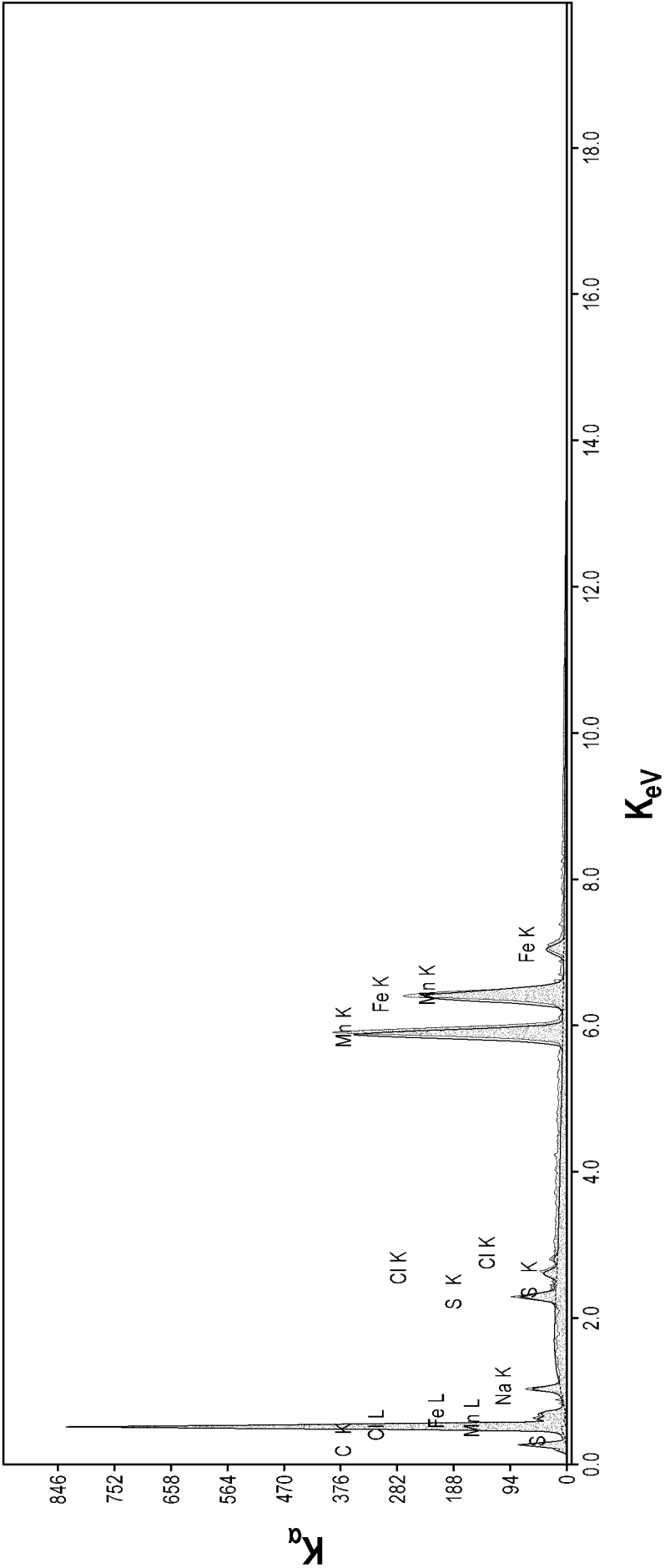
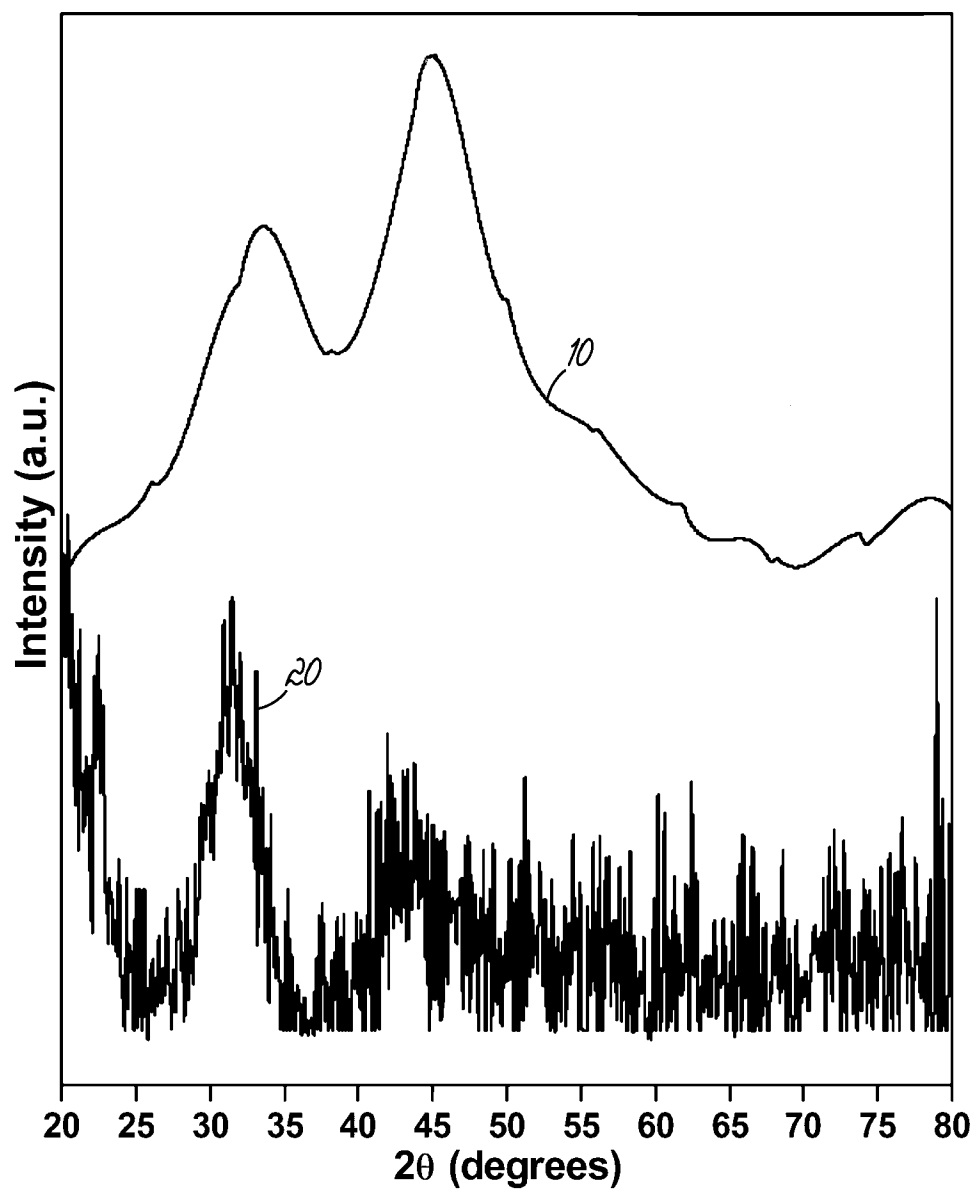


FIG. 1D

**FIG. 2**

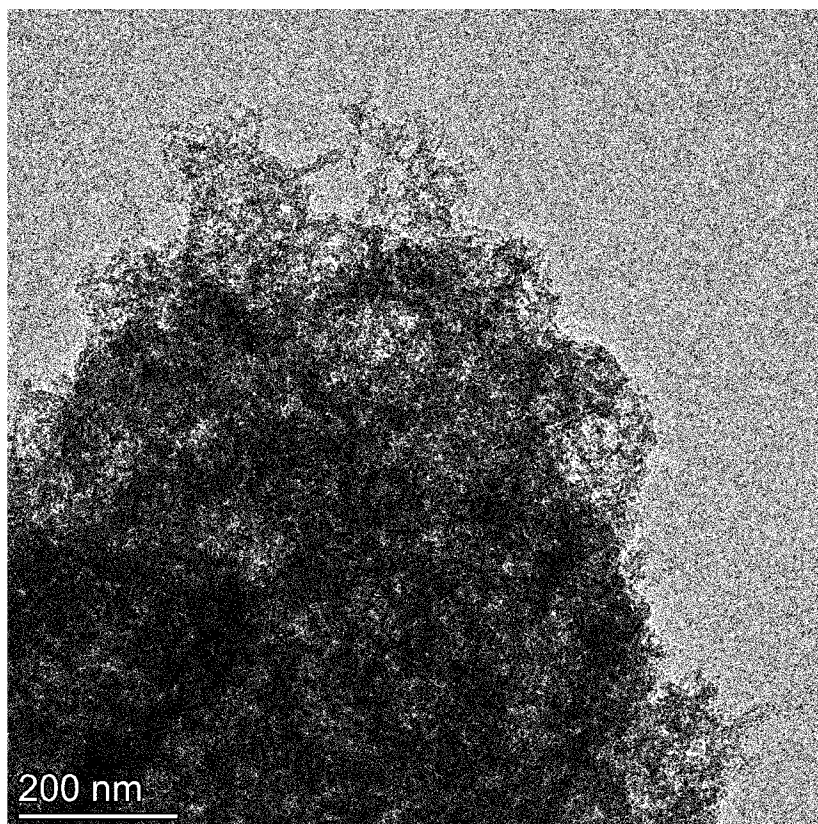


FIG. 3A

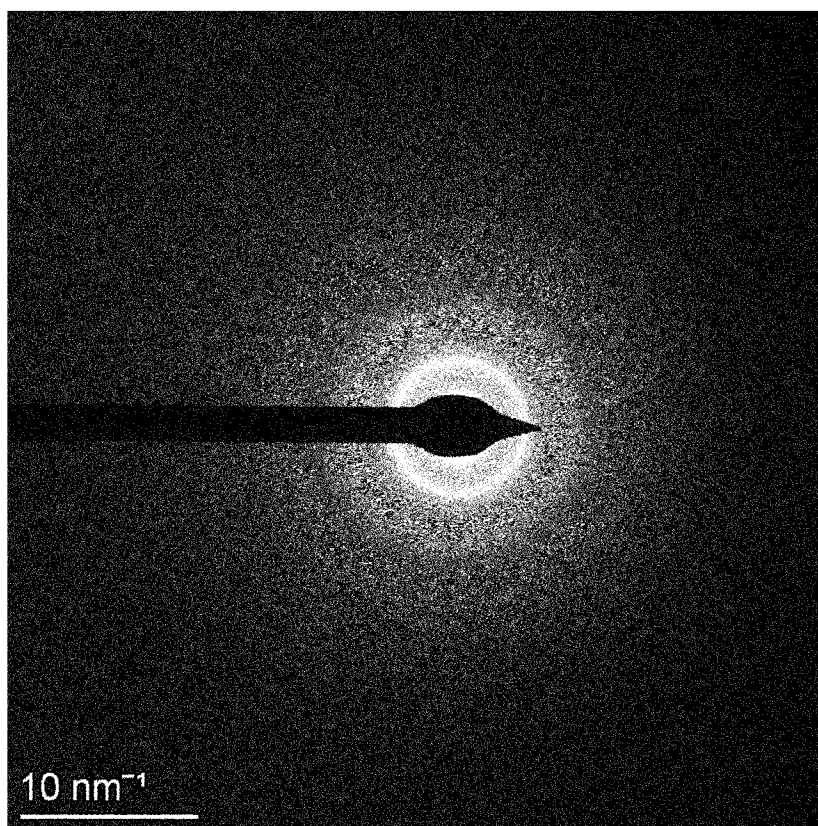


FIG. 3B

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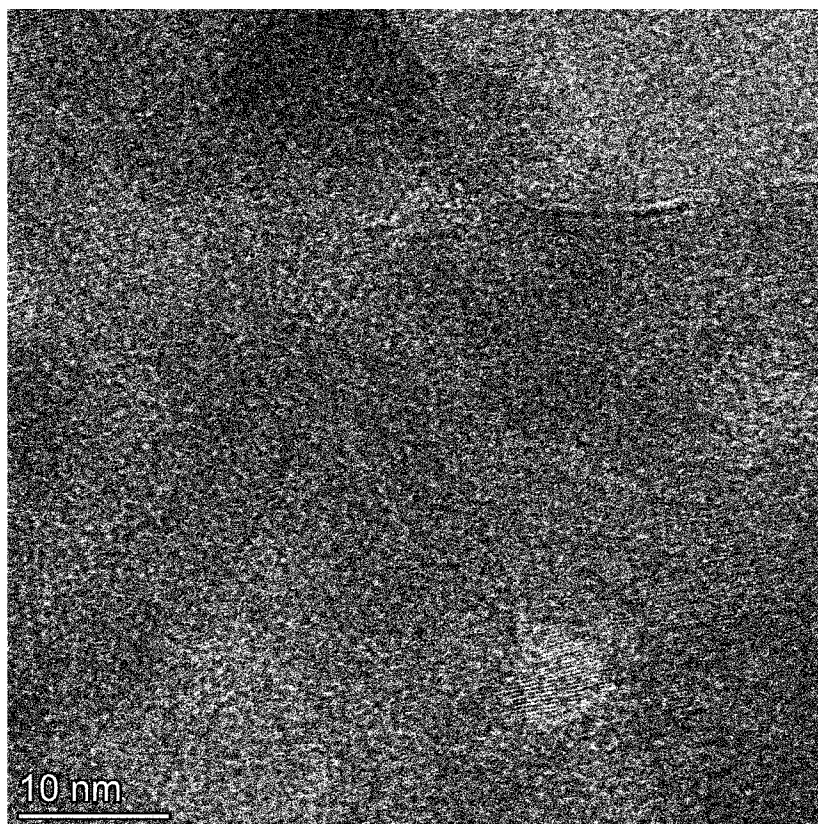


FIG. 3C

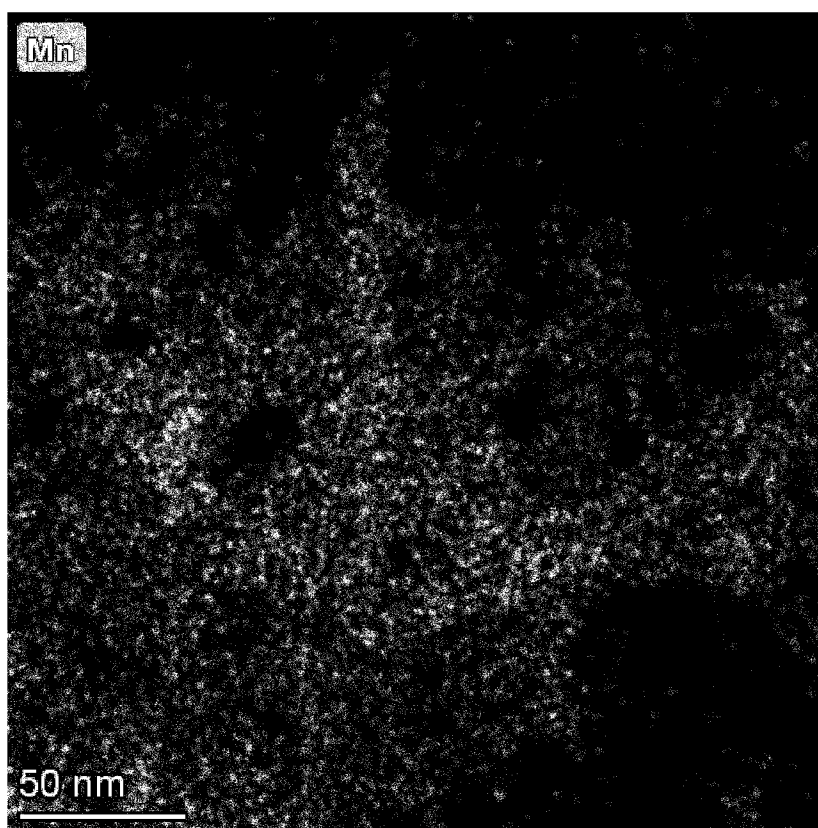


FIG. 3D

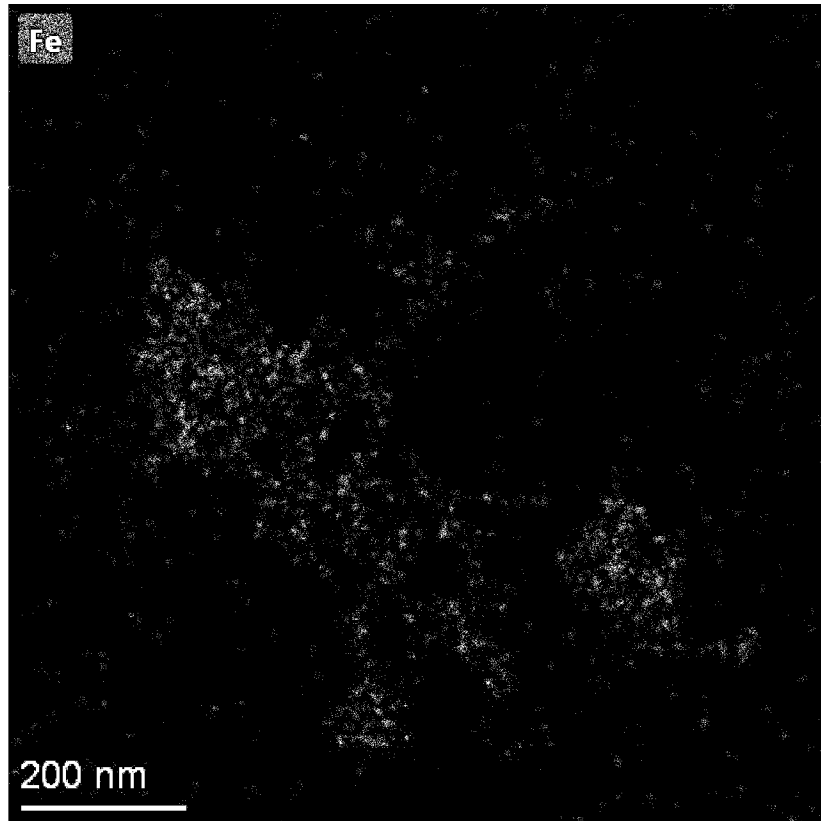


FIG. 3E

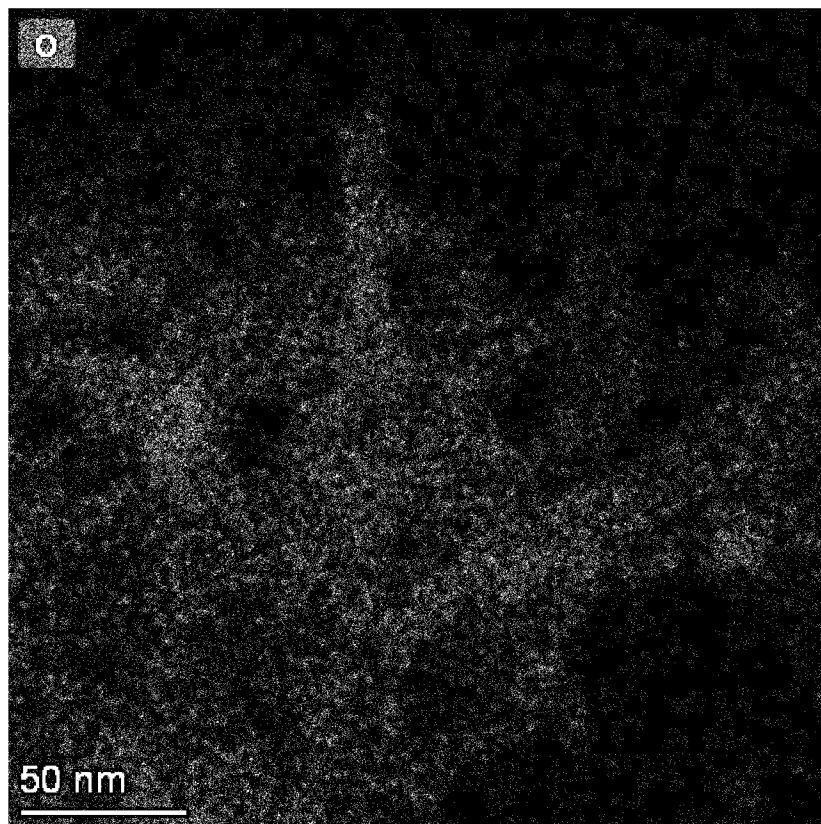


FIG. 3F

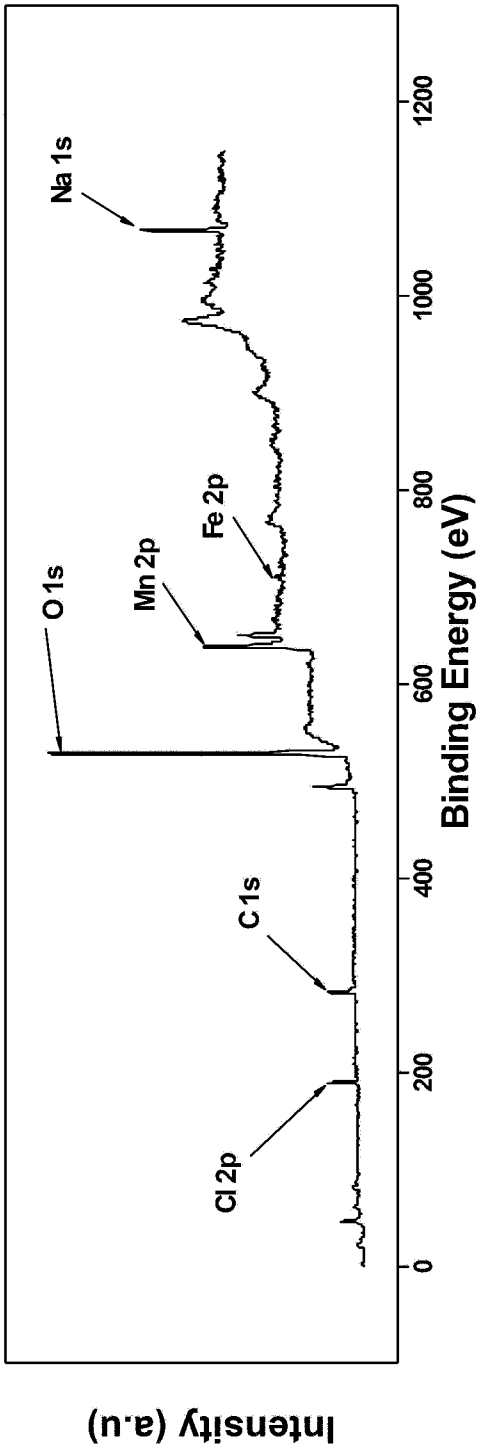
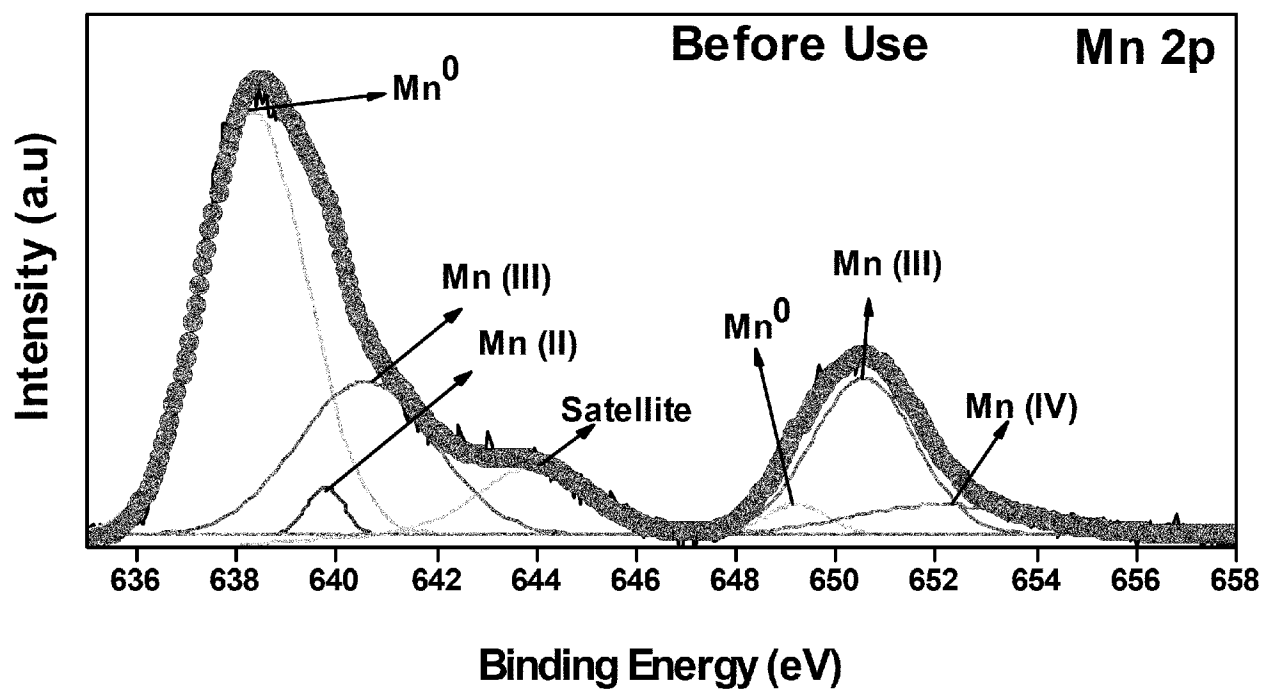
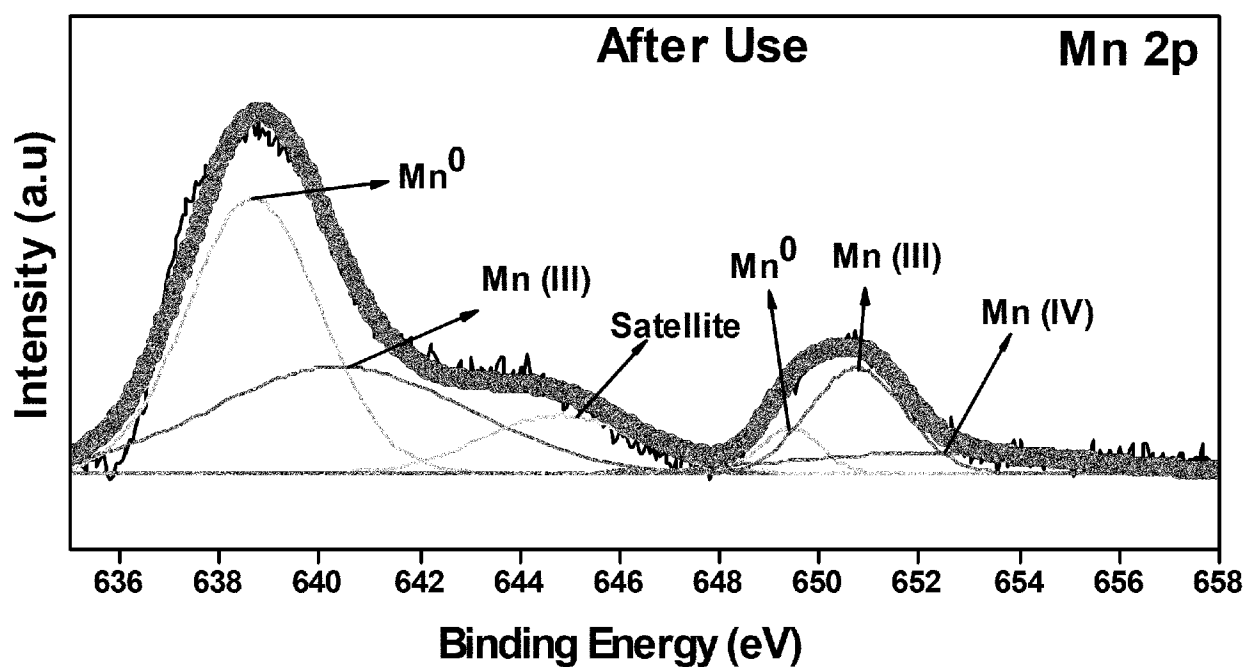
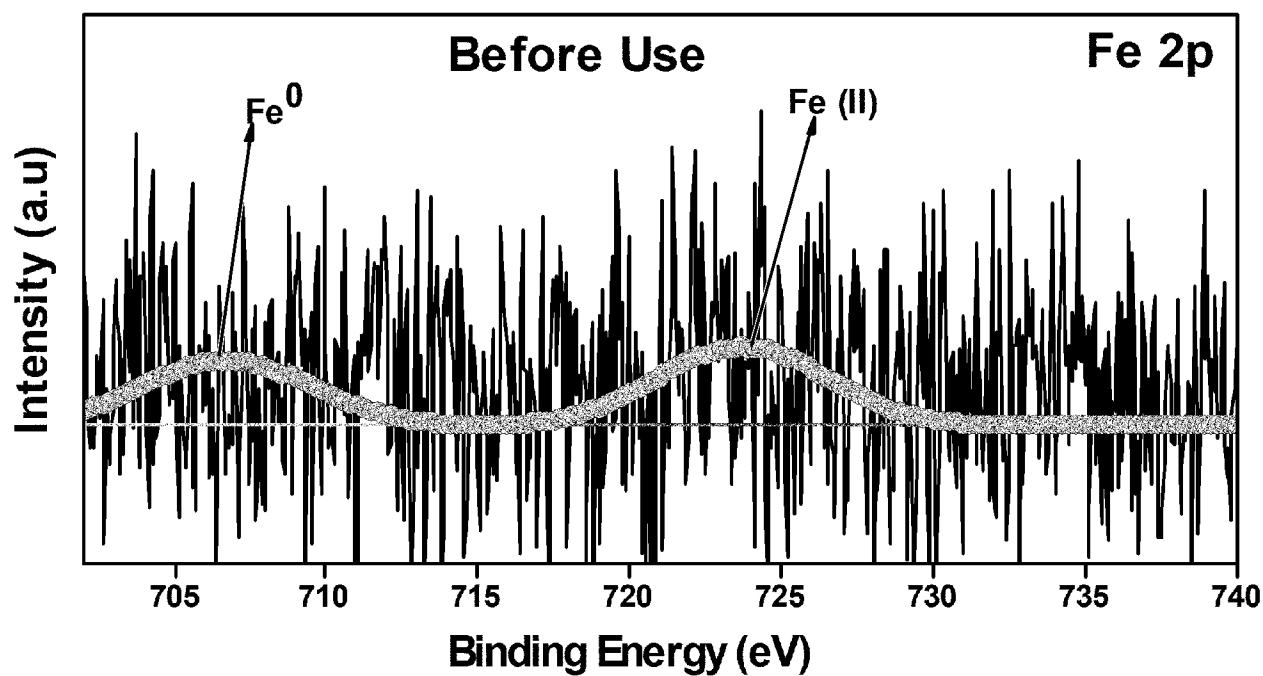
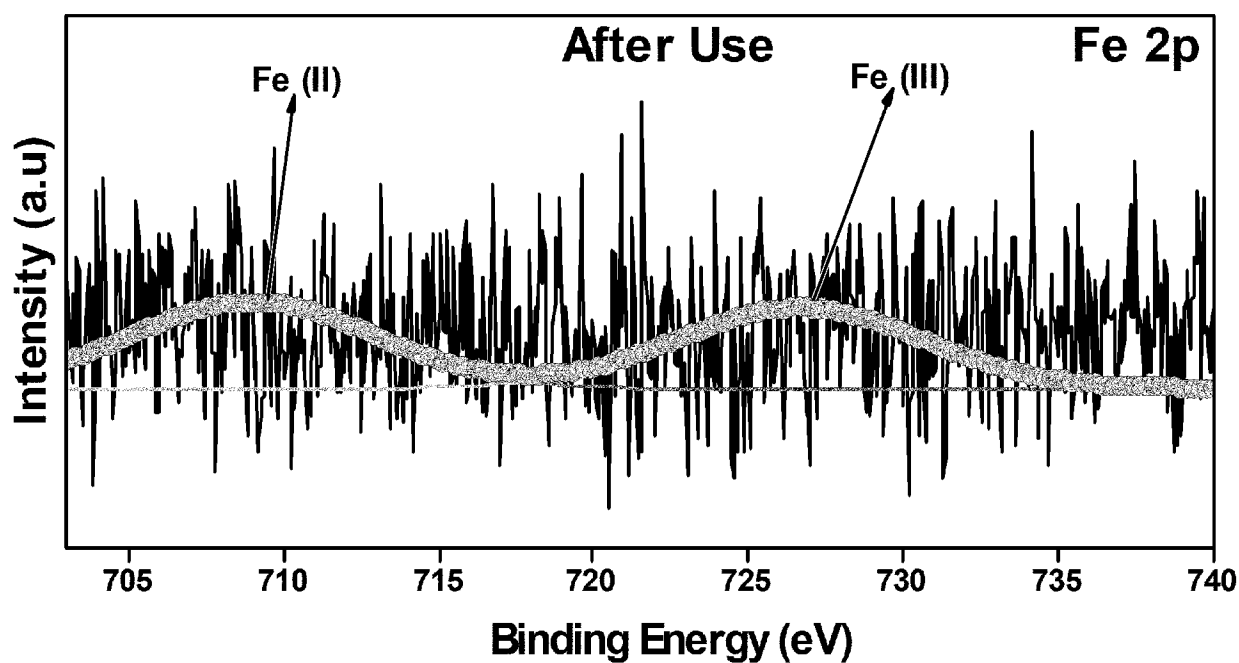


FIG. 4A

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**FIG. 4B****FIG. 4C**

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**FIG. 4D****FIG. 4E**

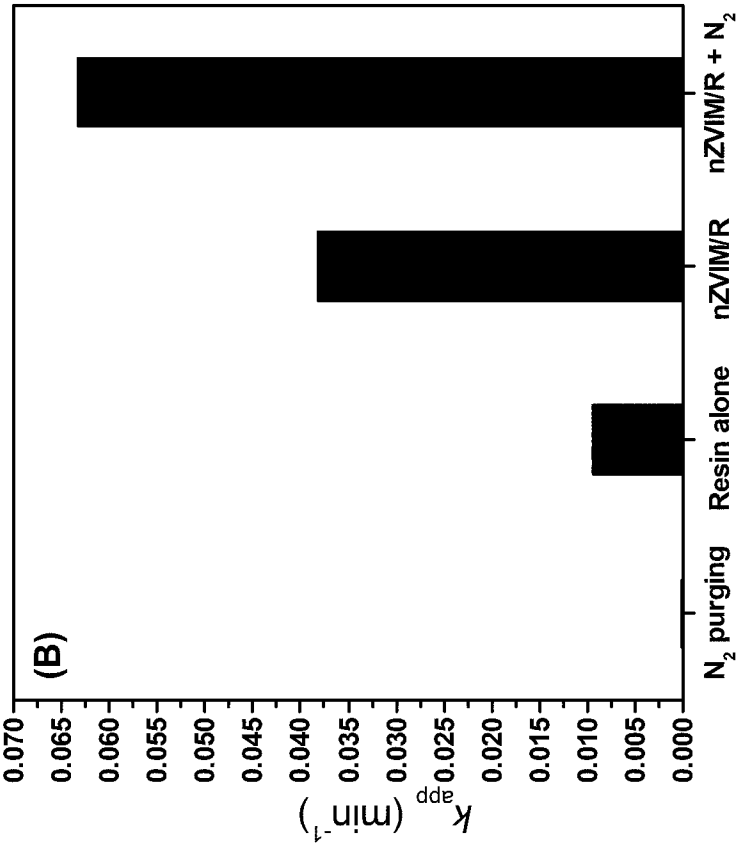


FIG. 5B

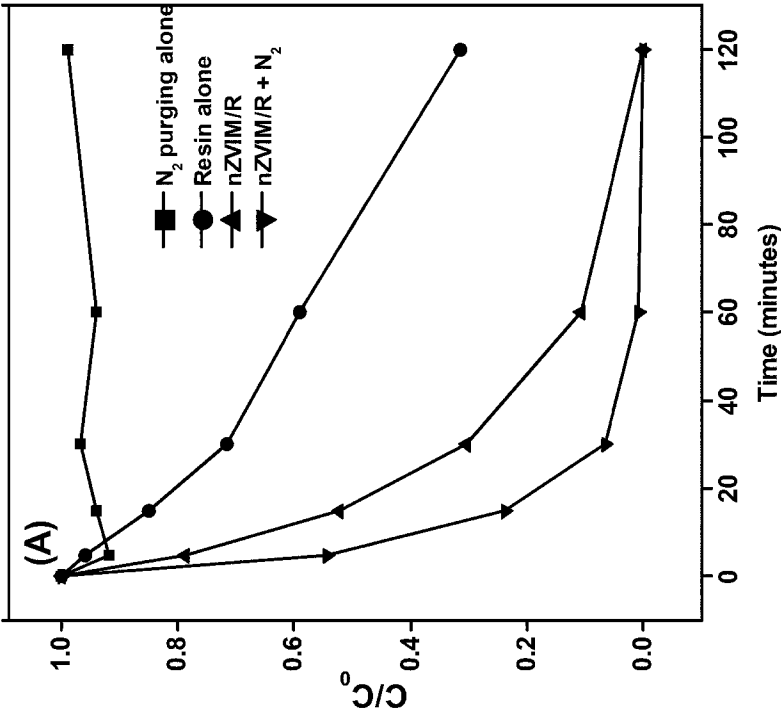


FIG. 5A

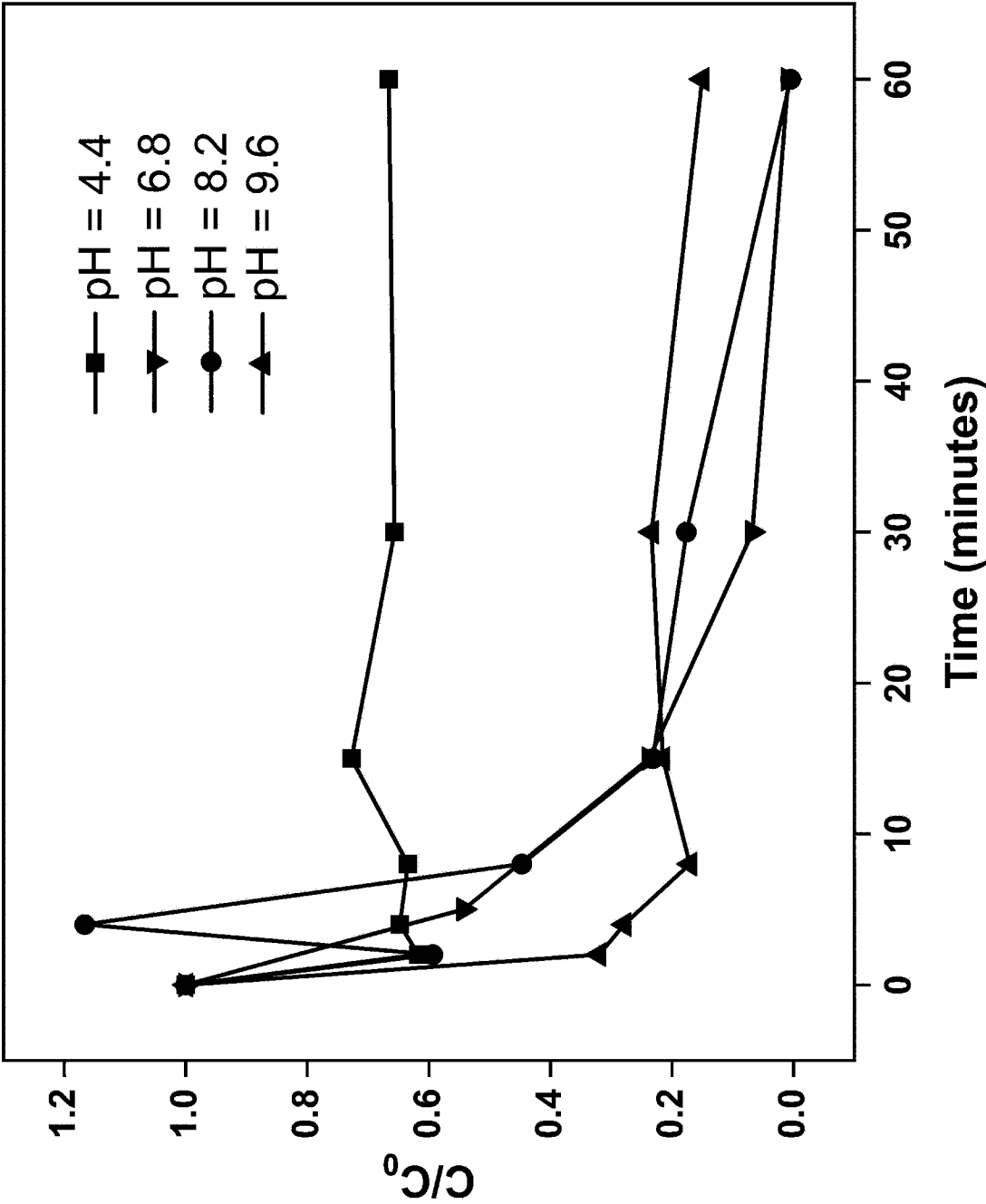


FIG. 6A

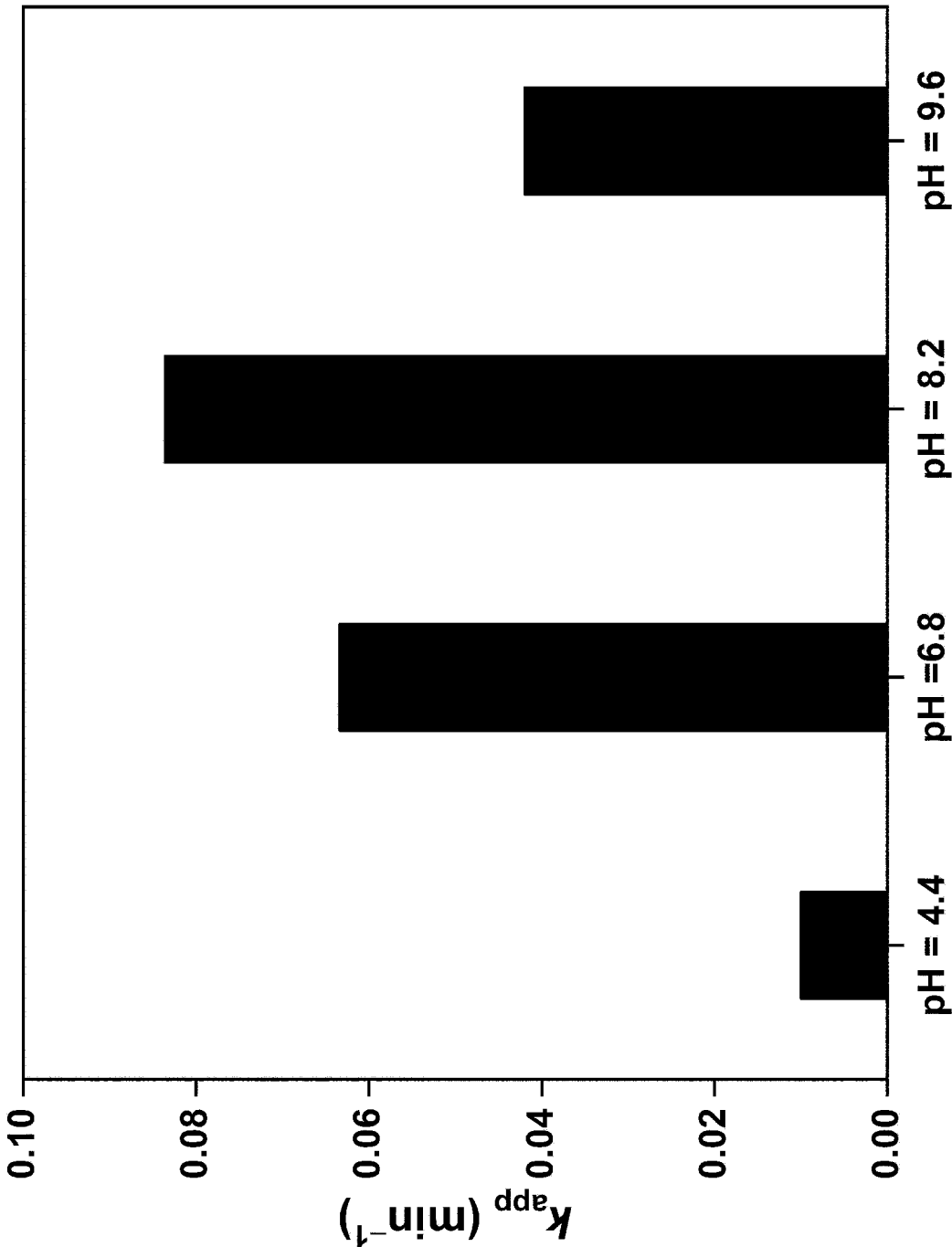


FIG. 6B

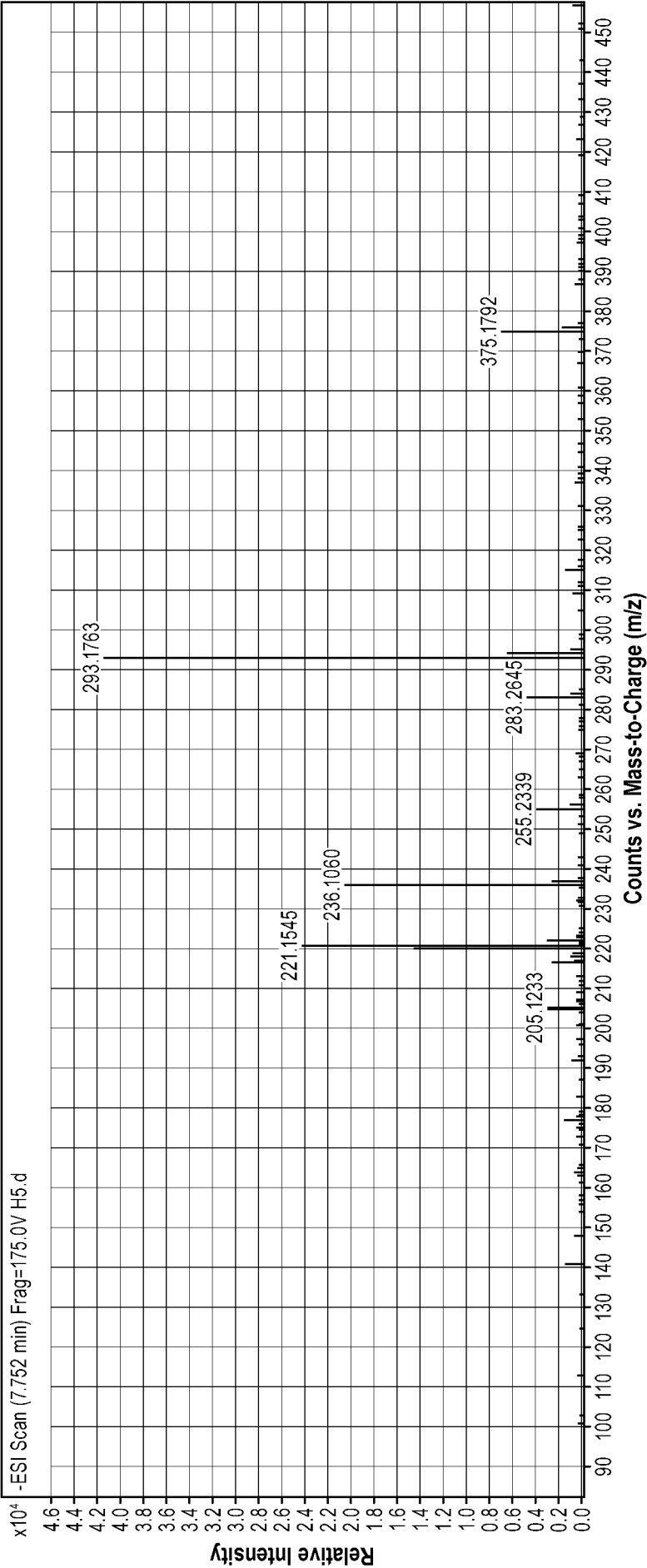


FIG. 7A

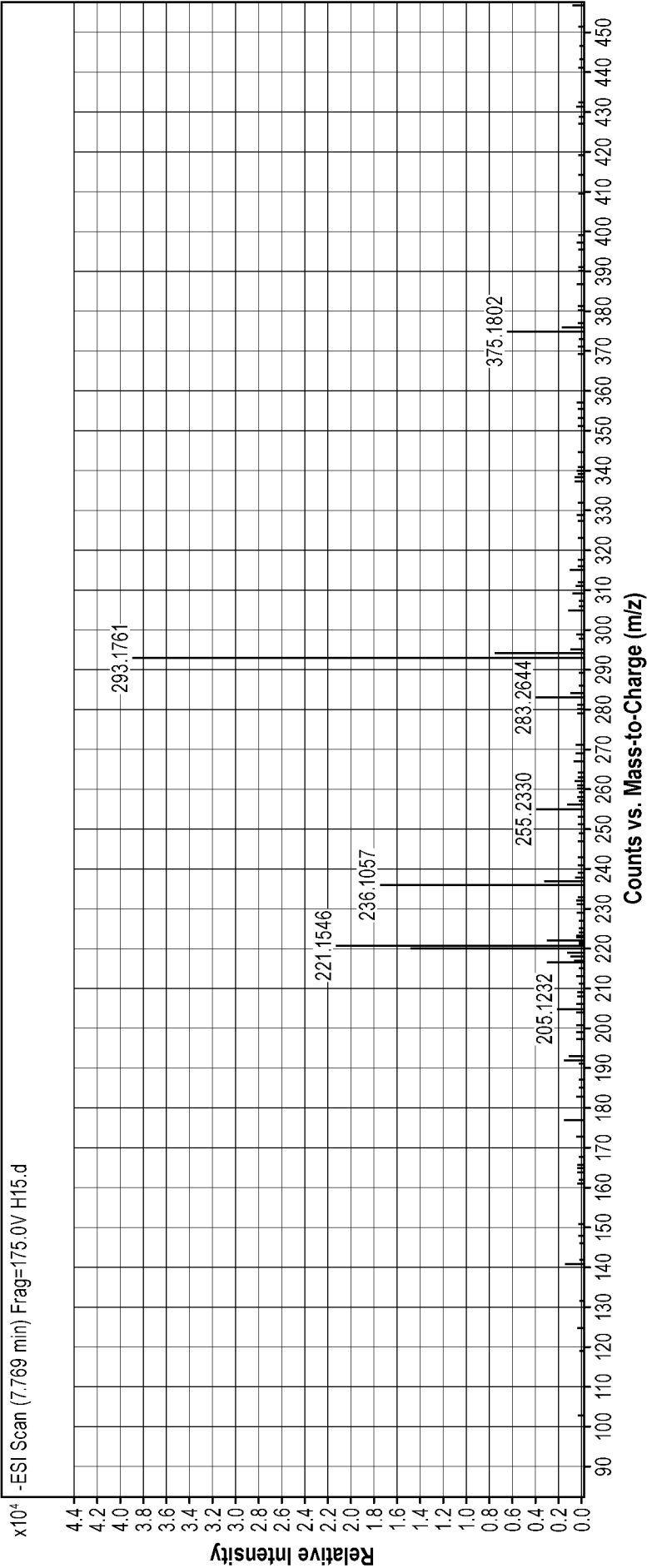


FIG. 7B

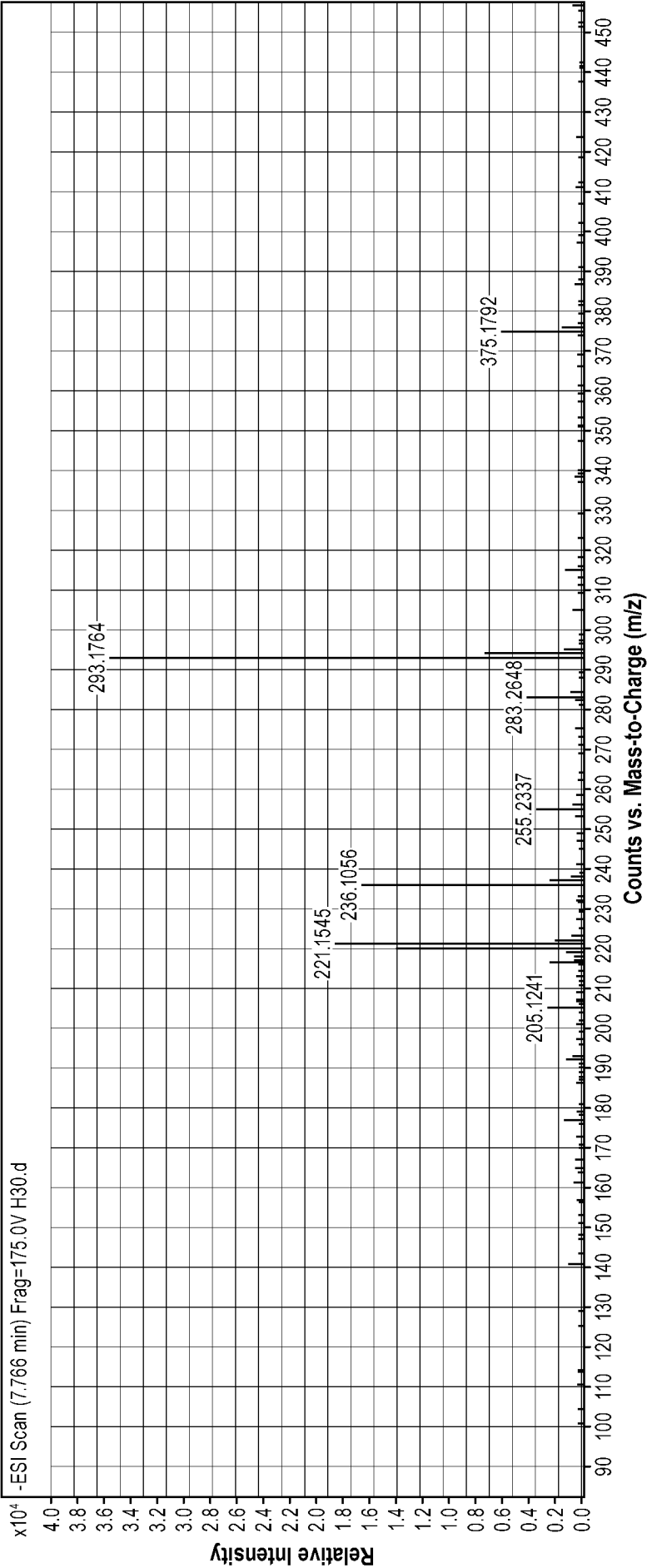


FIG. 7C

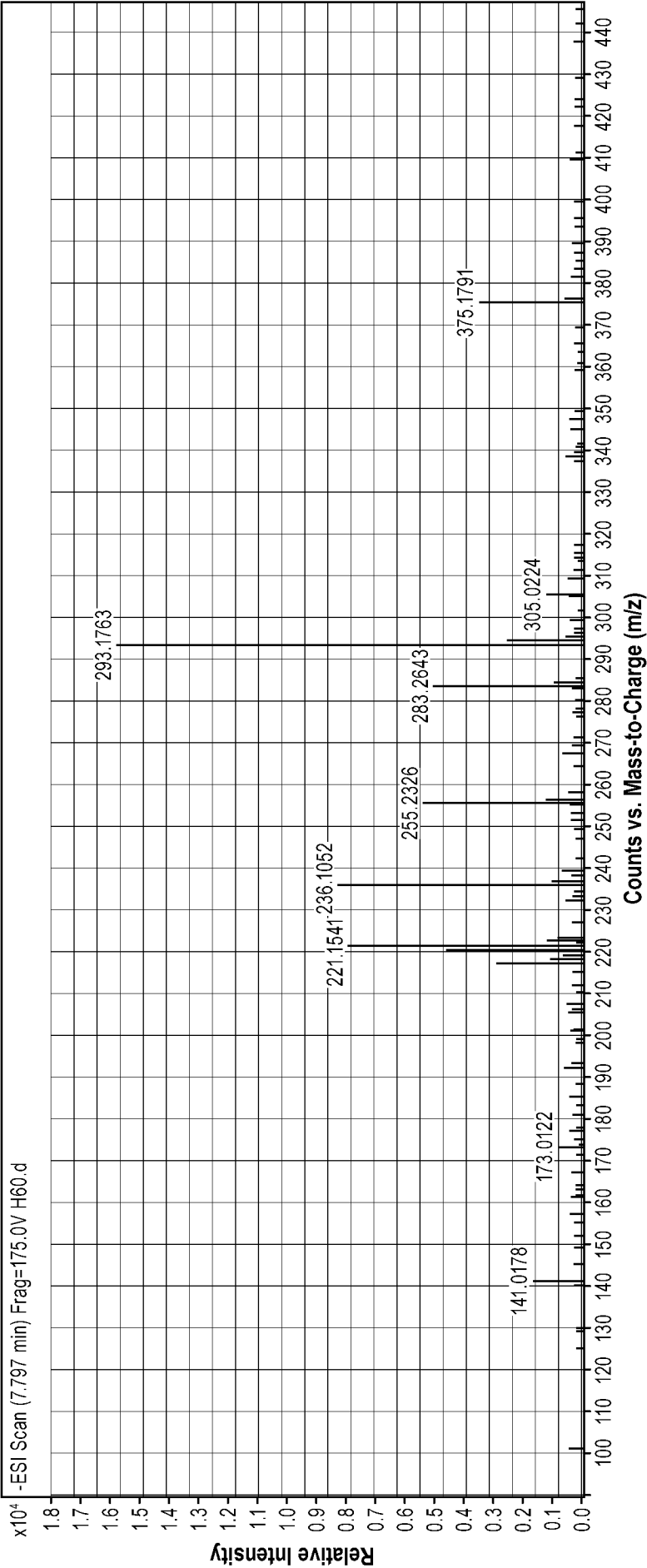


FIG. 7D

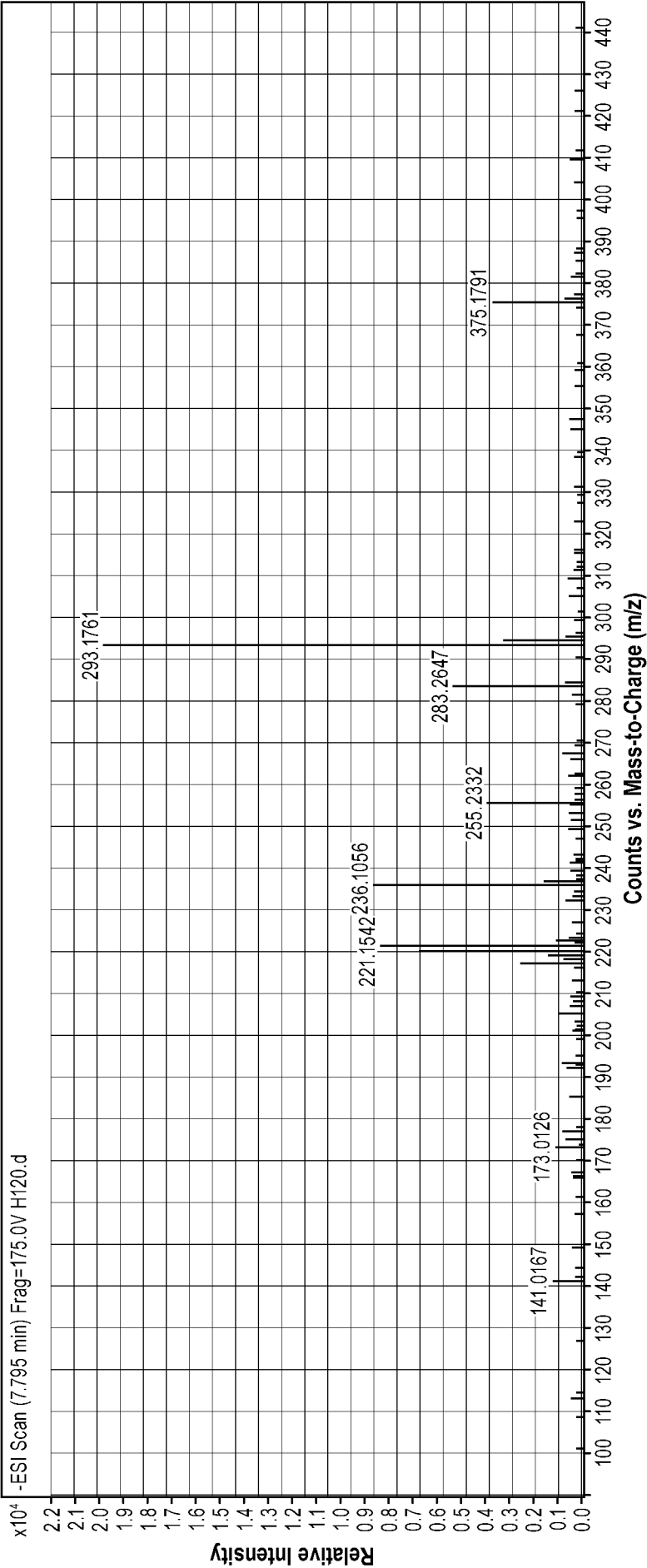


FIG. 7E

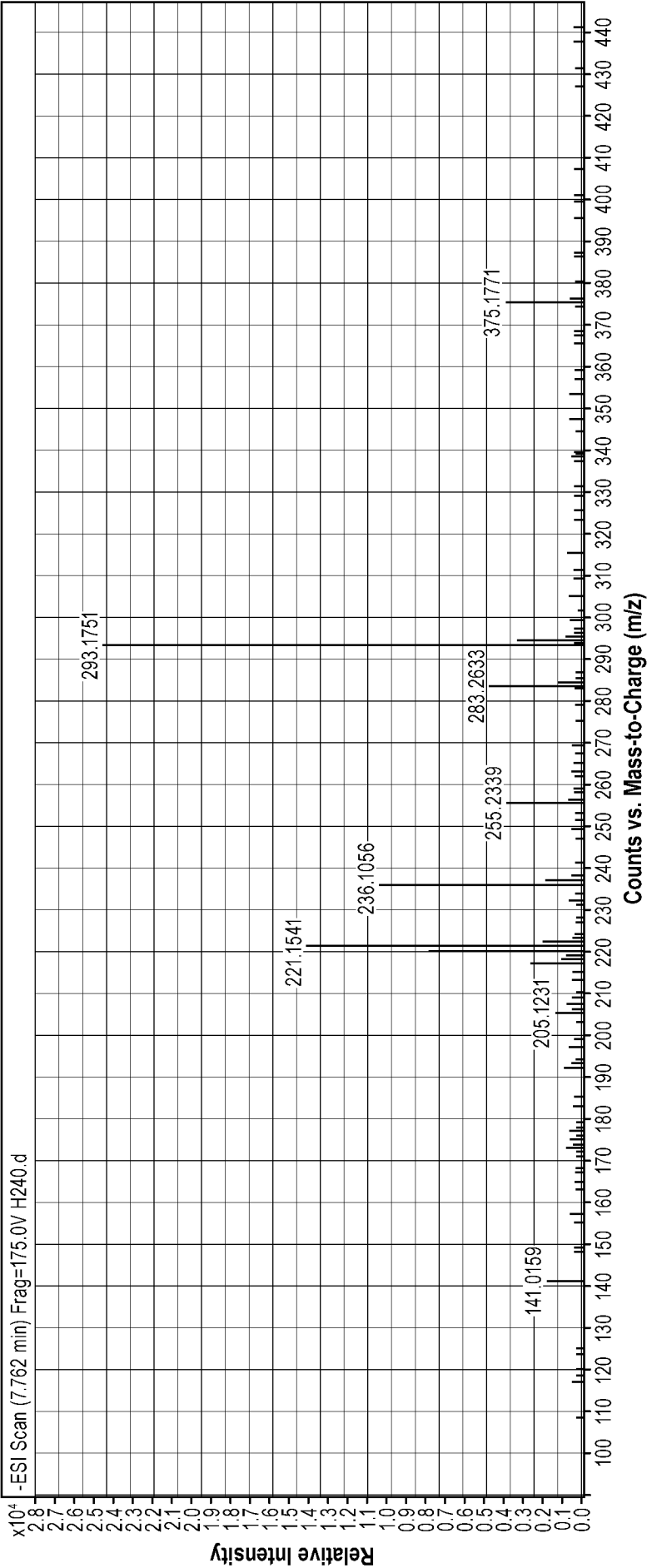


FIG. 7F

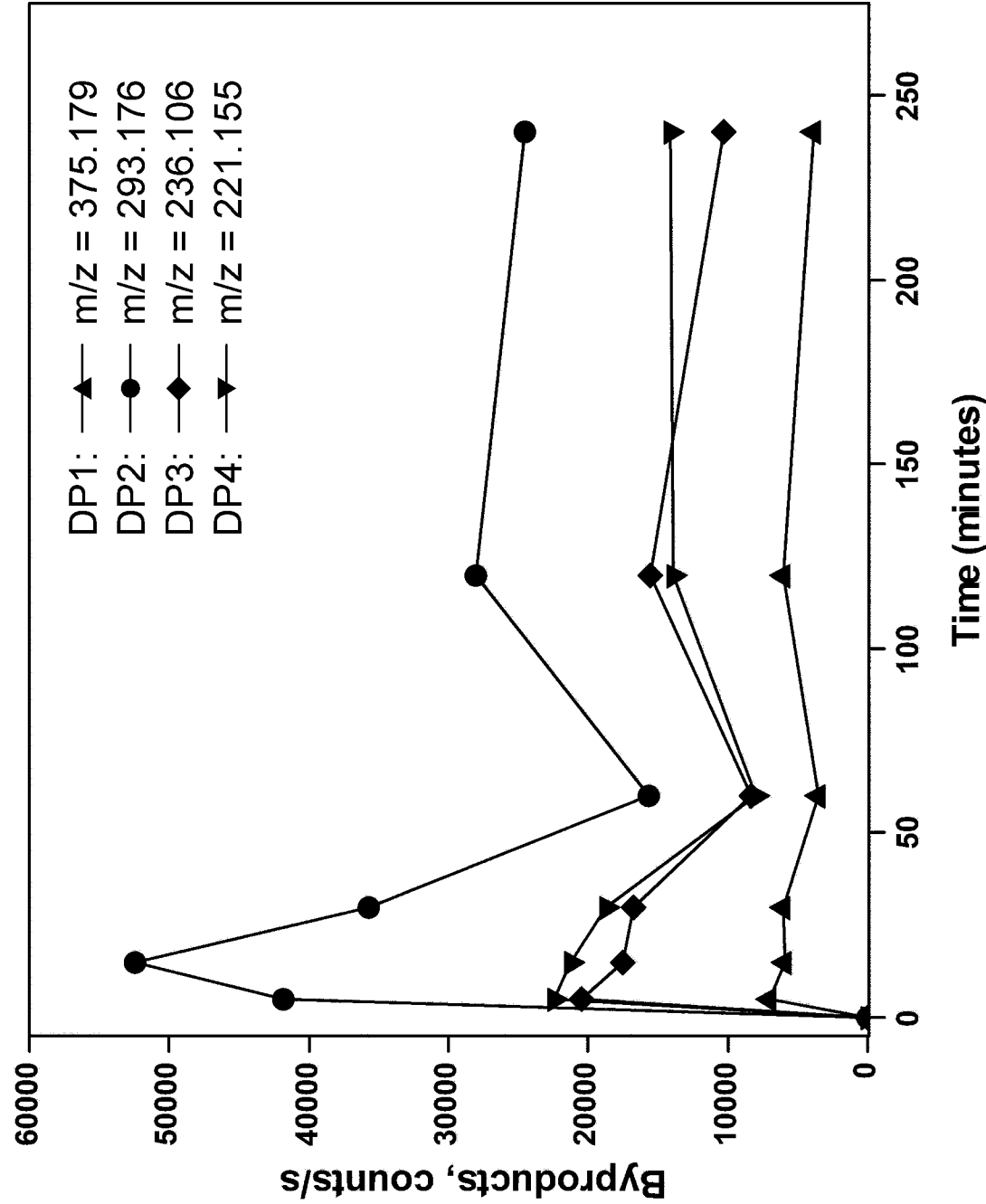
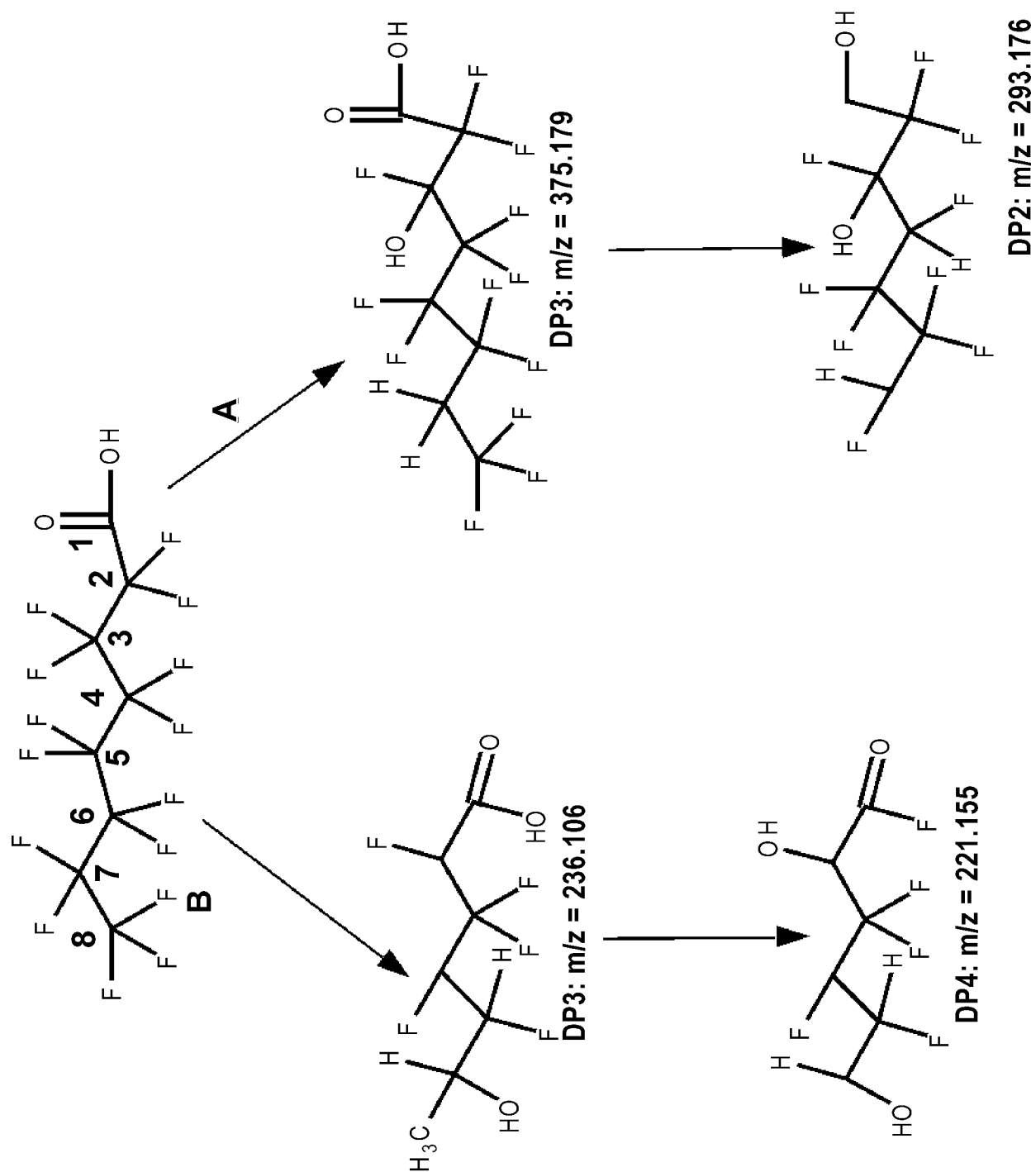


FIG. 8



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2024/036059

A. CLASSIFICATION OF SUBJECT MATTERIPC: **B01J 23/889** (2024.01); **B01J 35/45** (2024.01); **B01J 35/53** (2024.01); **B01J 41/12** (2024.01); **C02F 1/70** (2024.01); **C02F 101/36** (2024.01)CPC: **B01J 23/8892**; **B01J 35/45**; **B01J 35/53**; **B01J 41/12**; **C02F 1/705**; **C01P 2004/32**; **C02F 2101/36**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

See Search History Document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

See Search History Document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

See Search History Document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CN 113070102 A (NINGBO ZHENGGUANG RESIN CO., LTD) 06 July 2021 (06.07.2021) see machine translation	5-7
Y	CN 110947396 A (SHANGHAI INSTITUTE OF TECHNOLOGY) 03 April 2020 (03.04.2020) see machine translation	8-11
Y	CN 111804930 A (CHENGDU UNIVERSITY OF TECHNOLOGY) 23 October 2020 (23.10.2020) see machine translation	13, 14
A	CN 116143228 A (HEBEI UNIVERSITY OF TECHNOLOGY) 23 May 2023 (23.05.2023) see machine translation	1-15

☒ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

“A” document defining the general state of the art which is not considered to be of particular relevance

“D” document cited by the applicant in the international application

“E” earlier application or patent but published on or after the international filing date

“L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

“O” document referring to an oral disclosure, use, exhibition or other means

“P” document published prior to the international filing date but later than the priority date claimed

“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

“&” document member of the same patent family

Date of the actual completion of the international search

30 August 2024 (30.08.2024)

Date of mailing of the international search report

22 October 2024 (22.10.2024)

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US

Commissioner for Patents

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2024/036059

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WANG et al. Efficiently degradation of perfluorooctanoic acid in synergic electrochemical process combining cathodic electro-Fenton and anodic oxidation, Chemical Engineering Journal, Vol. 378, 15 December 2019 [Retrieved on 21 August 2024]. Retrieved from the Internet: <URL: https://www.sciencedirect.com/science/article/abs/pii/S1385894719314652?via%3Dihub >. entire document	1-4, 12, 15
Y		5-11, 13, 14

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2024/036059

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.: **1-15**

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees need to be paid.

Group I: claims 1-15 are drawn to catalysts for degrading perfluorooctanoic acid.

Group II: claims 16-48 are drawn to methods for catalyzing the degradation of perfluorooctanoic acid.

The inventions listed in Groups I and II do not relate to a single general inventive concept under PCT Rule 13.1, because under PCT Rule 13.2 they lack the same or corresponding special technical features for the following reasons:

The special technical features of Group I, catalysts for degrading perfluorooctanoic acid, are not present in Group II; and the special technical features of Group II, methods for catalyzing the degradation of perfluorooctanoic acid, are not present in Group I.

Additionally, even if Groups I and II were considered to share the technical features of a catalyst for degrading perfluorooctanoic acid, comprising: a plurality of bimetallic catalytic nanoparticles, wherein the bimetallic catalytic nanoparticles comprise metals selected from the group consisting of iron, manganese, cobalt, nickel, copper, and titanium, these shared technical features do not represent a contribution over the prior art as disclosed by "Efficiently degradation of perfluorooctanoic acid in synergic electrochemical process combining cathodic electro-Fenton and anodic oxidation" to Wang et al. (hereinafter, "Wang").

Wang teaches a catalyst for degrading perfluorooctanoic acid (Abstract), comprising: a plurality of bimetallic catalytic nanoparticles (pg 5 col 1 para 2 TEM result further revealed the detailed morphology and composition characters of Fe₁₀MnC. It can be seen from Fig. 3A that large amounts of nanoparticles were uniformly distributed.), wherein the bimetallic catalytic nanoparticles comprise metals selected from the group consisting of iron, manganese, cobalt, nickel, copper, and titanium (pg 5 col 2 para 3 the degradation rate of PFOA using Fe₁₀MnC...).

The inventions listed in Groups I and II therefore lack unity under Rule 13 because they do not share a same or corresponding special technical feature.