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(19) **United States**(12) **Patent Application Publication****Liou et al.**(10) **Pub. No.: US 2007/0089807 A1**(43) **Pub. Date: Apr. 26, 2007**(54) **METHOD FOR SPREADING NOBLE METAL
ON IRON PARTICLE SURFACE****Publication Classification**(51) **Int. Cl.**
C23C 22/72 (2006.01)(52) **U.S. Cl.** **148/242**(76) Inventors: **Ya-Hsuan Liou**, Danshuei Township
(TW); **Shang-Lien Lo**, Taipei City
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Township (TW)(57) **ABSTRACT**

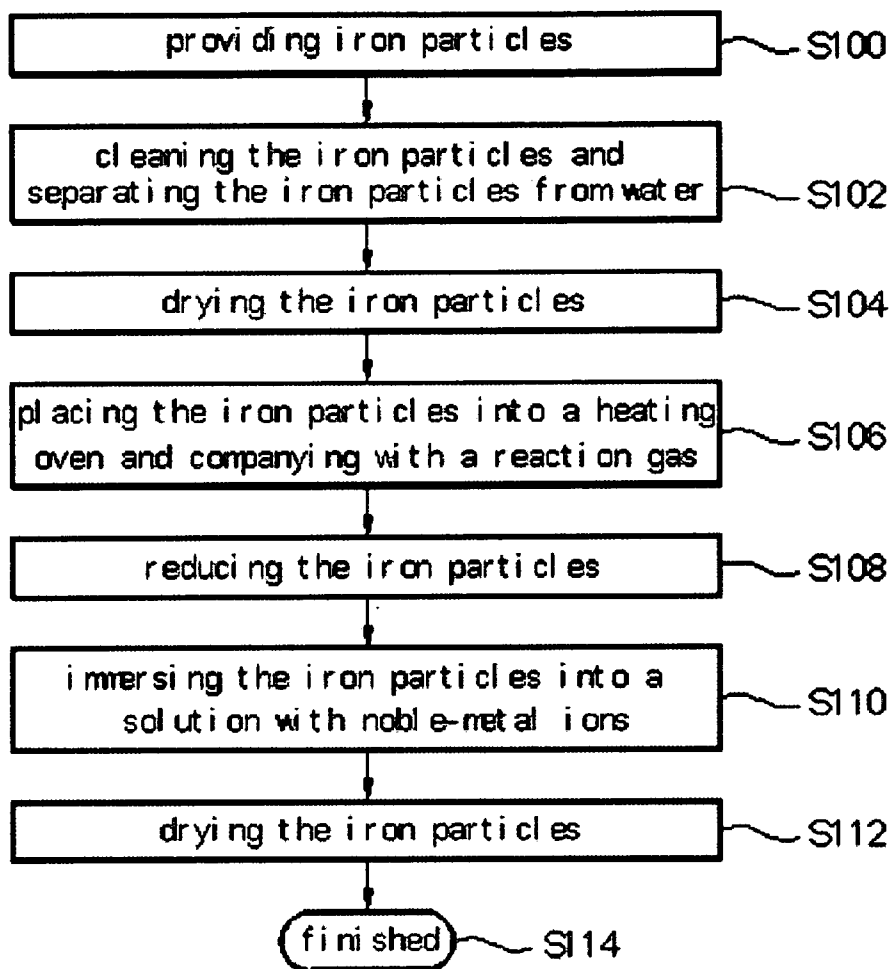
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A method for spreading noble metal on an iron particle surface includes: providing a plurality of iron particles, cleaning the iron particles up and separating the iron particles from cleaning water, drying the iron particles, placing the iron particles into a heater oven with a reaction gas, heating the iron particles for oxidation reduction, placing the iron particles into a noble-metal-ion solution for immersion plating, processing the iron particles with a solid-and-liquid separation, and then drying the iron particles. Wherein the heating temperature of the heating oven ranges from 300 to 500 degrees centigrade and the duration thereof ranges from 3 to 5 hours. Whereby, the iron particles are activated first in order to react with the noble metal so that the activity and the uniformity of the noble metal attached to the iron surface is improved.

(21) Appl. No.: **11/584,669**(22) Filed: **Oct. 23, 2006**(30) **Foreign Application Priority Data**

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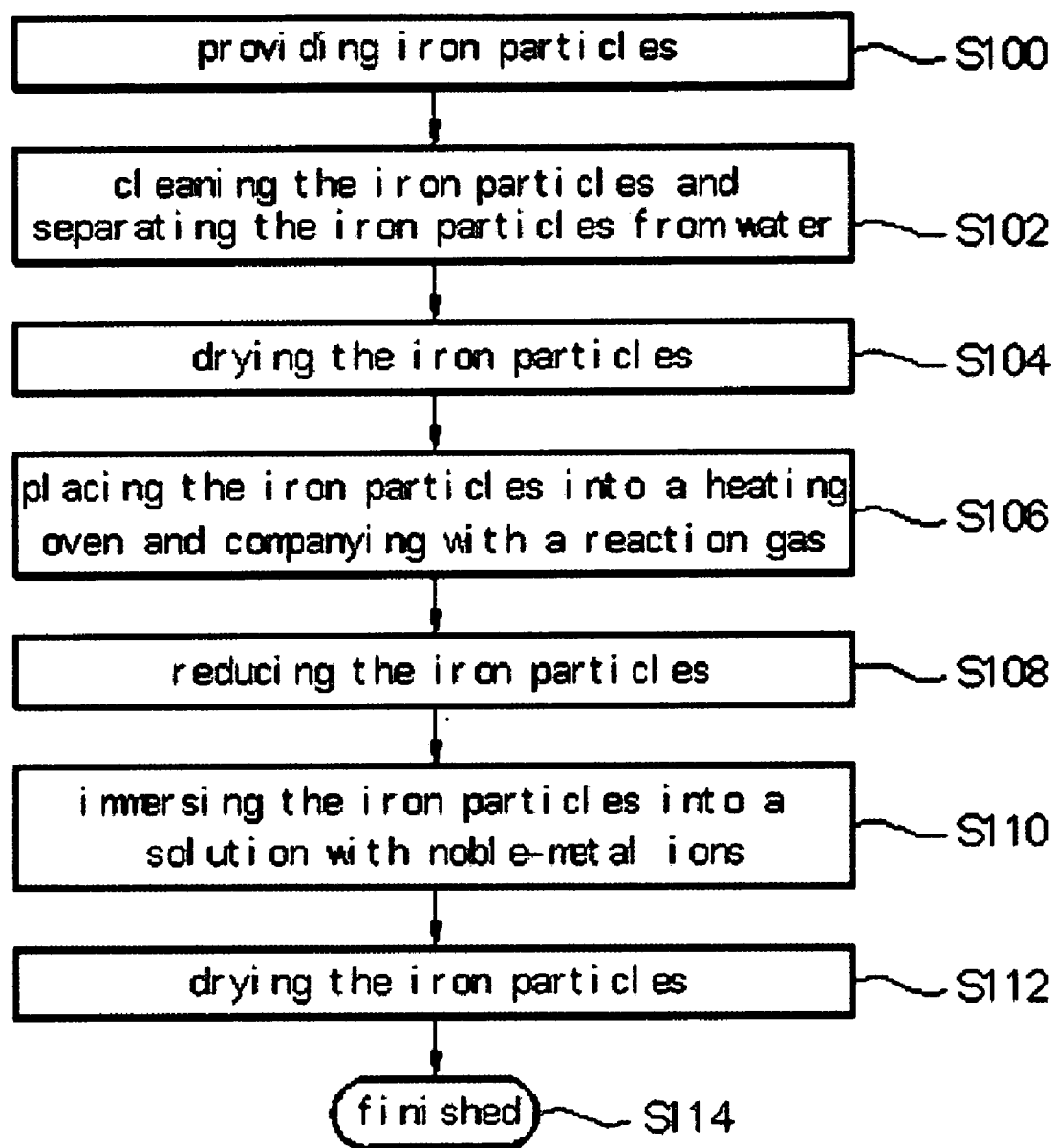


FIG. 1

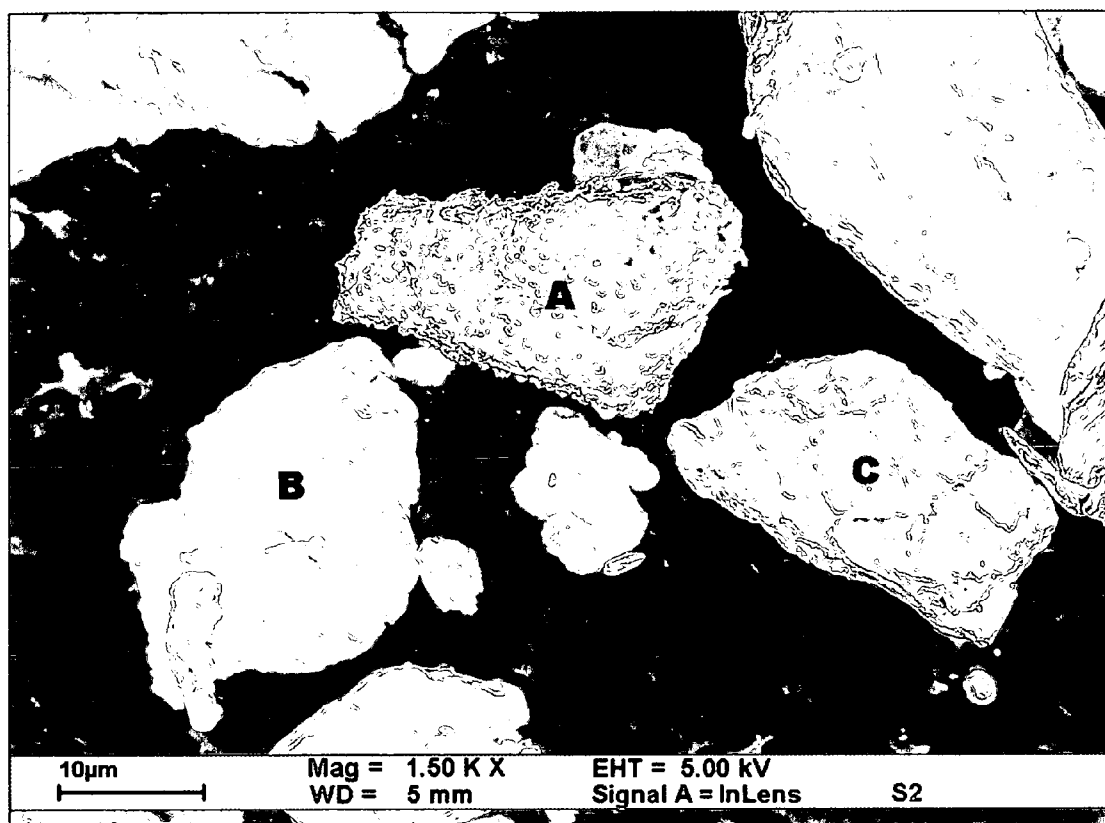


FIG. 2

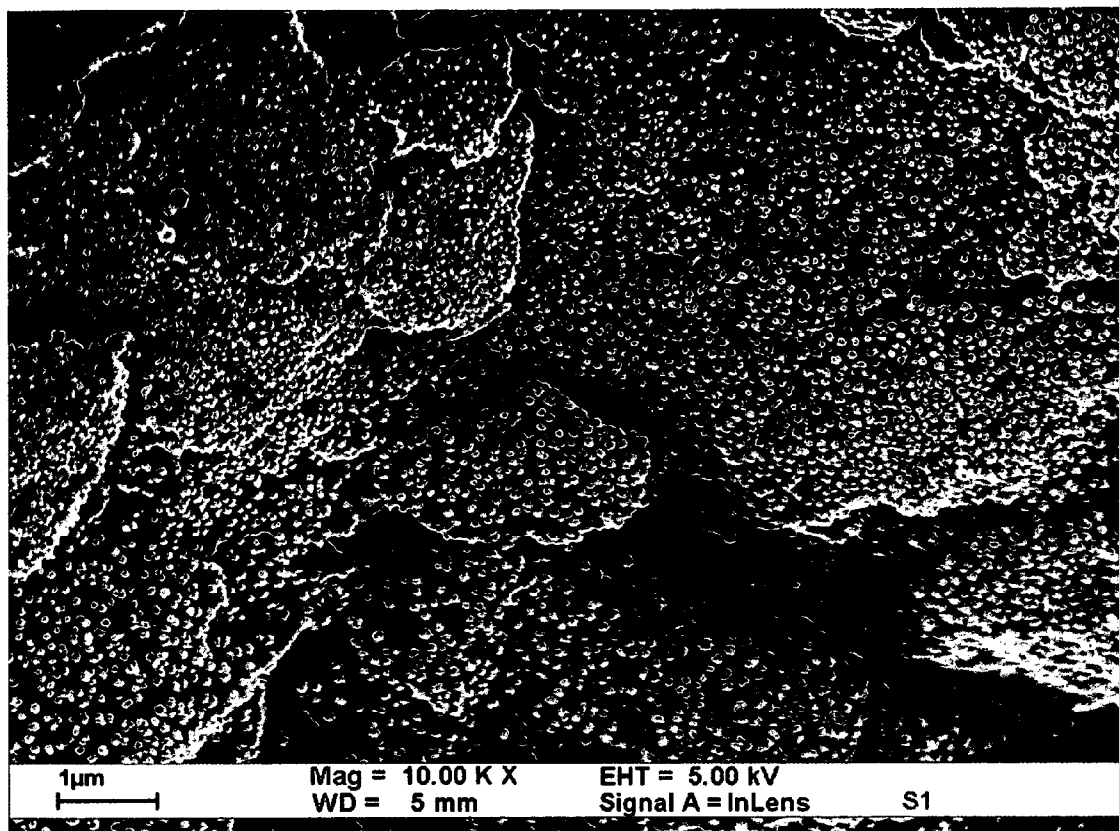


FIG. 3

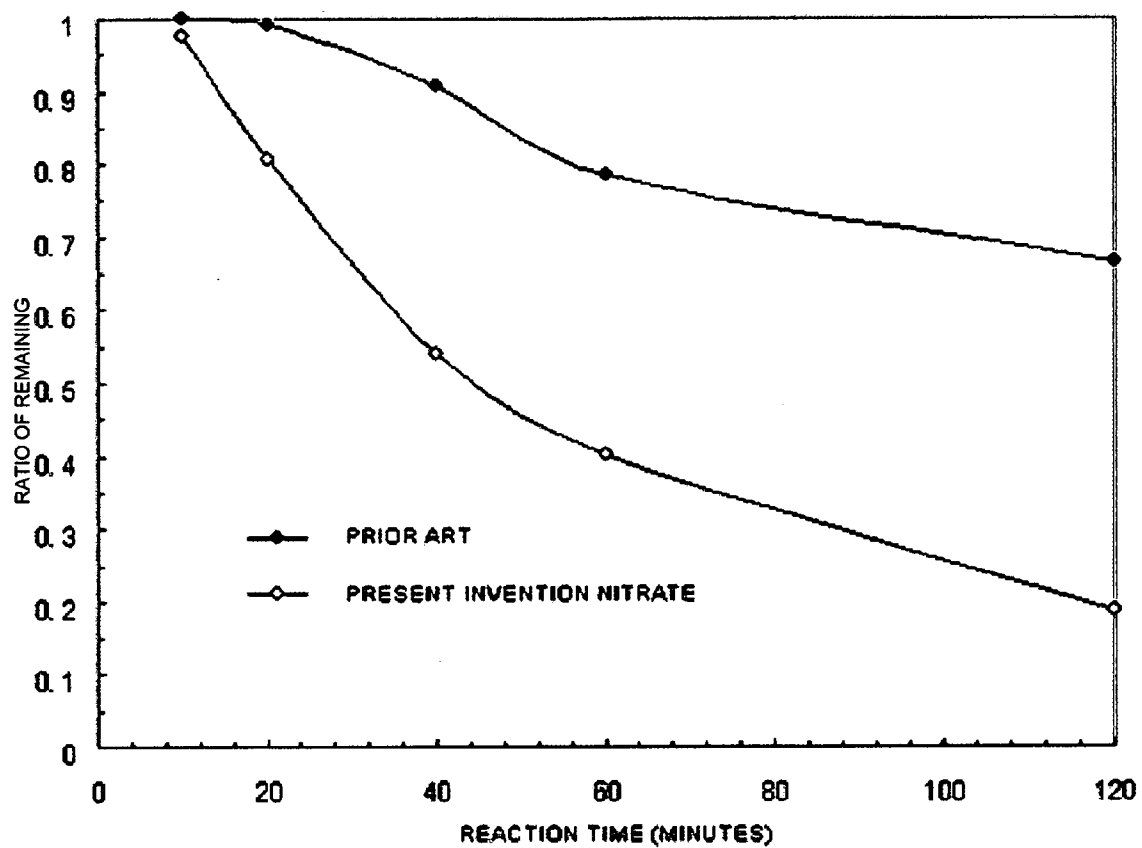


FIG. 4

METHOD FOR SPREADING NOBLE METAL ON IRON PARTICLE SURFACE

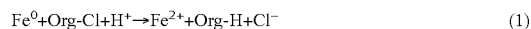
BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention

[0002] The present invention relates to method for distributing noble metal on the surface of iron particles uniformly, and especially to a method for treating the surface of iron particles and evening the activity of the surface of the iron particles.

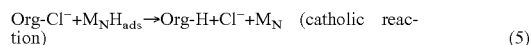
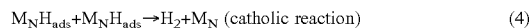
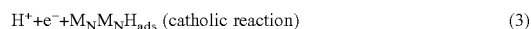
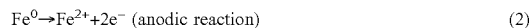
[0003] 2. Description of the Related Art

[0004] Conventionally, zero-valent iron (Fe^0) can spontaneously release electrons to reduce water pollutants, such as organic matter with chlorine, pesticides, stains, nitrates or radiation matter under natural conditions. This is similar to the process of rusting, in that a reaction (1), has organic matter with chlorine which acts as an oxidizing agent:



[0005] Without adding further additives or increasing the reaction temperature and pressure, zero-valent iron (Fe^0) can convert organic matter with chlorine, which may be carcinogenic, into a non-toxic hydrocarbon. Therefore, the applications of the zero-valent iron (Fe^0) are becoming more common and diverse due to their low cost and low-end technology level.

[0006] In conventional research, a small quantity of noble metals can be coated on the surface of the zero-valent iron (Fe^0), such as palladium (Pd), platinum (Pt) or copper (Cu), to increase surface activity. The noble metal increases the reaction rate of redox and degrades the pollutants. The reaction rate has been proven to be tens times than that of the zero-valent iron (Fe^0). Because of the potential difference between the zero-valent iron (Fe^0) and the respective noble metal, the zero-valent iron (Fe^0) is driven to release electrons to the surface of the noble metal. Hydrogen ions absorb the electrons and become hydrogen atoms with high reduction capacity. The hydrogen atoms can degrade the pollutants or combine with another hydrogen atom to form hydrogen gas. The steps mentioned above can be expressed by reactions (2) to (5) and are listed below:



[0007] Wherein M_N represents a respective noble metal, $\text{M}_\text{N} \text{H}_\text{ads}$ represents a hydrogen atom attached to the surface of the noble metal. A total reaction can be taken as a catalytic reaction for the noble metal catalyzing the zero-valent iron (Fe^0) and as a corrosion reaction of the organic matter with chlorine. In conventional immersion plating, the zero-valent iron (Fe^0) can be immersed in a solution with noble-metal ions and the noble-metal ions can be reduction to zero valence via the high active of the zero-valent iron (Fe^0), so that the zero-valent iron (Fe^0) is more highly active than the noble-metal ions. Therefore, the noble-metal ions can accept electrons to become noble-metal atoms attached to the surface of the zero-valent iron (Fe^0), such as the reaction (6) as shown below:



[0008] However, commercial iron, that has not received the appropriate pre-treatment, has a passive oxide layer formed its surface, for example, Fe_3O_4 , $\gamma\text{-Fe}_2\text{O}_3$, or the like. The passive oxide layer is formed due to the high temperature of the process or as a natural consequence of long-term storage. The zero-valent iron (Fe^0) with the passive oxide layer signifies uneven surface activity, and that means the replacement of noble metal will occur at some areas while at some other areas no replacement will occur at all. Thus, large-sized particles of noble metal are provided and the surface area is correspondingly small, so the catalysis efficiency decreases.

SUMMARY OF THE INVENTION

[0009] A method for spreading noble metal on an iron particle surface according to the present invention is provided to activate the surface of iron and react the iron particles with noble-metal ions, so that the uniformity and the activity of the noble metal attached to the iron surface can be both improved.

[0010] A method for spreading noble metal on the iron particle surface includes: providing a plurality of iron particles, cleaning-the iron particles up and separating the iron particles from cleaning water, drying the iron particles, placing the iron particles into a heater oven companied with a reaction gas, heating the iron particles to reduce oxidation, placing the iron articles to a noble-metal-ion solution for immersion plating, processing the iron particles with a solid-and-liquid separation, and drying the iron particles. Wherein the heating temperature of the heating oven ranges from 300 to 500 degrees centigrade and has a duration that ranges from 3 to 5 hours.

[0011] Whereby, the iron particles are first activated in order to react with the noble metal so that the activity and the uniformity of the noble metal attached to the iron surface are improved.

[0012] It is to be understood that both the foregoing general description and the following detailed description are exemplary, and are intended to provide further explanation of the invention as claimed. Other advantages and features of the invention will be apparent from the following description, drawings and claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] The various objects and advantages of the present invention will be more readily understood from the following detailed description when read in conjunction with the appended drawings, in which:

[0014] FIG. 1 is a flow chart of a method for spreading noble metal on the iron particle surface according to the present invention;

[0015] FIG. 2 is a SEM image of untreated commercial iron scanned by a scanning electron microscope (SEM in short);

[0016] FIG. 3 is a SEM image of commercial iron distributed with noble metal according to the present invention and scanned by a SEM; and

[0017] FIG. 4 is a diagram of commercial iron distributed with noble metal according to the present invention compared to untreated commercial iron reacting with a nitrate.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0018] A method for spreading noble metal on the iron particle surface according to the present invention is provided. A reaction gas, that includes hydrogen, mixes with nitrogen in a ratio of about 1:4. This process takes place under a heating temperature ranging from 300 to 500 degrees centigrade and a duration ranging from 3 to 5 hours for the reduction in order to reduce a passive oxide layer formed on a surface of zero-valent iron (Fe^0) particles. After the activity of the iron surface becomes uniform, a noble metal (represented by a characteristic w) can be processed with a displacement reaction. Referring to FIG. 1, an embodiment of the method according to the present invention prepares 0.5% Cu/Fe (w/Fe⁰; w represents Cu), and includes:

[0019] (1). Providing a plurality of iron particles (S100).

[0020] (2). Cleaning the iron particles robustly three times using distilled water so that the impurities and oil sludge are removed; putting the iron particles into a high-speed centrifugal dewaterer for at least 5 minutes at a rotation speed of 5000 rpm so that the iron particles are separated from the cleaning water (S102).

[0021] (3). Putting the iron particles into a freeze dryer as soon as possible for at least 12 hours to dry the iron particles in conditions of about -55 degrees centigrade and 0.2 Torr (S104) after which the iron particles become dehydrated.

[0022] (4). Providing approximately 5 g of dried iron particles into, a heater oven with a mixed reaction gas of hydrogen and nitrogen. The hydrogen and nitrogen are mixed in a ratio of about 1:4 is provided with a flow rate of about 120 milliliters per minute (120 mL/min) until the heating oven is filled. The temperature of the heating oven should be stable (S106).

[0023] (5). When the temperature of the heating oven is stable, the temperature of the heating oven starts to increase. The heater oven provides a heating profile that increases the temperature from room temperature to about 150 degrees centigrade (150° C.) at a rate of about 10 degrees centigrade per minute (10° C./min), and then remaining for about 30 minutes at about 150 degrees centigrade (150° C.) in order to remove all moisture. After this, the oven's temperature begins increasing to about 400 degrees centigrade (400° C.) at a rate of about 10 degrees centigrade per minute (10° C./min), remaining at 400 degrees centigrade (400° C.) for about 3 hours, and then returning back to room temperature. When the temperature of the heating oven returns to room temperature. The pure nitrogen gas cleans the iron particles via the flow rate of about 250 milliliters per minute (250 mL/min) for about 15 minutes (15 mins). After that, the iron particles can be removed from the heating oven (S108).

[0024] (6). The reduced iron articles are, then placed in a 250 mL solution of noble-metal-ion (containing a Cu-ion concentration of 100 mg/L) for immersion plating. The solution is then stirred slowly for 5 minutes (5 mins) (S110). The iron particles are immersed in the noble-metal-ion solution and the noble metal particles are formed and attach to the surface of the iron surface easily because the noble metal ions accept electrons easier than the zero-valent iron (Fe^0).

[0025] (7). The iron particles are then removed from the liquid via solid-and-liquid separation after the plating step via a high-speed centrifugal dewaterer. This step lasts at least 5 minutes at a rotation speed of about 5000 rpm. The iron particles are then dried by the freeze dryer as soon as possible for at least 12 hours at about -55 degrees centigrade and 0.2 Torr. Thus highly active dual metal 0.5% Cu/Fe (w/Fe⁰) particles (powders) are thereby manufactured (S114).

[0026] Another noble metal, such as Pd or Pt can be applied to the mentioned steps in the method to manufacture the dual metal, such as Pd/Fe (w/Fe⁰) or Pt/Fe (w/Fe⁰).

[0027] With respect to FIGS. 2 and 3, SEM images of conventional 0.5% Cu/Fe and the 0.5% Cu/Fe of the present invention caught by a scanning electronic microscope (SEM in short) are provided. The distinguish point between the two images is the particle size of the copper element attached to the iron element. The energy-dispersing X-ray (EDX in short) is applied to distinguish if any copper element exists from the distinguish point, and the size of most of the copper particles can be measured by the scale bar in SEM range from 750 and 850 nanometers (nm). In comparison, the size of most of the copper particles manufactured via the method of the present invention are about 150 nanometers (nm). Therefore, as the images show, the particle size of the dual metal according to the present invention is really small. Moreover, identified characters A, B and C represent three iron particles respectively, and only the particle of A can be plated the copper (Cu) which the size is around 750-850 nm, the particles of B and C can not be plated the copper due to the oxidation layers of the particles of are too thick in FIG. 2, but this phenomenon does not exist in FIG. 3. This proof shows that the distribution uniformity of the copper particles of the dual metal in FIG. 3 is much more than that in FIG. 2. The principle and operation of SEM or EDX is common knowledge and needn't further description.

[0028] Referring to FIG. 4, two solutions containing 40 mg/L of nitrate respectively react with the conventional method and the method of the present invention 0.5% Cu/Fe. After the process, the reaction rate of the present 0.5% Cu/Fe is 3.5 times faster than that of the conventional one. This is because the particle size of the present invention is less than that of the conventional method, and the effective surface area increases the rate of catalysis in the method of the present invention.

[0029] In the conventional method, a passive layer without special treatments exists on the surface of iron particles so that large-sized copper particles are generated at some specific areas and the other areas have no copper particles attached thereto. On the contrary, the dual metal according to the present invention with high activity reduces the catalysis time due to the increased effective surface area.

[0030] Although the present invention has been described with reference to the preferred embodiments thereof, it will be understood that the invention is not limited to the details thereof. Various substitutions and modifications have been suggested in the foregoing description, and others will occur to those of ordinary skill in the art. Therefore, all such substitutions and modifications are intended to be embraced within the scope of the invention as defined in the appended claims.

What is claimed is:

1. A method for spreading noble metal on an iron particle surface, comprising:

providing a plurality of iron particles;

cleaning the iron particles and separating the iron particles from cleaning water;

drying the iron particles;

placing the iron particles into a heater oven with a reaction gas;

heating the iron particles for oxidation reduction with a heating temperature ranging from 300 to 500 degrees centigrade and a duration ranging from 3 to 5 hours;

placing the iron articles in a noble-metal-ion solution for immersion plating; and

processing the iron particles with a solid-and-liquid separation after the immersion plating step, and then drying the iron particles.

2. The method as claimed in claim 1, wherein the step of immersion plating includes:

applying a high-speed centrifugal dewaterer for at least 5 minutes.

3. The method as claimed in claim 1, wherein the step of drying includes:

applying a freeze dryer for at least 12 hours in which conditions thereof are about -55 degrees centigrade and 0.2 Torr.

4. The method as claimed in claim 1, wherein the reaction gas includes hydrogen mixing with nitrogen.

5. The method as claimed in claim 4, wherein the hydrogen mixes with the nitrogen at a ratio of about 1:4.

6. The method as claimed in claim 4, wherein the hydrogen and the nitrogen are mixed and inputted into the heater oven at about 400 degrees centigrade (400° C.), the heater oven provides a heating profile that increases the temperature from room temperature to about 150 degrees centigrade (150° C.) at the rate of about 10 degrees centigrade per minute (10° C./min), maintains that temperature for about 30 minutes, then increases to about 400 degrees centigrade (400° C.), maintaining at about 400 degrees centigrade (400° C.) for about 3 hours, and returning back to room temperature.

7. The method as claimed in claim 6, wherein the iron particles are cleaned up by pure nitrogen gas the temperature in the heating oven returns back to room temperature.

8. The method as claimed in claim 7, wherein the pure nitrogen gas is provided for about 15 minutes with a flow rate of about 250 milliliters per minute (250 mL/min).

9. The method as claimed in claim 1, wherein the solution includes a noble-metal-ion at a concentration of 100 milligrams per liter (100 mg/L).

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