Preparation and mechanism of Fe_3O_4/Au core/shell super-paramagnetic microspheres

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Abstract   In the presence of Fe_3O_4 nano-particles, a new type of super-paramagnetic Fe_3O_4/Au microspheres with core/shell structures was prepared by reduction of Au^{3+} with hydroxylamine. The formation mechanism of the core/shell microspheres was studied in some detail. It was shown that the formation of the complex microspheres can be divided into two periods, that is, surface reaction-controlled process and diffusion-controlled process. The relative time lasted by either process depends upon the amount of Fe_3O_4 added and the initial concentration of Au^{3+}. XPS analysis revealed that along with increasing in coating amount, the strength of the characteristic peaks of Au increased, and the Auger peaks of Fe weakened and even disappeared. Size distribution analysis showed that the core/shell microspheres are of an average diameter of 180 nm, a little bit larger than those before coating.

Keywords: Fe_3O_4, gold, super-paramagnetic microspheres, core/shell structure.

The preparation and properties of super-paramagnetic microspheres coated with various polymers, biopolymers and inorganic materials have been studied intensively[1—3] due to their widespread uses in affinity chromatography[4], cell sorting[5], purification and separation of DNA[6] and targeting therapy[7], etc. Core/shell structured microspheres may be prepared by both physical and chemical methods. Considering the bio-compatibility and bio-degradability of Fe_3O_4[8] and the widespread uses of colloidal gold in clinical test[9,10], it was decided to prepare a new type of super-paramagnetic microspheres with core/shell structures. In the microspheres, gold was physically coated on Fe_3O_4 nano-particles. It is expected that the new type of microspheres may have the advantages of both components, that is, easy separation of super-paramagnetic particles and easy modification of gold surfaces, and make their applications more convenient and efficient.

It is a routine method to prepare nano-gold from organic/water two-phase system[11]. In a recent report, Brown et al.[12] described a method for preparing colloidal gold particles with uniform size distribution. In the preparation, nano-gold was used as seeds and hydroxylamine was used to reduce Au^{3+} which had been adsorbed on the seed surface. It seems that nano-gold functions as both seeds and catalyst for the reduction of Au^{3+}. Inspired by Brown and Natan's work, in the

present study, nano-Fe$_3$O$_4$ was used as seeds to adsorb Au^{3+} and hydroxylamine was used to reduce the adsorbed gold ions. Clearly, the nano-Fe$_3$O$_4$ particles coated with gold may function as catalyst for further reduction of adsorbed Au^{3+}. In this way, a core/shell type of complex Fe$_3$O$_4$/Au microspheres has been prepared and characterized by XPS and a laser size distribution analyzer. The main results, especially the preparation method and the formation mechanism of the complex microspheres, are presented in this paper.

1　Experimental

1.1　Materials and instruments

FeCl$_3$ • 6H$_2$O(99.0%), NH$_2$OH • HCl (98.5%), and AuCl$_3$ • HCl • 4H$_2$O were products of Xi'an Chemicals. FeCl$_2$ • 4H$_2$O(98.0%) was purchased from Shanghai Shanhai No. 2 Experimental Factory. All chemicals used were of analytical grade. Water was purified by deionization and double distillation before use.

Beckman DU-640 UV-VIS spectrometer was used for the absorbance measurement. PE PHI-5400 ESCA system was used for XPS determination, and the Mastersizer 2000 was used to determine the size distribution of the microspheres.

1.2　Synthesis of Fe$_3$O$_4$ ferrofluid

Fe$_3$O$_4$ ferrofluid was obtained by adding a concentrated solution of NaOH (10 mol/L) into a mixture of iron salts with a molar ratio of 1/2 (FeCl$_2$/ FeCl$_3$)[13]. The solution was stirred at 20℃ for 1 h and then heated to 90℃. After the heating, the system was incubated at the same temperature for another 1 h. Subsequently, Fe$_3$O$_4$ particles produced were separated by using external magnetic field and washed with plenty of water to achieve a neutral Fe$_3$O$_4$ suspension. Fe$_3$O$_4$ ferrofluid prepared in this way was used as seeds for the preparation of gold-coated magnetic particles. The solid content of this suspension is 5.6 mg/mL.

1.3　Synthesis of gold coated super-paramagnetic microspheres

The wet slurry was diluted with pure water for 10 times, withdraw a certain amount of the suspension and then mixed with 2.4 mL of HAuCl$_4$(0.1%, weight percent) and 0.1 mL of NH$_2$OH (80 mmol/L) in a cell. The reaction was monitored by measuring the absorbance of the system at 400 nm. This is because the absorbance of the reaction system at 400 nm depends linearly upon the concentration of Au^{3+} within a wide concentration range(eq.(1)):

$$A = 7.26C - 0.083, \tag{1}$$

where A stands for the absorbance of Au^{3+} at 400 nm, and C is the concentration of Au^{3+} in percentage.

It has been proved experimentally that both Fe$_3$O$_4$ and Fe$_3$O$_4$/Au microspheres have little absorbance or scattering at 400 nm. Therefore, it should be possible that the amount of gold ions adsorbed and reduced could be measured by recording the absorbance of the system at 400 nm. Even so, the suspension containing Fe$_3$O$_4$ or Fe$_3$O$_4$/Au microspheres has been adopted as blank

for the measurement.

2   Results and discussion

2.1   Adsorption of Au^{3+} onto Fe_3O_4 super-paramagnetic particle surface

No doubt, the effective adsorption of Au^{3+} onto the seed surface is absolutely necessary for the preparation of the core/shell microspheres. Therefore, the adsorption process was investigated first. 200, 300 and 400 μL Fe_3O_4 slurry was added, respectively, to a 1-cm quartz cell. And to the cell, 2.4 mL of $HAuCl_4$ solution (0.1%, weight percent), was added and mixed vigorously. A system with no $HAuCl_4$ was used as control. The absorbance of each system at different times after the mixing was recorded. The results are shown in fig. 1, revealing that in the presence of Fe_3O_4, the concentration of Au^{3+} in free state decreases with time, and the degree of decreasing depends upon the amount of Fe_3O_4 introduced. In contrast, the absorbance of the control system did not change within the experimental error and with time. Thus, it might be concluded that the decrease in Au^{3+} was caused by its adsorption on the particle surface.
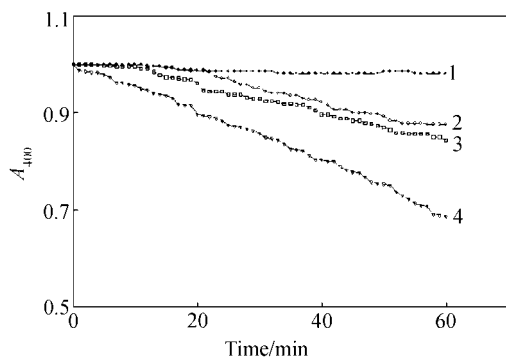

Fig. 1.   The adsorption of Au^{3+} on the different volumes of Fe_3O_4 particles. 1, Control; 2, 200 μL Fe_3O_4; 3, 300 μL Fe_3O_4, 4, 400 μL Fe_3O_4.

Fig. 1 can further reveal that the adsorption is a slow and self-catalyzing process. There is a short introduction period (about 10 min) in the system with a lower concentration of Fe_3O_4. After the period, the adsorption process speeds up. However, for the system with highest concentration of Fe_3O_4, the introduction period is almost zero. In addition, all adsorption curves are up-curved, showing that the adsorption is a typical self-catalyzing process.

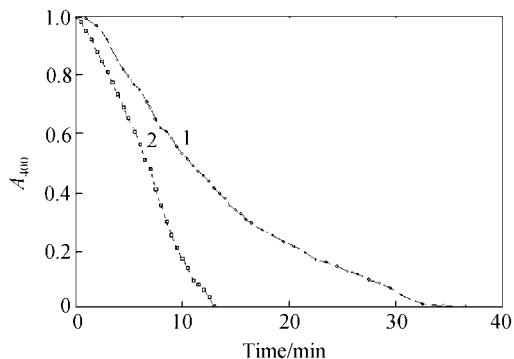### 2.2   Catalyzing reduction of Au^{3+} by hydroxyl-amine

The aqueous solution of $HAuCl_4$ can be reduced by NH_2OH. However, the reduction rate was significantly increased with the introduction of Fe_3O_4. As an example, fig. 2 shows some experimental results. It can be seen from the figure that the absorbance of the system with Fe_3O_4 decreases much faster with time than the corresponding control system. The catalytic reduction of Au^{3+} by NH_2OH may be rationalized by considering the large surface energy of Fe_3O_4 due to its small size. The large surface area favors the

Fig. 2.   Comparison of colloid Au formation between no seeds and using Fe_3O_4 particle as seeds. 1, Au^{3+}-NH_2OH; 2, Fe_3O_4-Au^{3+}-NH_2OH.

adsorption of Au^{3+}, and the high surface energy will make Au^{3+} be reduced more easily. Soon after the formation of the first layer of gold, the surface properties of the particles would have no difference with those of the pure gold, which had been proved to catalyze the reduction of Au^{3+} by NH$_2$OH. Therefore, it might be expected that the coating reaction continues until extinction of one of the reactants occurs.

The tentative conclusion that both Fe$_3$O$_4$ and gold-coated Fe$_3$O$_4$ particles have the ability to catalyze the reduction of Au^{3+} by NH$_2$OH was further supported by the experimental results shown in fig. 3. Obviously, the absorbance of the two systems with either particle decreases significantly faster than that of the control system. Furthermore, the particles coated with gold are much more active than pure Fe$_3$O$_4$ for the catalyzing process. This is in support of the result reported by Brown et al.[12]. The finding is important because it might be possible to control the particle size or the thickness of the gold shell by simply adjusting the concentration of Au^{3+} and/or NH$_2$OH in the reaction system.

Except the surface nature, the catalyzing reduction of Au^{3+} was also particle content dependence. Fig. 3 depicts the dependence of the reduction rate on the content of Fe$_3$O$_4$.

Clearly, by fixing the amount of the reactants, the more the particle added, the greater the reduction rate. It is also noted that the shape of curve 3 is significantly different from the others. It is composed of two parts. The first part stands for a fast reduction process and the second is a slow reduction process. The finding may be understood by

Fig. 3.   The whole reaction process at different situations. 1, No seeds; 2, 200 μL Fe$_3$O$_4$; 3, Fe$_3$O$_4$/Au as seeds; 4, 100 μL Fe$_3$O$_4$.

supposing that the fast reduction process is a surface reaction controlled process, and the second is a diffusion controlled process. This rationalization was further confirmed by the results from a designed experiment (fig. 4). In the experiment, the content of Fe$_3$O$_4$ was fixed and the initial concentration of Au^{3+} was varied. With reference to the figure, it can be revealed that each curve, except the one with 0.1% Au^{3+}, was also composed of two parts. The first process lasted longer for the system with higher concentration of Au^{3+}. This phenomenon may be understood by considering
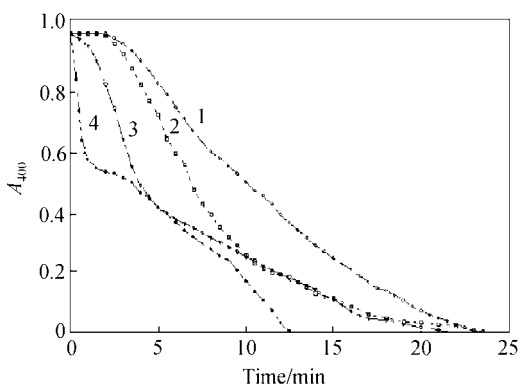

Fig. 4.   The effect of reductive process on different initial Au^{3+} solutions. 1, 0.1% Au^{3+}; 2, 0.075% Au^{3+}; 3, 0.05% Au^{3+}; 4, 0.025% Au^{3+}.
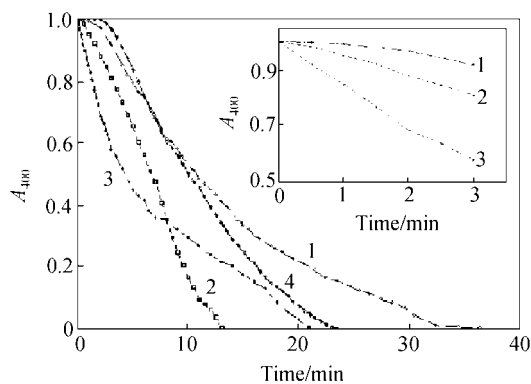
the proposed mechanism that the reaction rate should depend upon the surface area available for the reaction. For any of the systems mentioned, there is no difference in this respect because the content of Fe_3O_4 had been fixed. Therefore, the greater concentration of reactant will make this process last longer only when the concentration of the reactant decreases to a certain amount at which the reactant consumed by surface reduction is just complemented by that arriving at the surface, the reduction becomes diffusion controlled. As for the system with highest concentration of Au^{3+}, the concentration of Au^{3+} remaining in the system is so large that the consumption of Au^{3+} by the surface reaction is always lower than that diffused to the particle surface.

2.3 Synthesis of gold coated super-paramagnetic particles

As mentioned earlier, preparation of core/shell super-paramagnetic particles with gold as coatings is of great value both theoretically and practically. Considering that addition of Fe_3O_4 nano-particles will significantly accelerate the reduction of Au^{3+} by NH_2OH, it might be possible to prepare the structured microspheres by using the above-mentioned method. However, it is noted that Au^{3+} can be also reduced by NH_2OH in the absence of Fe_3O_4. Therefore, it is important to make sure that only gold-coated magnetic particles rather than the mixture of pure gold and the core-shell structured particles are produced.

It can be observed that before coating the seeds, Fe_3O_4, was black, and after the coating reaction was finished the particles became dark-red. This is a clear evidence for the successful coating of gold onto Fe_3O_4 particles. In addition, the whole particles precipitated quickly when the beaker containing the gold-coated particles was put on a permanent magnetite. In contrast, the control system without treatment with external magnetic field remained to be a colloid for quite a long time, another evidence for the coating of gold on the magnetic particle surface. To confirm the result further, pure colloid gold was prepared also and the response of the colloids to external magnetic field was also tested. It was found that treatment with external magnetic field could not induce precipitation of the colloids. All the results described above show clearly that in the system containing Fe_3O_4 particles the gold-coated magnetic particles are the main products if appropriate reaction condition was selected.

Fig. 5 shows the XPS spectra of the naked Fe_3O_4 particles and the core/shell particles with different amounts of gold coatings. In fig. 5 curve 1 is the XPS spectrum of naked Fe_3O_4, curve 2 is the XPS spectrum of the core/shell particles with less gold coatings, and curve 3 is that of the core/shell particles with more gold coatings. The Auger peaks, and characteristics of Fe, appear clearly in curve 1. Curve 2 shows clearly that with gold coating, the characteristic $Au4f^5$ and $Au4f^7$ peaks of Au appear significantly, and at the same time the Auger peaks of Fe decrease. Reference curve 3 reveals that with more gold coatings the Auger peaks of Fe almost disappear completely, and strength of O1s is also weakened. By contrast, the curve is characterized by various gold peaks including $Au4f^5$, $Au4f^7$, $Au4d^3$, $Au4d^5$, and $Au4p^3$, etc. It is known that the doublet peaks at 87.5 and 83.8 eV ($Au4f^5$ and $Au4f^7$) shown in fig. 5(b) are the characteristics of Au^0 [14].

The high intensity of these peaks indicates clearly that the core/shell particle surface is mainly composed of pure gold.
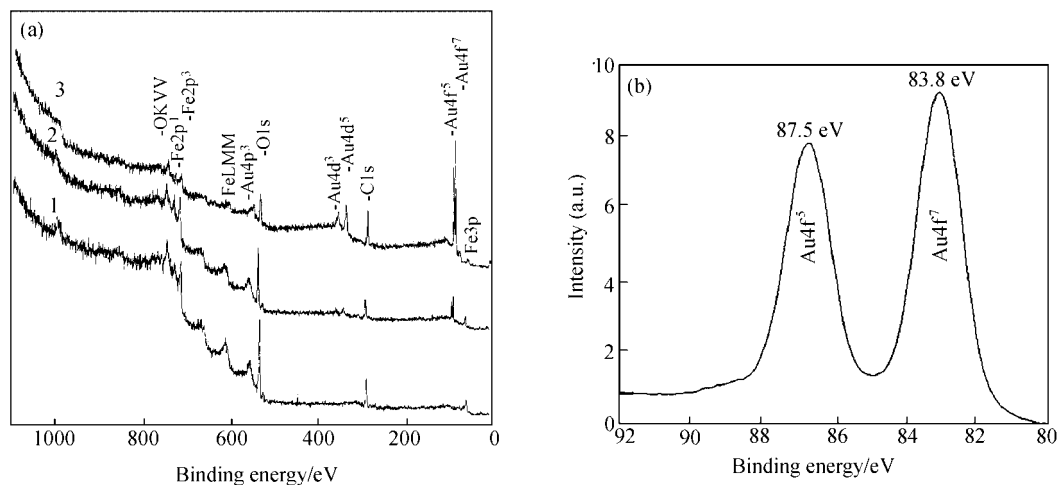

Fig. 5.   XPS spectra of naked and coated particles.

Fig. 6 is the size distribution of the naked and core/shell super-paramagnetic microspheres. The average diameter, d (0.5), of the naked Fe_3O_4 particles is 175 nm. The naked particles aggregated slightly during the determination, which was evidenced by the appearance of a small tail in curve 1. The aggregation disappeared after coating with gold. However, there are two distinct components in the core/shell microspheres as revealed by the size distribution (curve 2). The small one with a diameter of about 10 nm may be pure gold particles formed during reduction of Au^{3+}.

Anyway, the main component is the core/shell microspheres which are of an average diameter of about 180 nm, a little bit larger than those before coating. The preparation of core/shell type Fe_3O_4/Au microspheres with uniform composition and size distribution will become one of the important tasks to fulfill in the near future.
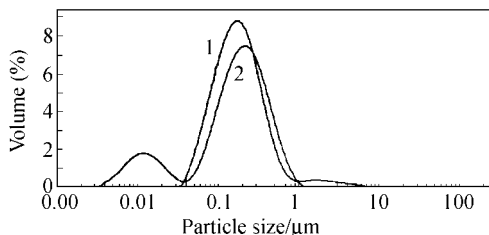

Fig. 6.   The size distribution of the naked and complex particles. 1, Size distribution of Fe_3O_4; 2, size distribution of Fe_3O_4/Au.

3   Conclusions

In the presence of super-paramagnetic Fe_3O_4 particles and excess of hydroxylamine, Au^{3+} could be reduced quickly at the particle surface. The reduction process may be divided into two parts, that is, the surface reaction controlled process and the diffusion controlled process. The time lasted by either process depends upon both the amount of Fe_3O_4 particles used and the initial concentration of Au^{3+}. In this way a new type of super-paramagnetic Fe_3O_4/Au microspheres with core/shell structures may be prepared easily. The degree of the coatings can be controlled by sim-

ply adjusting the composition of the reaction system and/or by repeating the coating process.

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