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Synthesis of surfactant-stabilized Co/Au bimetallic nanoparticles with a core-shell structure

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Well-defined surfactant-stabilized "Co-shell Au-core" bimetallic nanoparticles were successfully prepared in the presence of the mixture of two surfactant molecules. The formation of these core-shell structures is driven by the thermal deposition of $Co(CO)_8$ by refluxing *p*-xylene solution in the presence of the pre-formed gold nanoparticles which were prepared by $NaBH_4$-reduction of $HAuCl_4$. Continuous layer of cobalt without vacancies wrapping the gold core was revealed by TEM observation and the obtained bimetallic nanoparticles could be dispersed stably.

Key words: nanoparticle, bimetallic, cobalt, gold, magnetic, composite materials

1. INTRODUCTION

Nanoparticles have drawn interest due to their specific magnetic, optic, electronic, and catalytic properties, that arise from the quantum size effects and large surface areas that are characteristic of these materials.[1] Particularly, recent intensive efforts have been focused on the development of multimetallic nanoparticles in order to improve such specific properties of monometallic ones.[2] Bimetallic nanoparticles can be prepared by simultaneous reduction of the corresponding two precursor metal salts or by successive reduction of one metal over the nuclei of the other.

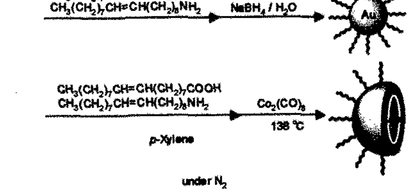
Bimetallic nanoparticles of a noble metal and a transition metal are also widely investigated. Carpenter et al.[3] and Yamamoto et al.[4] have reported synthesis of Fe/Au bimetallic nanoparticles with reverse micelles. They applied these nanoparticles as magnetic materials. Fe/Pt bimetallic nanoparticles proposed by Sun et al. have a very large magnetic property thanking to a special crystalline structure.[5] Wiggins et al. prepared a novel nanomagnetic materials, called "metal nano-onions", which exhibited a GMR effect.[6]

In this report, we demonstrate the preparation of core-shell type bimetallic Co/Au nanoparticles by combination of $NaBH_4$-reduction of gold ions and thermal decomposition of a cobalt carbonyl compound.

2. EXPERIMENTAL

All preparative processes were carried out under nitrogen in order to avoid oxidation of nanoparticles. In this study, we have selected a successive metal atom generation procedure to form Co/Au bimetallic nanoparticles with a controlled structure. All reagents were used as received. Solvents used here were HPLC grade of Kanto Chemicals. Water was purified by a Mili-Q system (> 18 MΩ).

Preparation of Co/Au bimetallic nanoparticles is shown in Scheme 1. At the first stage, gold nanoparticles as the core material were prepared by a modified Brust's method.[7] Into an aqueous solution of $HAuCl_4$ (0.494 g in 40 cm^3), a toluene solution of the phase transfer reagent, tetra-*n*-octylammonium bromide (TOAB, 2.92 g in 110 cm^3) was injected dropwise. After 1h-stirring the two-phase mixture, the aqueous phase became colorless and the toluene phase turned into red. This indicates that $AuCl_4^-$ was transferred into the toluene phase by formation of ion complex with TOAB. Toluene phase was then transferred to another flask and a mixture of oleyl amine (3.6 mmol) and oleic acid (3.6 mmol) was injected again dropwise under stirring. Previous mixing of these two surfactant reagents increased the viscosity of the surfactant liquid intensively. Then, an aqueous solution of $NaBH_4$-(0.227 g in 35 cm^3) was injected slowly by using a syringe pump. The color of the dispersion instantly turned from red into dark brown. After 3h stirring, the obtained dispersion was filtered over a membrane filter with a pore size of 0.45 μmϕ and was concentrated to the total volume of approx. 20 cm^3. This concentrated dispersion was centrifuged at 7000 rpm for 15 min and black powder was obtained



Scheme 1. Preparation scheme of Co/Au bimetallic nanoparticles.

(preformed Au nanoparticles).

The obtained Au nanoparticles were re-dispersed into *p*-xylene (110 cm^3) and the dispersion was bubbled with pure nitrogen. Then, in this dispersion, cobalt octacarbonyl ($Co(CO)_8$, 1.23 g), and a mixture of oleyl amine (3.6 mmol) and oleic acid (3.6 mmol) were introduced. The mixed dispersion was refluxed for 1h. The obtained dispersion was again filtered, concentrated, and centrifuged as described above in order to obtain Co/Au bimetallic nanoparticles in powder form.

Transmission electron microscopic observation was carried out with a Hitachi H-6000 at the acceleration voltage of 75 kV. TEM samples were made by casting a droplet onto carbon coated copper grids.

3. RESULTS AND DISCUSSION

Core-shell nanoparticles are often prepared by successive deposition method, that is, deposition of the secondary generated 0-valent metal atoms onto pre-formed metal nanoparticles of the other metal element.

Gold nanoparticles were prepared by a modified Brust's two-phase method with oleylamine and oleic acid as stabilizers instead of thiol compounds.[7] Although $NaBH_4$ is a strong reducing reagent and gold ions were reduced immediately after addition of $NaBH_4$, the obtained nanoparticles dispersion was enough stable and could be purified to obtain gold nanoparticles in powder form by filtration and centrifugation. Figure 1 shows the TEM image of the obtained surfactant-stabilized gold nanoparticles. Usually, thiol-stabilized gold nanoparticles prepared by Brust's method are very small with their diameter less than 5 nm[7], or in some cases, ca. 1.5 nm.[8] However, by using the mixture of oleylamine and oleic acid, the particles grew much larger. The diameter of these particles is in the range of 8 – 10 nm. The structure of the particles is not spherical but cubic or hexyagonal and shows clear edges. The contrast changes and fringes in the particles indicated that they are well crystallized. Some particles are fused on the TEM grid. Probably the lack of strong coordination between the stabilizing reagents (oleylamine and oleic acid) and the gold nanoparticle surface introduces this structural transformation.

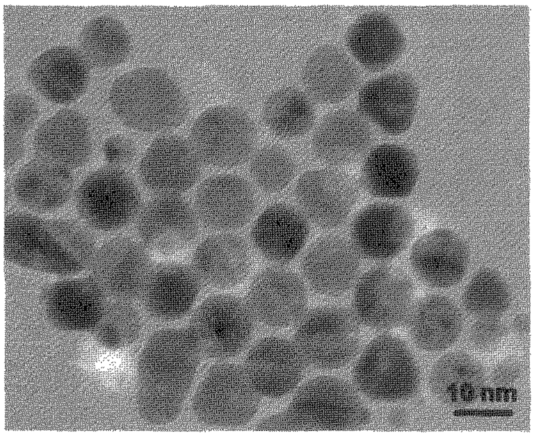


Figure 1 TEM image of gold nanoparticles stabilized by the mixture of oleylamine and oleic acid. The reducing reagent was $NaBH_4$.

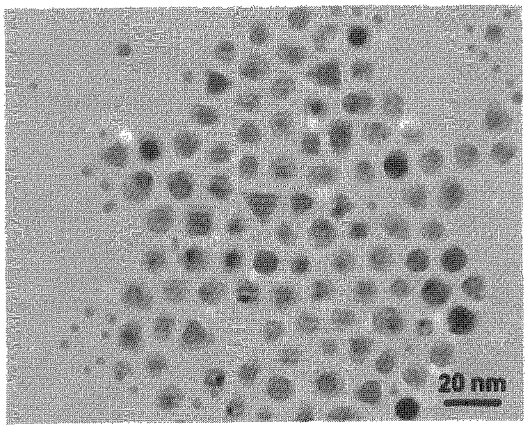


Figure 2 TEM image of $\text{Co}_{\text{shell}}\text{Au}_{\text{core}}$ bimetallic nanoparticles prepared by deposition of 0-valent Co atoms onto pre-formed gold nanoparticles. The stabilizers used here was the 1/1 (mol/mol) mixture of oleylamine and oleic acid. Co layers (grey area) continuously cover Au nanoparticles (black dot). Some small Au nanoparticles are also observed in the image.

The obtained black powder of gold nanoparticles could be readily re-dispersed into *p*-xylene which have a boiling temperature enough high (138 °C) in order to decompose $Co(CO)_8$ to generate 0-valent cobalt atoms. After refluxing *p*-xylene dispersion for 1h, no obvious precipitate was observed.

Figure 2 shows the typical TEM image of the Co/Au bimetallic nanoparticles prepared by sequential generation of gold and cobalt atoms. In this image, black dots are covered by grey surrounding layer. Black dots are gold nanoparticles as in Figure 1 and grey layer can be attributed to cobalt. This image clearly indicates that cobalt atoms, which were generated by thermal decomposition of $Co(CO)_8$, were successfully deposited onto the pre-formed gold nanoparticles and most of the particles obtained here have $\text{Co}_{\text{shell}}\text{Au}_{\text{core}}$ structure. Unfortunately, the variation of the particle size of Co/Au bimetallic nanoparticles is obviously larger than pre-formed Au nanoparticles and the thickness of the cobalt layer is not quite unique. But no distinct fragmentation of cobalt layer can be observed in this TEM image.

Preliminary SQUID data of these bimetallic nanoparticles showed superparamagnetic behavior as other small nanoparticles.[4]

Preparation of more uniform core-shell type Co/Au bimetallic nanoparticles is now under investigation. Further detailed magnetic properties will be reported separately.

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