

IMMOBILIZATION OF MAGNETITE ON CORE-SHELL PARTICLES

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ABSTRACT

A method for magnetite-immobilization on Au-SiO₂ core-shell (Au/SiO₂) particles is proposed. A colloid solution of 2.4×10^{-4} M Au nanoparticles with an average size of 16.9 ± 1.2 nm was prepared by mixing HAuCl₄ at 2.4×10^{-4} M and sodium citrate at 1.6×10^{-3} M in water at 80°C. Au/SiO₂ particles with an average size of 47.3 ± 3.5 nm were prepared by using a sol-gel method at 35°C in ethanol with 2.0×10^{-5} M (3-aminopropyl) trimethoxysilane as a silane coupling agent, 5.0×10^{-4} M tetraethylorthosilicate as a silica source, 10.7 M H₂O and 5.0×10^{-4} M NaOH as a catalyst in the presence of 4.3×10^{-5} M Au nanoparticles. The Au/SiO₂ particles were surface-modified with 1.0 g/L poly-diallyldimethylammonium chloride at 4.3×10^{-5} M Au. Preparation of colloid solution of magnetite nanoparticles with an average of 7.3 ± 1.6 nm was performed with a salt-base reaction at room temperature in aqueous solution containing 7.2×10^{-2} M FeCl₃, 3.6×10^{-2} M FeCl₂, 3.6×10^{-2} M HCl and 4.0×10^{-1} M NaOH. The magnetite nanoparticles were immobilized on the Au/SiO₂ particles (Au/SiO₂/magnetite) by mixing the Au/SiO₂ particle colloid solution with an Au concentration of 8.6×10^{-5} M and the magnetite nanoparticle colloid solution with Fe concentrations of 3.0×10^{-4} – 3.0×10^{-3} M. The Au/SiO₂/magnetite particles prepared at the Fe concentrations of 1.2×10^{-3} M and above were well drawn close to magnet. These results confirmed that the proposed method was suitable to magnetite-immobilization.

Key words: Core-shell, Particle, Au, Silica, Magnetite

I. INTRODUCTION

Iodine compounds have been used as X-ray contrast agents in medical examination [1], because of their strong absorption for X-ray. Since X-ray contrast agents that are commercially available are iodine compounds dissolved homogeneously in solvents at molecular level, the iodine compound molecules flow fast in blood tubes. Accordingly, they cannot stay in living bodies for a long period: It is hard to take X-ray images steady for a long term by using the solution-type iodine compounds.

Apart from the iodine compounds, gold is also available as the contrast agent because of its high-absorption ability for X-ray. The Au nanoparticles have been examined toward contrast agents for imaging tissues in living bodies at nanometer level [2-7].

The iodine compounds cannot be used for patients, who may be provoked adverse events like allergic reactions in [8]. For metallic nanoparticles, toxicity in living bodies has also been suggested in several kinds of metallic nanoparticles [9-13].

The above-mentioned problems can be solved by forming particles of contrast agents and coating the particles with shell of materials inert for living bodies. Moving of particles is resisted by liquid flow strongly compared to that of molecules, and the shell prevents the particles from contacting with living bodies, which decreases their toxicity. Coating of nanoparticles with silica, which is inert for living bodies, has been extensively studied by various researchers, whose methods are based on a sol-gel method [14-17]. Our research group has extended the sol-gel method to silica-coating of Au nanoparticles (Au/SiO₂) [18-21]. In our previous work [21], X-ray imaging ability was demonstrated for the Au/SiO₂ particle colloid solution.

Nanoparticles of magnetic materials, in which magnetite (Fe₃O₄) is representative, have been extensively studied, because of their wide applications such as high-density storage, magnetic resonance imaging, drug delivery, and separation of biochemical products [22, 23]. Particles composed of magnetite nanoparticles and our Au/SiO₂ particles will have both magnetic property and X-ray imaging ability.

In the present work, methods based on an electrostatic interaction between particles are examined for immobilization of magnetite on Au/SiO₂ particles (Au/SiO₂/magnetite).

II. EXPERIMENTAL

A. Chemicals

Hydrogen tetrachloroaurate (III) trihydrate (HAuCl₄•3H₂O, > 98%) and trisodium citrate dihydrate (Na-cit, 99%) were used as a starting chemical and a reducing reagent for preparing Au nanoparticles, respectively. (3-Aminopropyl) trimethoxysilane (APMS, 97.0%) and tetraethylorthosilicate (TEOS, 95 %) were a silane coupling agent between Au and silica and a silica source for silica-coating, respectively. NaOH (1 M) and ethanol (99.5 %) were used as a catalyst and a solvent in a sol-gel reaction of TEOS for silica-coating, respectively. poly-diallyldimethylammonium chloride (PDADMAC, Mw: 70000) was used for surface-modification of the Au/SiO₂ particles. Starting reagents for preparation of magnetite nanoparticle colloid solution were FeCl₂•4H₂O (99-102%) and FeCl₃ (99.9%). HCl (35-37%) and NaOH (1 M) were used for preventing Fe(OH)₂ from being produced at high pH and for precipitating Fe ions as iron hydroxide or iron oxide, respectively. HAuCl₄•3H₂O, APMS and PDADMAC were purchased from Sigma-Aldrich, and other chemicals from Kanto Chemical. All the chemicals were used as received. Water that was ion-exchanged and distilled with Yamato WG250 was used in all the preparations.

B. Preparation

Au/SiO₂ nanoparticles

Au nanoparticles were prepared by reduction in the gold salt with Na-cit [24]. Freshly prepared Na-cit aqueous solution was added to HAuCl₄ aqueous solution at a constant temperature of 80°C under vigorous stirring. Initial concentrations of Au and Na-cit were adjusted to 2.4×10^{-4} and 1.6×10^{-3} M, respectively, which resulted in production of mostly-spherical Au nanoparticles with an average diameter of 16.9 ± 1.2 nm [20].

The Au nanoparticles were silica-coated by performing a sol-gel method using TEOS, APMS, and NaOH in the presence of Au nanoparticles (Au/SiO₂). To H₂O/ethanol solution were added the Au

nanoparticle colloid solution, APMS/ethanol solution and TEOS/ethanol solution in turn. Finally, NaOH aqueous solution was added to the Au/H₂O/TEOS/ethanol solution for initiating a sol-gel reaction of TEOS. The reaction temperature and time were 35°C and 24 h, respectively. Initial concentrations of Au, H₂O, NaOH, APMS, and TEOS were 4.3×10^{-5} , 10.7, 5.0×10^{-4} , 2.0×10^{-5} , and 5.0×10^{-4} M, respectively, which resulted in production of Au/SiO₂ core-shell particles with an average diameter of 47.33.5 nm.

Magnetite nanoparticles

Magnetite nanoparticles were prepared with a salt-base reaction between Fe ions and NaOH. Aqueous solution that contained FeCl₂ and HCl was mixed with FeCl₃ aqueous solution. NaOH aqueous solution was added to this mixture, and stirred for 1 h to complete the reaction. Initial concentrations of FeCl₃, FeCl₂, HCl and NaOH were 7.2×10^{-2} , 3.6×10^{-2} , 3.6×10^{-2} and 4.0×10^{-1} M, respectively. The particles were washed by repeating a treatment composed of centrifugation, removal of supernatant, addition of water, and shake with a vortex mixer three times. A total Fe concentration was adjusted to 1.2×10^{-1} M by varying the amount of water added at the final treatment.

Au/SiO₂/magnetite particles

Immobilization of the magnetite nanoparticles on the Au/SiO₂ particles, *i.e.*, fabrication of Au/SiO₂/magnetite particles, was performed by utilizing an electrostatic force of attraction. The Au/SiO₂ particle surface was cationized by immersing the Au/SiO₂ particles into PDADMAC aqueous solution, in which concentrations of Au and PDADMAC were 4.3×10^{-5} M and 1.0 g/L, respectively. The cationized particles were washed by repeating a treatment composed of centrifugation, removal of supernatant, addition of water, and shake with a vortex mixer three times. Then, the magnetite colloid solution was added to the colloid solution of the cationized Au/SiO₂ particles, in which concentrations of Au and Fe were 8.6×10^{-5} and $3.0 \times 10^{-4} - 3.0 \times 10^{-3}$ M, respectively. The pH of the solution was adjusted to 9. The reaction temperature and time were 20°C and 24 h, respectively.

C. Characterization

The particles were characterized by X-ray diffractometry (XRD), TEM, zeta potential analysis using electrophoretic light scattering and ultra violet-visible (UV-VIS) spectroscopy. XRD chart was recorded with a Rigaku RAD-C X-ray diffractometer operated at 20 kV and 40 mA with CuK α radiation. Samples for the XRD were prepared by repeating a treatment composed of centrifugation, removal of supernatant, addition of water, and shake with a vortex mixer three times, and by drying the sediment after the final supernatant removal. TEM was performed with a JEOL JEM-2000FXII microscope operated at 200 kV. Samples for TEM were prepared by dropping and evaporating the particle suspensions onto a collodion-coated copper grid. ζ -Potentials of particles were measured with a Brookhaven Instruments ZetaPALS zeta potential analyzer.

III. RESULTS AND DISCUSSION

A. Magnetite nanoparticles

Fig. 1 shows an XRD pattern and a TEM image of the magnetite nanoparticles. All the peaks detected could be indexed to Fe_3O_4 (JCPDS card No 19-629). The particles might have contained $\gamma\text{-Fe}_2\text{O}_3$, because a diffraction pattern of $\gamma\text{-Fe}_2\text{O}_3$ (JCPDS card No 39-1346) is quite similar to Fe_3O_4 . Since both Fe_3O_4

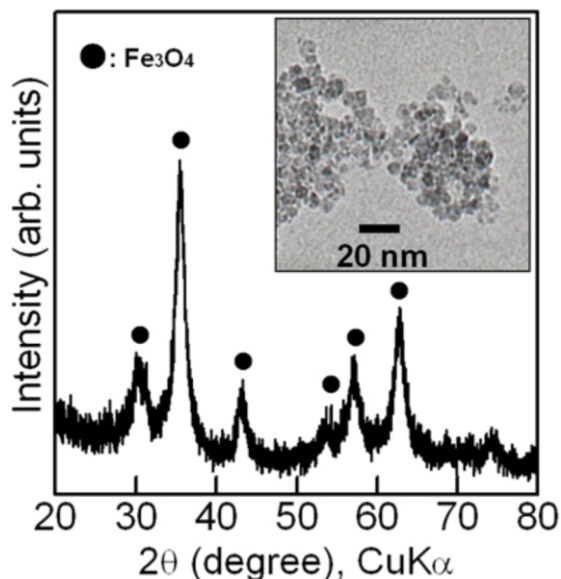


Fig. 1. XRD pattern of magnetite nanoparticles, Inset show their TEM image.

and $\gamma\text{-Fe}_2\text{O}_3$ are ferromagnetic, the aim of making the Au/SiO_2 particles have magnetic property is not lost. The particles had an average diameter of 7.3 ± 1.6 nm. Fig. 2 shows ζ -potential of the magnetite nanoparticles as a function of pH. An isoelectric point of the particles was 8.2.

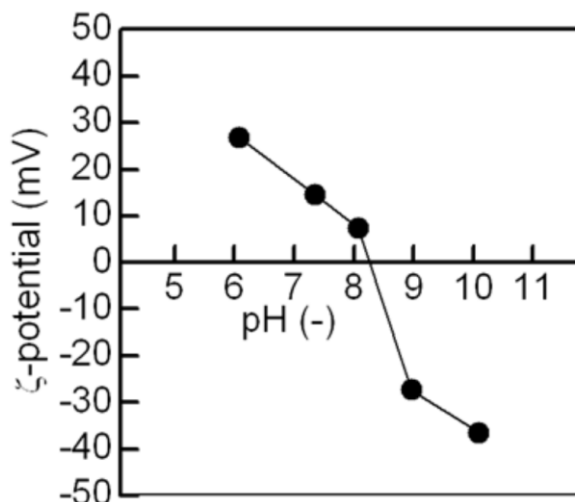


Fig. 2. ζ - Potential of the magnetite nanoparticle versus pH of the particle colloid solution

B. Au/SiO_2 /magnetite particles

Since the magnetite nanoparticles had the isoelectric point of 8.2, they were anionic at pH9. Accordingly, the magnetite nanoparticles were expected to be immobilized electrostatically on the cationized Au/SiO_2 particle surface by the pH adjustment to 9.

Fig. 3 shows an XRD pattern of the Au/SiO_2 /magnetite particles. Peaks due to Fe_3O_4 were detected. Besides the peaks, peaks appeared at 38.2, 44.1, 64.6 and 77.4 degree, which were attributed to face-centered cubic structured Au (JCPDS card No 4-784). This result indicated that crystal structures of metallic Au and magnetite were not damaged during the magnetite-immobilization procedure, and implied successful magnetite-immobilization for the Au/SiO_2 particles.

Fig. 4 shows photographs of as-prepared Au/SiO_2 /magnetite particle colloid solutions. All the colloid solutions examined were colloiddally stable. The color of Au/SiO_2 colloid solution was wine red.

concentration, because the magnetite nanoparticle colloid had a color of dark brown.

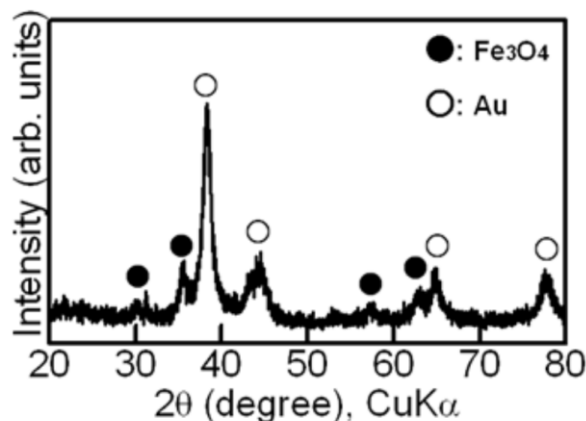


Fig. 3. XRD pattern Au/SiO₂ magnetite particles

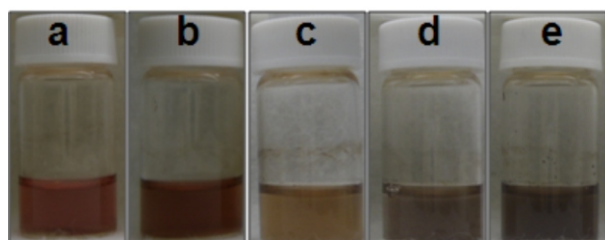


Fig. 4. Photographs of as - prepared Au/SiO₂/magnetite particle colloid solutions prepared at Fe concentrations of (a) 3.0×10^{-4} , (b) 6.0×10^{-4} , (c) 1.2×10^{-3} , (d) 2.1×10^{-3} , and (e) 3.0×10^{-3} M

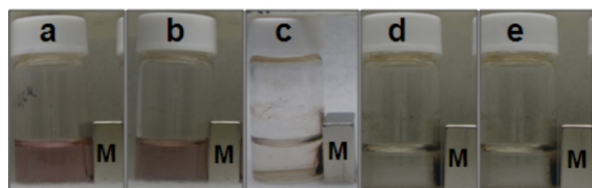


Fig. 5. Photographs of Au/SiO₂/ magnetite particle colloid solutions after placing a magnet on the sample bottle wall. The samples were the same as in Fig. 4. M: magnet.

Fig. 5 shows photographs of Au/SiO₂/magnetite particle colloid solutions after placing a magnet on the sample bottle wall. For Fe concentrations of 1.2×10^{-3} M and above, the particles were dominantly gathered on the inside wall of bottle near magnet, and

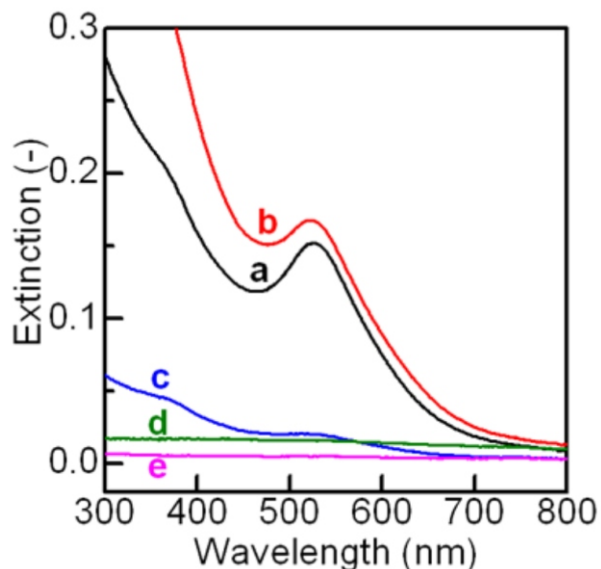


Fig. 6. UV-VIS extinction spectra of colloid solutions after placing a magnet on the sample bottle wall and separating the gathered particles from the Au/SiO₂/magnetite particle solutions. The samples

were the same as in Fig. 5. the solutions became clear. Fig. 6 shows UV-VIS extinction spectra of colloid solutions after placing a magnet on the sample bottle wall and separating the gathered particles from the Au/SiO₂/magnetite particle solutions. At Fe concentrations of 3.0×10^{-4} and 6.0×10^{-4} M, peaks attributed to surface plasmon resonance of Au nanoparticles were observed at ca. 520 nm. The Fe concentrations were not enough for the amount of Au/SiO₂ particles. Consequently, all the Au/SiO₂ particles were not magnetite-immobilized, and such Au/SiO₂ particles with no Fe₃O₄ were not gathered with magnet, which provided their remaining in the solution. In contrast, no dominant peaks were detected for the Fe concentrations of 1.2×10^{-3} M and above. This indicated that the magnetite nanoparticles were successfully immobilized on most Au/SiO₂ particles because of the enough Fe concentrations. As a result, many particles in the colloid solution were efficiently gathered with magnet.

IV. CONCLUSION

A method for preparing Au/SiO₂ core-shell particles, on the surface of which magnetite nanoparticles was immobilized (Au/SiO₂/magnetite), was proposed. Au nanoparticles that were prepared by mixing HAuCl₄ and Na-cit were silica-coated with a sol-gel method using APMS, TEOS, water and NaOH

in ethanol. The Au/SiO₂ particle surface was cationized with PDADMAC for efficient magnetite-immobilization. Magnetite nanoparticles were prepared by means of a salt-base reaction between iron ions and NaOH in water. Au/SiO₂/magnetite particles were successfully fabricated by mixing the surface-cationized Au/SiO₂ particle colloid solution with the magnetite nanoparticle colloid solution. The obtained Au/SiO₂/magnetite particles were well gathered with magnet. Accordingly, the Au/SiO₂/magnetite particles are expected to have dual functions of ferromagnetism and X-ray imaging ability. Further investigation towards practical use for medical examination is now in progress.

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