

Synthesis of gold-coated iron nanoparticles by a reverse micelle method

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Gold-coated iron nanoparticles were fabricated by a two-step reverse micelle method. The core-shell structure of nanoparticles where an Fe core is surrounded by Au shell was revealed by TEM, XRD and EDS. This structure shows that the Au shell was formed on the surface of the Fe core before the coalescence of nanoparticles. The UV-vis absorption spectrum of colloidal nanoparticles exhibited an absorption band at 526 nm and magnetic measurements indicated that the nanoparticles are superparamagnetic at room temperature.

Key words : Nanoparticles, Core-shell structure, Reverse micelle method, Magnetic property.

Introduction

Magnetic nanoparticles have attracted much attention due to their potential applications in magnetic sealing [1], magnetic resonance imaging (MRI) [2, 3], and cell tagging and sorting [4]. Recently, considerable progress has been made in the synthesis of various magnetic nanoparticles [5] and now particle size, particle shape, and surface properties may be controlled. In particular, core-shell structured nanoparticles are of special interest due to the structural stabilization where a shell layer prevents a core from oxidation and corrosion. In addition, the shell layer can be modified so as to give new properties and functions [6]. Magnetite (Fe₃O₄) nanoparticles with polymer shells have been studied extensively [7] and iron nanoparticles with gold [8, 9] or oxide shells [10] have also been fabricated. In this study, we fabricated gold-coated iron (Fe@Au) nanoparticles using a two-step reverse micelle process and characterized their structures and magnetic properties.

Experimental

Fe@Au nanoparticles were prepared using a reverse micelle method which is also called the water-in-oil microemulsion method [8, 9]. The preparation was carried out under flowing argon gas in a glove box. In the first step, Fe nanoparticles were obtained by reducing Fe²⁺ with NaBH₄. The oil solution was prepared by adding 10.2 g cetyl-trimethyl-ammonium bromide (CTAB) and 8.5 g 1-butanol into 34 g octane oil, as a surfactant and a cosurfactant,

respectively. Then, a 5 ml aqueous solution containing 0.05 M FeSO₄·7H₂O was added to this oil solution and another 5 ml aqueous solution containing 1.0 M NaBH₄ was added via a double-ended needle under vigorous stirring at room temperature. The size of the reverse micelle was controlled by the molar ratio of water to surfactant.

In the second step, a Au shell was formed by reducing HAuCl₄. After stirring the above solution for 1 h, 10 ml aqueous solution containing 0.042 M HAuCl₄ was added into it. Notice that no more NaBH₄ was added here. The remaining NaBH₄ in the first step is supposed to have worked in this step. The mixture was left stirring at room temperature overnight. Finally, dark precipitates were collected using a strong permanent magnet and washed with a mixture of chloroform and methanol several times before being dried in a vacuum. All materials were purchased from Aldrich and used without further purification. Distilled water was used throughout and all the liquid starting materials were degassed for 2 h prior to the experiments.

The morphologies, sizes, and structures of nanoparticles were determined by TEM (JEOL EM-2010). TEM samples were prepared as follows; the synthesized particles were dispersed into ethanol under ultrasonic vibration for 5 minutes, and a drop of this solution was placed onto an amorphous carbon-covered copper grid and evaporated in air. About 100 particles on different parts of the grid were used to evaluate the average particle size and their distribution. XRD measurements were performed using a Rigaku D/max III instrument (Cu-K) and UV-visible absorption (UV-vis) spectra were measured from a CARY 500 Scan spectrometer. Magnetic hysteresis curves were recorded with a Lake Shore 7400 vibrating sample magnetometer.

Results and discussion

The XRD pattern of the synthesized nanoparticles is

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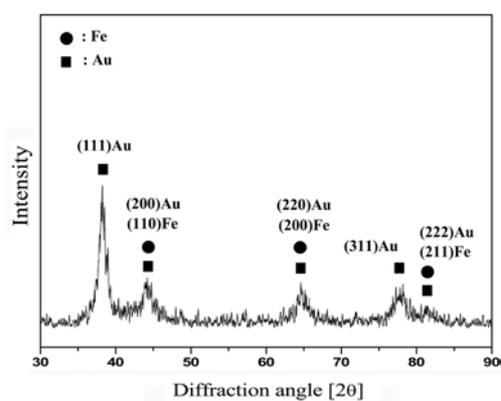


Fig. 1. XRD pattern of the synthesized nanoparticles.

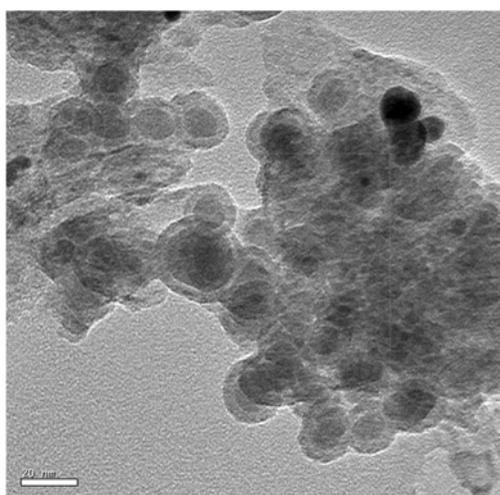


Fig. 2. TEM micrograph showing the shapes of the synthesized nanoparticles and their aggregates. The dark inner regions of nanoparticles are the cores and the bright outer regions the shells. The white bar on a lower left corner indicates 20 nm.

shown in Fig.1 The pattern shows the presence of both α -Fe and Au with some peaks overlapping, consistent with the previous reports [8, 9]. Notably, no iron oxide's peak was found in Fig. 1 and also no oxygen was detected in EDS measurements. This indicates clearly that the iron core was protected by the gold shell from oxidation.

Fig. 2 shows typical morphologies of the synthesized nanoparticles and their aggregates. Since the Fe nanoparticles are magnetic at room temperature, they tend to aggregate on the grid. The core-shell structure of the nanoparticles is evident in Fig. 2 This core-shell structure means that the formation of Au layers on the surface of the pre-existing Fe nanoparticles was preferred to the homogeneous nucleation of pure Au nanoparticles. This preference could be caused either by the minimization of the interfacial energy as in heterogeneous nucleation or by the large population of reducing agents (NaBH_4) around the pre-existing Fe nanoparticles. In this experiment, the former is believed more probable since the Au reduction proceeded under vigorous stirring.

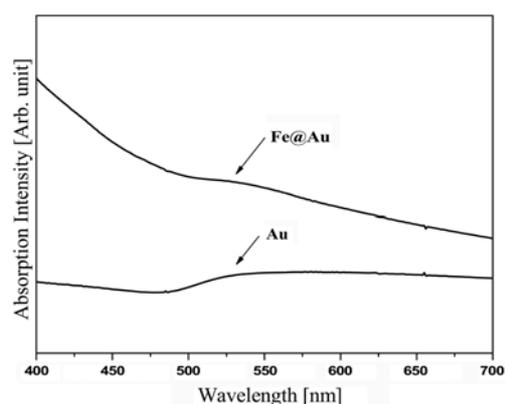


Fig. 3. UV-vis absorption spectra of pure Au and Au-coated Fe nanoparticles.

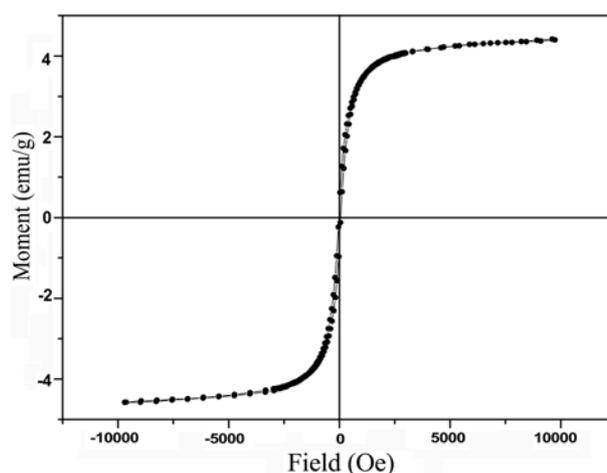


Fig. 4. Magnetic hysteresis of the synthesized Fe@Au nanoparticles obtained from VSM measurement.

The UV-vis spectra for the Fe@Au and pure Au nanoparticles are shown in Fig. 3 Both Fe@Au and Au nanoparticles show a broad absorption band around 526 nm indicating the aggregations and wide size distributions that were found in TEM. The solution containing Au nanoparticles exhibited a reddish color while that containing Fe@Au nanoparticles a dark-red color. Magnetic hysteresis for the synthesized Fe@Au nanoparticles is shown in Fig. 4 This shows no remanent magnetization, which indicates that the nanoparticles are paramagnetic even at room temperature, *i.e.*, superparamagnetic.

Conclusions

Gold-coated iron nanoparticles were synthesized by a two-step reverse micelle method. In this method, the reducing agent, NaBH_4 , was not added in the second step where the Au shells were formed. The core-shell structures of the synthesized nanoparticles were revealed clearly in TEM micrographs. VSM measurement of the synthesized nanoparticles showed a superparamagnetic property.

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