

Synthesis of Monodisperse FeAu Nanoparticles with Tunable Magnetic and Optical Properties

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Magnetic nanoparticles are always receiving considerable attention because of their great potential applications in magnetic recording devices, bioseparation, medical diagnoses, magnetically targeted therapy, and magneto-optical systems. In the past several years, significant efforts have been made on their preparation via the thermal decomposition or reduction of organometallic complexes because the resultant magnetic nanoparticles usually exhibit good monodispersity and high crystallinity. The most typical example is FePt nanoparticles. Other examples include many magnetic alloy nanoparticles (e.g., FePd, FeCo, FeMo, CoPt, and CoNi) and core-shell nanoparticles (e.g., FePt@Fe₃O₄, Pt@Fe₂O₃, Co@Pt, Pt@Co, and Ni@Pd). In general, by controlling the reaction conditions and compositions, the particle size and size-related properties could be tuned. As compared to these magnetic nanoparticles with potential applications in high-density data storage and high-performance permanent magnets, significantly fewer efforts have been made on the synthesis of metallic alloy nanoparticles simultaneously with magnetic and optical properties.



FeAu nanoparticles are expected to exhibit the magnetic property of Fe and the surface plasmon resonance property of Au. Their preparation has not been reported until now. This is the first study on the synthesis of FeAu nanoparticles via the high-temperature organometallic route. Typically, iron pentacarbonyl, gold acetate, and 1,2-hexadecanediol were dissolved in a dioctylether solution of oleic acid and oleylamime under an Ar atmosphere. After stirring for 1 h at room temperature, the temperature was raised to 250 ° C and the reaction mixture was refluxed for 1 h under a flow of Ar to form FeAu nanoparticles. In the absence of gold acetate or iron pentacarbonyl, pure Fe and Au nanoparticles could be obtained.

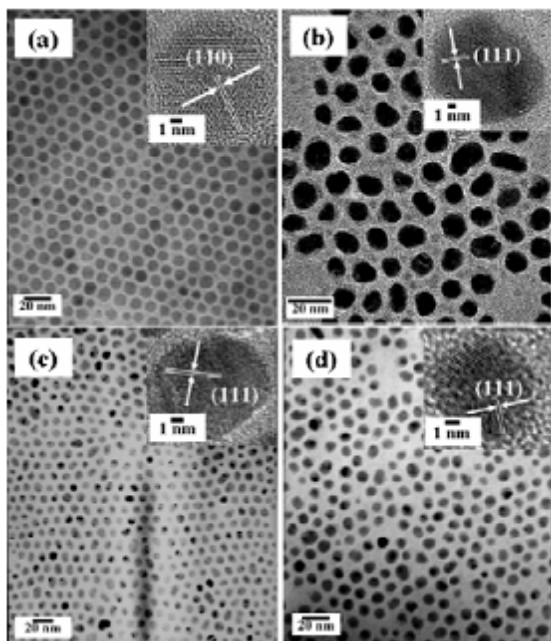


Fig. 1. TEM images of pure Fe (a) and FeAu nanoparticles with the Au/Fe molar ratios of 0.25(b), 0.5(c), and 1(d) obtained at 250 ° C and 1 h. The insets indicate the high-resolution TEM images.

From TEM analysis (Fig. 1a), it was found that the resultant Fe nanoparticles were monodisperse with a mean diameter of 8.9 ± 0.8 nm and well arranged into a 2-D nearly hexagonal close-packed array. The high-resolution TEM image further revealed they had a highly crystallinity, and the lattice spacing of 2.00 Å related to the (110) plane of bulk body-centered cubic (bcc) Fe. The FeAu nanoparticles obtained under the same reaction conditions essentially remained nearly monodisperse (Figs. 1b-d). When Au/Fe=0.25, 0.5, and 1, the mean diameters were 9.8 ± 1.1 , 7.7 ± 0.9 , and 8.9 ± 0.9 nm, respectively. The variation of particle size with composition might be referred to the difference in nucleation process. Since the reduction rate of gold acetate was faster than the decomposition rate of iron pentacarbonyl, Au nuclei might be formed preferentially and used as seeds to accelerate the decomposition of iron pentacarbonyl and formation of FeAu nanoparticles. So, a higher Au/Fe molar ratio might lead to a smaller particle size due to the increase in the number of seeds. However, when the concentration of iron pentacarbonyl was fixed, the increase in the Au/Fe molar ratio implied the increase in the total metal precursor concentration. Hence, when the Au/Fe molar ratio was too high, particle size might increase contrarily owing to the increased collision probabilities of metal atoms or nuclei. In addition, from EDX analysis, we demonstrated that the compositions in the products were roughly consistent with those in the feed solutions, confirming the formation and composition of alloy nanoparticles.

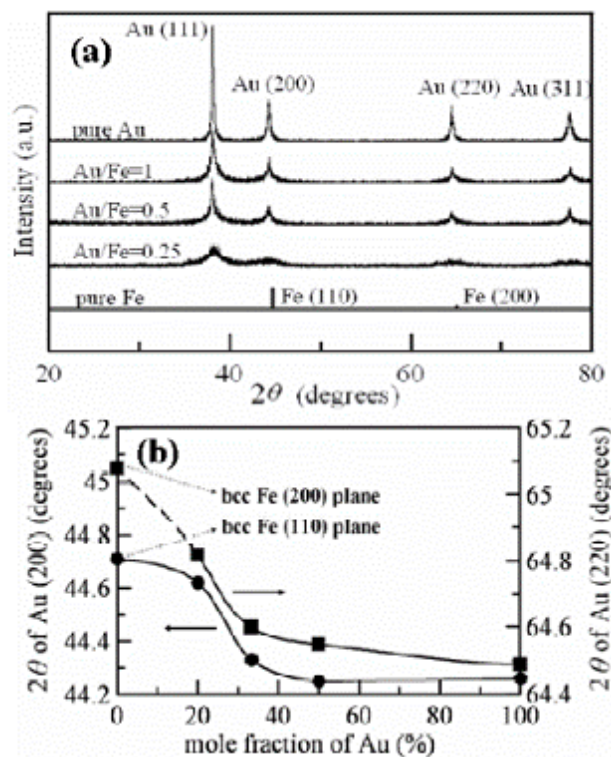


Fig. 2. (a) XRD patterns of Au, Fe, and FeAu nanoparticles with various Au/Fe molar ratios. (b) Composition-dependences of the diffraction angle at (200) and (220) planes.

When Au/Fe ratios were 0.25, 0.5, and 1, the lattice spacings were found to be 2.22, 2.24, and 2.21 Å respectively. They all related to the (111) plane of face centered cubic (fcc) FeAu alloys. Furthermore, the XRD patterns of FeAu nanoparticles exhibited four similar characteristic peaks as Au nanoparticles did (Fig. 2a). The characteristic peak was broader at a lower Au/Fe molar ratio, implying the crystallinity of FeAu nanoparticles was poorer than that of Au nanoparticles. In addition, the characteristic peaks for the (200) and (220) planes of fcc Au or FeAu nanoparticles were quite close to those for the (110) and (200) planes of bulk bcc Fe. The dependences of their diffraction angles on the composition (Fig. 2b) indicated that the diffraction angles for both the characteristic peaks decreased significantly when Au atoms were incorporated into the bcc structure of Fe. This might be attributed to the structural change from bcc to fcc.

In addition, we also examined the effects of reaction time and temperature on the synthesis of FeAu nanoparticles. It was found that then increases in reaction time or reaction temperature did not lead to the structural change. Longer reaction time (>3 h) or higher reaction temperature (297 ° C) led to smaller mean diameter and broader particle size distribution due to the atom rearrangement and faster nucleation rate, respectively. Also, the reduction rate of gold acetate and the deposition rate of Au atoms on the nuclei were enhanced more significantly by increasing reaction temperature than the decomposition rate of iron pentacarbonyl and the deposition rate of Fe atoms on the nuclei.

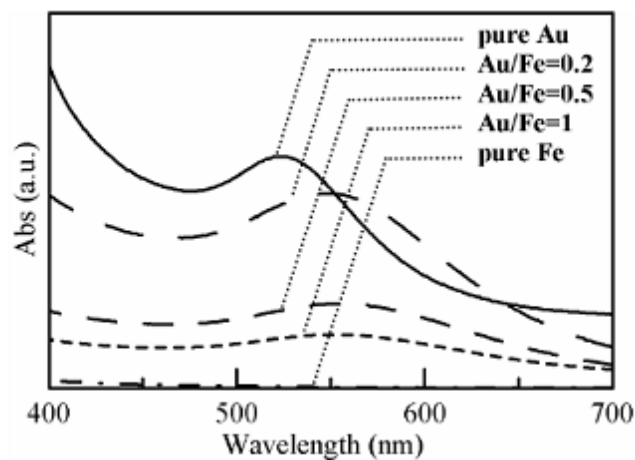


Fig. 3. UV-VIS absorption spectra of Fe, Au and FeAu nanoparticles with various molar ratios in hexane.

As expected, the UV-VIS absorption spectra (Fig. 3) revealed that FeAu nanoparticles exhibited the characteristic absorption bands similar to that of Au nanoparticles. Also, with decreasing the Au/Fe molar ratio, the characteristic absorption band red-shifted and the absorbance decreased because the electron cloud oscillation of surface Au atoms was perturbed by Fe atoms.

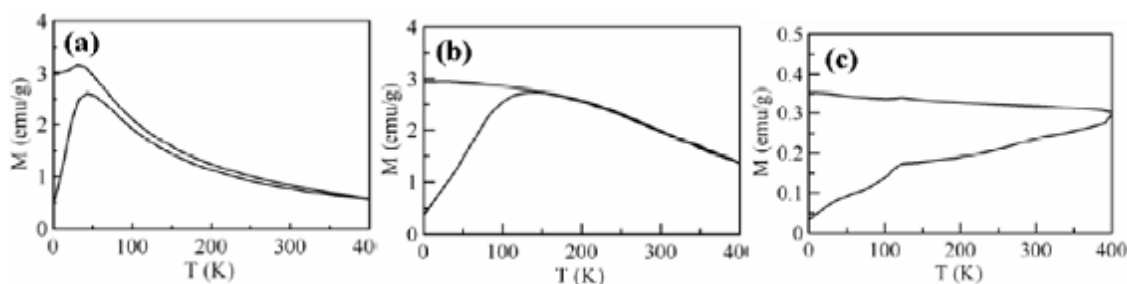


Fig. 4. ZFC/FC curves of Fe (a) and FeAu nanoparticles with the Au/Fe molar ratios of 0.25 (b), and 0.5 (c) obtained at 1 h and 250 ° C. The external magnetic field is 100 Oe.

Of course, FeAu nanoparticles were also expected to possess the magnetic property of Fe. By measuring the field cooled (FC) and zero field cooled (ZFC) curves of Fe and FeAu nanoparticles under an external magnetic field of 100 Oe (Fig. 4), we found that the blocking temperatures (T_B) of Fe and FeAu nanoparticles at Au/Fe=0.25 were 42.7 and 143 K, respectively. Because their T_B values were significantly lower than room temperature, they were expected to be superparamagnetic at room temperature. When Au/Fe=0.5, the magnetization decreased significantly and T_B was above 400 K. Further analyzing the field-dependences of the magnetization at 300 K for Fe and FeAu nanoparticles (as shown in Fig. 5), it was found that the hysteresis phenomenon was weak for each case. This could be attributed to the fact that they were quite small and nearly superparamagnetic. The corresponding saturation magnetization (M_s), remnant magnetization (M_r), and coercivity (H_c) were listed in Table 1, together with the T_B values. Obviously, the increase in the Au content led to the decrease in magnetization and the deviation from the superparamagnetic property.

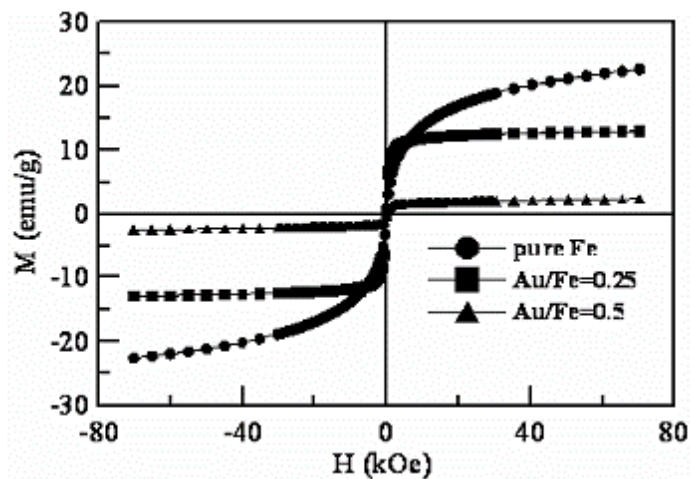


Fig. 5. Magnetic hysteresis loops at 300K for Fe and FeAu nanoparticles with various Au/Fe molar ratios obtained at 1 h and 250 ° C.

Table 1. A list of the T_B , M_s , M_r , and H_c values for Fe and FeAu nanoparticles with various Au/Fe molar ratios obtained at 1 h and 250 ° C.

Au/Fe molar ratio	T_B [K]	M_s [emu g^{-1}]	M_r [emu g^{-1}]	H_c [Oe]
0	42.7	22.6	0.09	14.3
0.25	143	13.0	0.3	23.7
0.5	>400	2.4	0.12	55.9

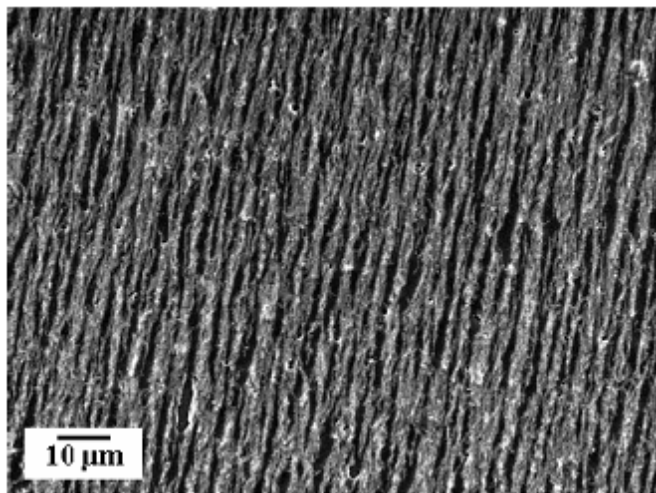


Fig. 6. SEM image of self-assembled line pattern of FeAu nanoparticles with a Au/Fe molar ratio of 0.25 under an external magnetic field. The FeAu nanoparticles were obtained at 1 h and 250 ° C.

By dropping the FeAu nanoparticles-containing alcohol solution of polyethyleneimine on the transparency film on a permanent magnet, it was found that these nanoparticles were quickly aligned into stripes in the direction of magnetic field (Fig. 6). Such a 1-D pattern has the potential applications as the anisotropic optical, magnetic, or conducting materials.

In conclusion, the synthesis of monodisperse FeAu nanoparticles was achieved by a high-temperature organometallic route. The effects of composition, reaction time, and reaction temperature on their size,

structure, and optical and magnetic properties were studied and well discussed. The resultant FeAu nanoparticles indeed possessed the optical property of Au nanoparticles and the magnetic property of Fe nanoparticles. This is novel product is expected to be useful in optical, magnetic, and biotechnological fields.

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