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Simultaneous agglomeration of Fe/Au nanoparticles with controllability of magnetic dipole interaction

Tomoyuki Ogawa,[a,*] Hiroaki Kura[a] and Migaku Takahashi[a,b]

[a]Department of Electronic Engineering, Graduate School of Engineering, Tohoku University, 6-6-05 Aza-Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan
[b]Center for Nanobioengineering and Spintronics, Chungnam National University, 220 Gung-Dong, Yuseong-Gu, Daejeon 305-764, Republic of Korea

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Assemblies of α-Fe/Au nanoparticles (NPs) with various volume fractions of α-Fe NPs were prepared by simultaneous agglomeration of α-Fe NPs and Au NPs in solution. Only the dipole interaction was affected by the magnetic interaction between α-Fe NPs in this system. The magnetic properties were significantly changed according to the volume fraction of the α-Fe NPs, with a high α-Fe NP volume fraction assembly exhibiting good soft magnetic properties.

Keywords: Iron; Nanocrystalline metal; Granular materials; Soft magnetic materials

The assembly of ferromagnetic nanoparticles (NPs) is expected to have a unique effect on the magnetic properties, such as superferromagnetism and the superspinglass state, in contrast to isolated NP systems, due to magnetic dipole interactions [1–7]. The characteristic magnetic properties of magnetic NP assemblies with well-controlled volume fraction were investigated because the magnitude of the dipole interaction correlates strongly with interval of the NPs. Control of the volume fraction in magnetic NP assemblies has generally been performed by freezing of ferrofluids with known concentrations [8–10]. However, this method is problematic in that magnetic NPs are locally concentrated by aggregation during the freezing process, and measurement of the magnetic properties cannot be performed at temperatures higher than the melting point of the matrix solvent [11,12]. To obtain stable and well-controlled volume fractions of NP assemblies with homogeneity, it is necessary to develop a new concept for the preparation of NP assemblies. We propose a new method for the preparation of magnetic/non-magnetic NP assemblies by simultaneous agglomeration in solution and clarify the influence of magnetic dipole interaction on the magnetic characteristics. The NPs are dispersed in non-polar solvents such as hexane and toluene and rapidly coagulate by the addition of a polar solvent such as acetone or ethanol to produce a precipitate [13]. From a mixture of two different NP solutions, a random structure consisting of both NPs is expected to be formed from precipitation. Simultaneous agglomeration allows the volume fraction of magnetic NPs to be easily controlled by modifying the mixture ratio of both NP solutions.

In this work, α-Fe/Au NPs assemblies with various volume fractions of α-Fe NPs (ρ_{Fe}) were prepared by a novel simultaneous agglomeration method and the influence of magnetic dipole interaction on the magnetic properties was investigated. Chemically synthesized α-Fe NPs are the most appropriate materials for the study of dipole interaction in an assembly of magnetic NPs, due to the specific magnetic properties of α-Fe, such as high saturation magnetization, low magnetic anisotropy, single domain and narrow size distribution [14,15]. Au NPs were selected as non-magnetic NPs because Au is stable and rarely forms alloys with Fe.

The synthesis of α-Fe NPs and preparation of α-Fe/Au NP assemblies were performed in an Ar-purged glove box (Miwa Mfg. Co., Ltd., DBO-2LNKP) with O_2 and H_2O limited to less than 0.1 ppm to prevent oxidation. α-Fe NPs were synthesized by the modified thermal decomposition of an $Fe(CO)_5$-oleylamine reacted precursor [14]. Au NPs were synthesized by reduction of $HAuCl_4$ in oleylamine in the atmosphere [16]. After purification, the Au NPs were transferred to the glove box and mixed with the α-Fe NP solution in hexane.

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* Corresponding author. Tel.: +81 22 795 7134; fax: +81 22 263 9402; e-mail: tomoyuki@ecei.tohoku.ac.jp

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α–Fe/Au NP assemblies were obtained as precipitates by adding an appropriate amount of ethanol to the mixture. The precipitates were dried at room temperature under vacuum of approximately 1 Pa, and then uniaxially pressed at 300 MPa to yield $2 \times 2 \times 0.5\ \text{mm}^3$ specimens for various measurements. The average diameter and size distribution of α-Fe and Au NPs were determined from transmission electron microscopy (TEM; JEOL, JEM-2100) observations. The nanostructures of the α-Fe/Au NP assemblies were directly observed using cross-sectional TEM techniques. The macro- and microscopic chemical compositions were determined by X-ray fluorescence (XRF; Rigaku, RIX 2100) analysis and energy-dispersive X-ray spectroscopy (EDX; EDAX, Genesis). Magnetic data were obtained using a superconducting quantum interference device magnetometer (Quantum Design, Inc., MPMS-5) and a physical property measurement system (Quantum Design, Inc.).

Figure 1a and b shows cross-sectional TEM images of α-Fe/Au NP assemblies with Fe:Au atomic ratios of (a) 12:88 and (b) 34:66, which were estimated by XRF analysis. The thicknesses of the specimens for cross-sectional TEM analysis were approximately 30 nm. The average diameter and size distribution of α-Fe and Au NPs in these samples were estimated to be 8.7 ± 0.7 and 10.8 ± 1.6 nm, respectively. There was no direct contact between individual NPs because the α-Fe NPs and the Au NPs were covered by an oleylamine surfactant. Assuming that the NPs establish a fully formed close-packed structure and a 1.7 nm gap between two particles [17], then the α-Fe NP volume fractions by total volume were $\rho_{\mathrm{Fe}} = 3.8\%$ and 11.3%, respectively. However, the actual value may be slightly smaller due to inhomogeneity in the structure. Figure 1(c and d) and (e and f) shows EDX elemental mapping images for Fe and Au taken in the same field as that shown in Figure 1a and b, respectively. The Fe element distribution was random and homogeneous for both samples, which is indicated by the very-low-contrast particles in the bright-field image. This indicates that the Fe NPs were present in the Au NP matrix without significant segregation. A maximum ρ_{Fe} of 43% was obtained for the assembly consisting of only α-Fe NPs, and ρ_{Fe} should be widely controllable below this value. Therefore, α-Fe/Au NP assemblies obtained by the simultaneous agglomeration method are good candidates for the investigation of magnetic dipole interactions.

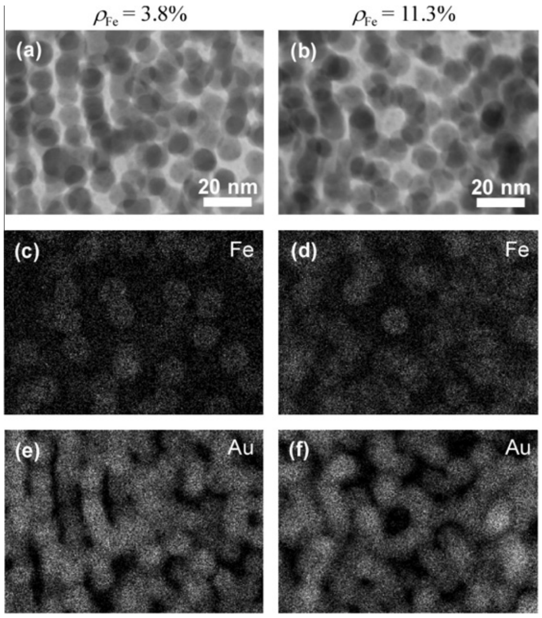

Figure 1. Cross-sectional TEM images of α-Fe/Au NPs assemblies with ρ_{Fe} at (a) 3.8 and (b) 11.3%. Fe and Au elemental mapping images for ρ_{Fe} at (c and e) 3.8 and (d and f) 11.3% in the same field as shown in (a) and (b), respectively.

To investigate the influence of ρ_{Fe} on the magnitude of magnetic dipole interaction and collective magnetic behavior, the temperature-dependent AC magnetic susceptibility of α-Fe/Au NPs assemblies with various ρ_{Fe}s (0.5%, 1.6%, 4.5%, 11.5% and 23.5%) was measured. Figure 2a and b shows the absolute value of AC magnetic susceptibility χ and phase delay δ under an AC magnetic field of 3 Oe as a function of temperature for various frequencies; $f = 101$, 1009 and 9973 Hz. The temperature for the peak position of χ and that at which δ disappears agrees qualitatively with the freezing temperature of the magnetic moment T_{m}, which can be obtained from the intersectional temperature between temperature-dependent DC susceptibility curves under zero-field-cooled and field-cooled conditions. In the temperature range higher than T_{m}, the α-Fe/Au NP assembly exhibits superparamagnetism. In order to clarify the contribution of ρ_{Fe} to the temperature dependence of the AC magnetic susceptibility T_{m}, the temperature at the peak position of δ (T_{δ}) and the peak height of δ (δ_{peak}) for a frequency of 101 Hz are plotted as a function of ρ_{Fe} in Figure 3. T_{m} increased monotonically from around 70 K to over

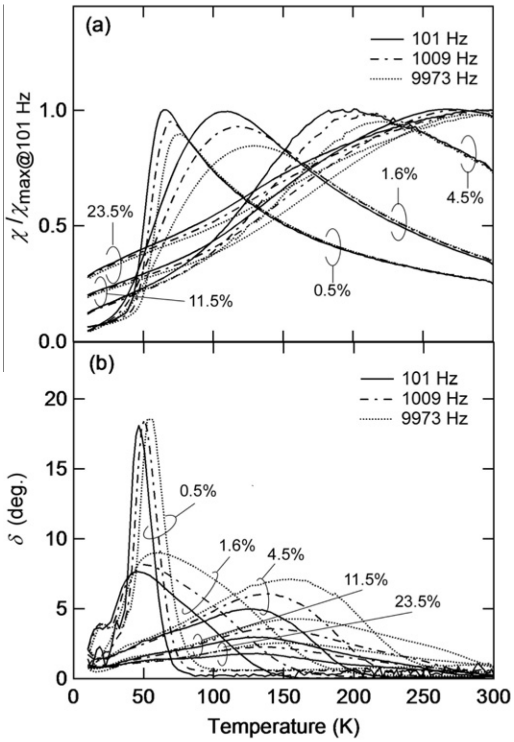

Figure 2. Temperature-dependent (a) χ and (b) δ for α-Fe/Au NPs assemblies with ρ_{Fe} at 0.5%, 1.6%, 4.5%, 11.5% and 23.5% for various measurement frequencies: $f = 101$, 1009 and 9973 Hz.