Formation of Ferromagnetic Iron Core-Shell Nanocubes on a H-Terminated Si(100) Surface by Electrodeposition

L. Y. Zhao, H. Jalili, N. Panjwani, T. Chan, Z. H. He, N. F. Heimg, and K. T. Leung

WATLab and Department of Chemistry, and Department of Physics, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

Near-monosized and uniformly distributed cubic Fe core–shell nanoparticles (with an average side length of 56 nm) were electrodeposited on H-terminated Si(100) in a FeCl$_3$ solution. X-ray photoelectron spectroscopy analysis indicates chemical states of the Fe nanocubes characteristic of predominant ferromagnetic metallic Fe cores covered by Fe$_3$O$_4$ shells. Glancing-incidence X-ray diffraction analysis reveals a body-centered cubic (bcc) lattice structure. A nanometer-thick film consisting of 2–3 layers of cuboidal nanoparticles of the same bcc Fe core and Fe$_3$O$_4$ shell can be obtained when the amount of charge transfer is increased. The prominent magnetic domains of those nanocubes can be illustrated by magnetic force microscopy.

© 2007 The Electrochemical Society. [DOI: 10.1149/1.2759604] All rights reserved.


Magnetic nanoparticles (NPs), particularly iron with its low-cost advantage, have attracted recent attention due to their potential applications in spin-based electronics, data storage, and targeted drug delivery. Because NPs with different shapes should have different electronic, magnetic, and catalytic properties, various synthetic techniques have been developed to obtain iron NPs with different shapes and morphologies. In particular, near-spherical Fe NPs with diameters ranging from 6 to 35 nm were obtained by thermal evaporation and condensation of bulk metal in an inert atmosphere. Various electronic, optical, magnetic, and catalytic properties of these NPs are investigated with well-defined shapes uniformly, a considerable amount of controlled fabrication of such a layer of magnetic NPs, or patterns thereof, may have significant practical applications.

In the present work, we show that cubic Fe NPs with a considerably thinner passivating oxide layer (i.e., a significant Fe core) can be obtained by replacing the Fe(III) ions with Fe(II) ions in electrochemical deposition on a H-Si(100) surface (from an aqueous FeCl$_3$ solution). Unlike electroplating in which Fe is usually deposited as a film, we demonstrate controlled electrodeposition of Fe in the form of discrete metallic NPs, and by increasing the amount of charge transfer a thin film consisting of cuboidal NPs of Fe can be obtained. The morphology of the cubic Fe NPs is determined by field-emission scanning electron microscopy (SEM), while the chemical states and bulk crystal structures of these Fe NPs are characterized by X-ray photoelectron spectroscopy (XPS) and glancing-incidence X-ray diffraction (GIXRD), respectively. The magnetic properties of these cubic Fe NPs with their large Fe cores are investigated by magnetic force microscopy (MFM). The prominent MFM features suggest the presence of sub-μm magnetic domains in the nanometer-thick film of these cuboidal Fe nanostructured deposits.

Experimental

Details of our electrodeposition experiment and the three-electrode cell setup have been discussed elsewhere. Si(100) (p-type, 30 × 15 mm, 0.4 mm thick, 1.0–1.5 mM cm) substrate was cleaned using the RCA method, etched in aqueous HF (2%) solution to remove the native oxide layer, and rinsed with Millipore water. The resulting H-Si(100) is flat and terminated with hydrides (Si$_{2n}$H$_n$; n = 1, 2, or 3), and is found to be suitable for uniform deposition of nanoparticles. In a fresh deoxygenated aqueous solution of 10 mM FeCl$_3$ and 0.2 M H$_3$BO$_3$ (pH 3.6), Fe NPs were deposited on the H-Si(100) substrate by amperometry potentiostatically at −1.4 V (relative to the Ag/AgCl reference electrode). After the deposition, the Si substrate was thoroughly rinsed with Millipore water and dried in N$_2$. The surface morphology of the Fe nanodeposits was characterized by SEM. The corresponding chemical composition was analyzed by XPS with a monochromatic Al K$_x$ X-ray source (1486.6 eV), and at a typical energy resolution of 0.4–0.5 eV full width at half-maximum. The binding energy scale was calibrated to that of the Si 2p$_{3/2}$ photopeak of bulk Si (99.3 eV), because of recent reports of changes in the C 1s binding energy position.
an incidence angle $\omega = 0.6^\circ$, with the Cu K\alpha characterization of the nanodeposits was determined by GIXRD at a graded multilayer parabolic X-ray mirror, and the X-ray spot size cuboidal Fe NPs were found to always codeposit along with a Fe shaped nanorod electrodeposition involving FeCl$_3$. Distorted NPs evidently led to shape distortion and clustering, resulting in a charge transfer increased to 70 mC at a deposition potential different from 5 to 3.6 V, while the weak broad feature at 102.4 eV can be attributed to Si 2p of silicon suboxide (SiO$_2$)$_x$. The presence of the latter SiO$_2$ feature therefore indicates partial oxidation of the Si substrate, likely induced by the electrodeposition. The formation of SiO$_x$ is also consistent with the strong characteristic O 1s feature at 532.2 eV, shown in Fig. 1d. The weak O 1s feature found at 529.9 eV can be attributed to Fe$_2$O$_3$. In the Fe 2p region (Fig. 1e), the features at 706.8 eV (720.1 eV) and 711.1 eV (724.7 eV) are consistent with the characteristic Fe 2p$_{3/2}$ (2p$_{1/2}$) states for metallic Fe and Fe$_2$O$_3$, respectively. Both the O 1s and Fe 2p XPS data therefore indicate the presence of an Fe$_2$O$_3$ shell with metallic Fe as the core of the cubic NP. Even though we also performed XPS depth-profiling experiments (not shown), it was difficult to determine the contribution of the Fe core from these data because ion sputtering has been found to cause reduction of Fe oxides to metallic Fe. However, using the attenuation theory, we were able to estimate the thickness of the Fe$_2$O$_3$ shell to be 2.5 nm using the ratio of the intensities of the Fe 2p$_{3/2}$ photoelectrons of Fe and Fe$_2$O$_3$. In our recent work involving electrodeposition in an FeCl$_3$ solution, the as-deposited oval-shaped nanorod Fe particles were found to consist of Fe cores with composite FeOOH and FeO shells, while the spherical NPs correspond to Fe cores with composite Fe$_2$O$_3$ and FeO shells. In the present cubic NP case, there is a sizable Fe 2p feature corresponding to metallic Fe before sputtering, which was not observed in the case of the oval-shaped nanorods and spherical NPs. This confirms that the oxide shell for the cubic NPs must not only be thinner than those of the oval-shaped nanorods and spherical NPs but also less than the escape depth of the Fe 2p photoelectron at 780 eV kinetic energy ($\sim$ 6 nm). Conversely, the relative amount of the Fe core in the cubic NPs is larger than those for the oval-shaped nanorods and spherical NPs. The surface morphology and the chemical composition of the Fe electrodeposits can therefore be effectively controlled by manipulating the oxidation states of the Fe salts used in the electrodeposition.

Figure 2 shows the GIXRD patterns of the Si(100) substrate with and without the Fe nanodeposits. The features at 50–60° are found to be in good accord with the strong characteristic O 1s feature found at 532.2 eV, shown in Fig. 1d. The weak O 1s feature found at 529.9 eV can be attributed to Fe$_2$O$_3$. In the Fe 2p region (Fig. 1e), the features at 706.8 eV (720.1 eV) and 711.1 eV (724.7 eV) are consistent with the characteristic Fe 2p$_{3/2}$ (2p$_{1/2}$) states for metallic Fe and Fe$_2$O$_3$, respectively. Both the O 1s and Fe 2p XPS data therefore indicate the presence of an Fe$_2$O$_3$ shell with metallic Fe as the core of the cubic NP. Even though we also performed XPS depth-profiling experiments (not shown), it was difficult to determine the contribution of the Fe core from these data because ion sputtering has been found to cause reduction of Fe oxides to metallic Fe. However, using the attenuation theory, we were able to estimate the thickness of the Fe$_2$O$_3$ shell to be 2.5 nm using the ratio of the intensities of the Fe 2p$_{3/2}$ photoelectrons of Fe and Fe$_2$O$_3$. In our recent work involving electrodeposition in an FeCl$_3$ solution, the as-deposited oval-shaped nanorod Fe particles were found to consist of Fe cores with composite FeOOH and FeO shells, while the spherical NPs correspond to Fe cores with composite Fe$_2$O$_3$ and FeO shells. In the present cubic NP case, there is a sizable Fe 2p feature corresponding to metallic Fe before sputtering, which was not observed in the case of the oval-shaped nanorods and spherical NPs. This confirms that the oxide shell for the cubic NPs must not only be thinner than those of the oval-shaped nanorods and spherical NPs but also less than the escape depth of the Fe 2p photoelectron at 780 eV kinetic energy ($\sim$ 6 nm). Conversely, the relative amount of the Fe core in the cubic NPs is larger than those for the oval-shaped nanorods and spherical NPs. The surface morphology and the chemical composition of the Fe electrodeposits can therefore be effectively controlled by manipulating the oxidation states of the Fe salts used in the electrodeposition.

Figure 2 shows the GIXRD patterns of the Si(100) substrate with and without the Fe nanodeposits. The features at 50–60° are found to be in good accord with the (311) plane of the p-Si(100) substrate reported in the literature. All the remaining peaks found for the Fe NPs shown in Fig. 2a can be ascribed to the (110), (200), (211), (220), and (310) planes of the bcc lattice of Fe (JCPDS 06-0696). After taking into account the instrumental linewidth (deduced from the GIXRD pattern of commercial metallic Fe powders obtained separately under the same experimental conditions), we estimated the particle size to be $\sim$ 57 nm by using the Scherrer equation (with the Scherrer constant of 0.9), in excellent agreement with our SEM results (Fig. 1a). No evidence of Fe$_2$O$_3$ was found from the XRD data, which indicates that either the amount of Fe$_2$O$_3$ was insufficient to be detected by GIXRD or more likely the surface Fe$_2$O$_3$ species is amorphous. Together with our earlier work involving FeCl$_3$ solution, we demonstrate that three types of Fe NPs with different shapes and compositions can be obtained by appropriate manipulation of the electrodeposition parameters, including different Fe salts and different electrolyte solutions. The oval shape of the nanorod nanostructure could be due to codeposition of FeOOH (formed by hydrolysis in an aqueous FeCl$_3$ solution) during electrodeposition. Because hydrolysis could not occur in FeCl$_3$ solution
and individual well-defined Fe NPs are probably single crystalline (bcc), the deposited metallic Fe NP could only be of cubic shape.

To illustrate the strong magnetic moments found in these Fe cuboidal NPs, we show in Fig. 3 AFM and MFM images of the Fe cuboidal nanoparticles deposited with the higher charge transfer 70 mC (Fig. 1b). The image correlation coefficient between the AFM and MFM images is found to be 0.0486, suggesting that the topography effect is negligible in the MFM image. Although the spatial distribution of the magnetic moments of individual NPs could form complicated patterns of magnetic interactions, the bright and dark regions of the observed MFM features are generally attributed to domains with magnetic moments pointing in opposite directions (i.e., upward and downward out of the sample plane). The presence of the extended magnetic domains with approximate segment widths of 0.5 μm and lengths of 1–3 μm is clearly found in the MFM image (Fig. 3b), which provides evidence for longer range magnetic ordering of these magnetic NPs. Superconducting quantum interference device (SQUID) measurements have been attempted without success due to the insufficient amount of nanodeposits present.

Conclusion

Uniformly distributed cubic Fe NPs with an average side length of 56 nm and a narrow size distribution were deposited potentiostatically by amperometry from an FeCl₂ and H₃BO₃ solution onto a H-Si(100) substrate. XPS analysis shows that the individual NPs consist of a substantial Fe core and a thin Fe₂O₃ shell (2.5 nm thick), while the corresponding GIXRD data indicate the crystal structure of the Fe core to be bcc. Given the relatively large amount of the Fe core compared to the Fe₂O₃ shell, and that bcc Fe is known to be ferromagnetic, our MFM measurements reveal some of the interesting magnetic properties of these cubic Fe core-shell NPs.

Acknowledgments

This work was supported by the Natural Sciences and Engineering Research Council of Canada. We are indebted to Dr. Roman Engel-Herbert and Dr. Thornton Hesjedal for helpful discussions.

References