Mapping magnetic fields of Fe$_3$O$_4$ nanosphere assemblies by electron holography

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Crystalline Fe$_3$O$_4$ nanospheres with averaged diameters of 150 nm have been synthesized by a facile solvothermal method and characterized using transmission electron microscopy and electron holography. The nanospheres can self-assemble into either chain-like or ring-like shapes with sizes of a few micrometers, where large magnetic moments are found for individual particles at the remanent state and lead to strong fringing field in vicinity of the assemblies. Magnetic dipolar moments can be aligned both within and out of the sample plane, with a typical length scale on the order of 500 nm. © 2013 American Institute of Physics. [http://dx.doi.org/10.1063/1.4798500]

I. INTRODUCTION

Magnetite (Fe$_3$O$_4$) nanocrystals have attracted much attention due to their unique magnetic properties and good biocompatibility for prospective applications in magnetic resonance imaging, drug delivery, and bio-separation. 1–3 Fe$_3$O$_4$ has also been demonstrated as an excellent storage material for lithium-ion battery in nanostructured form. 4 To form such morphologies, nanoparticles of Fe$_3$O$_4$ with uniform size distribution show a pronounced self-assembly behavior and thus serve as building blocks for superstructures and mesocrystals, where magnetic interactions determine the morphology. 5 It is of great importance to identify the magnetic interactions in assembly systems, in particular, to probe the magnetization within individual nanocrystal as well as to determine the fringing field in the vicinity. 5

Among various magnetic imaging techniques, magnetic force microscopy (MFM) is primarily sensitive to out-of-plane field and its tip may affect the magnetization of specimen during the long scanning process; Lorentz microscopy has poor resolution and less quantification to detect nano- or macrodipolar magnetic fields. 6 In contrast, off-axis electron holography (EH) based on transmission electron microscopy (TEM) provides a unique approach to retrieve the quantum-mechanical phase change of the electron wave passing through the specimen. 5 The phase is more sensitive to the electromagnetic fields within and around the sample than the amplitude, which usually does not change even if being magnetized or electrically biased. Therefore, quantitative mapping of magnetic field in and around these nanocrystals is achievable to determine domain structures as well as stray fields. 7,8

Previous EH studies have been applied to a variety of nanoparticle systems, including magnetic bacteria, 9 cobalt, 10 iron, 11 permalloy, 12 and magnetite 13 nanoparticle assemblies. In those circumstances, the particle size is a few tens of nanometers, typically below 50 nm, and of regular shapes, such as cubes, octahedrons, and spheres, which are favorable for acquiring electron holograms and retrieving phase information. Also due to the simple geometry, it is relatively trivial to analyze the magnetization within the nanocrystals. In this study, the average size of Fe$_3$O$_4$ particles is about 150 nm; the entire assembly size can be up to a few microns. Thus, it is a dilemma to simultaneously determine precise phase shifts within individual particles and obtain large-scale overview with enough resolution. Herein, we solve this issue by detecting the fringing fields around an assembly, and we use this approach to characterize the magnetic properties of two representative Fe$_3$O$_4$ nanosphere assemblies.

II. EXPERIMENTAL

Fe$_3$O$_4$ nanospheres were synthesized through a simple solvothermal method. In a typical process, FeCl$_3$·6H$_2$O (4 mmol) was added into the mixture of 15 ml ethylene glycol (EG) and 15 ml dimethylformamide (DMF), and dissolved by magnetic stirring at room temperature. Then, CO(NH$_2$)$_2$ (18 mmol) was added and the obtained solution was transferred into a 50 ml Teflon-lined stainless steel autoclave and maintained at 200 °C for 12 h in an oven. The product was naturally cooled in air and washed by purified water and ethanol for several times. The power product was dispersed in solution and transferred onto copper grids with amorphous carbon film support for TEM observations.

The sample was characterized by X-ray diffraction (XRD, Rigaku D/max-γ/B), TEM (JEOL 2100 FEG), and EH. The TEM was operated in Lorentz mode, where the normal objective lens was deactivated and the column was degaussed to create magnetic-field-free environment. During EH observation, an in situ field can be applied by slightly exciting the immersive objective lens to magnetize the sample. Details have been described elsewhere. 14,15

III. RESULTS AND DISCUSSION

Figure 1 displays XRD pattern of the as-prepared product, in which strong and sharp diffraction peaks indicate that...
the sample has been well crystallized. The diffraction peaks can be readily indexed to an inverse spinel Fe$_3$O$_4$ structure (JCPDS No. 65-3107) with lattice constant of $a = 0.8391$ nm. No diffraction peaks for notable impurities (e.g., hematite) are found.

Figure 2(a) shows a TEM micrograph displaying an overview of as-prepared Fe$_3$O$_4$ nanoparticles. The Fe$_3$O$_4$ particles are in spherical shape with size distributed in the range of 100–200 nm. A close-up view was taken on an individual particle, as shown in the high-resolution TEM image in Figure 2(b). It is clearly indicated that the nanospheres are composed of single crystals, and the resolved lattice spacing of 0.42 nm is corresponding to the (200) planes of Fe$_3$O$_4$. It is worth noting that the nanoparticles are mostly solid spheres though a small population exhibits a hollow morphology, attributed to Ostwald rippening. Figures 2(c) and 2(d) indicate representative morphologies of the solid and hollow spheres, respectively. This solid-hollow morphology evolution has been systematically studied and the controllable growth of such Fe$_3$O$_4$ nanostructures was successfully achieved in prior studies. In the current study, we are more focused on the magnetic properties of the Fe$_3$O$_4$ particles, i.e., the magnetization distribution and its behavior in response to an external magnetic field.

After dispersing Fe$_3$O$_4$ particles into more dilute concentrations and transferring them onto carbon supporting TEM grid, it is found that the nanospheres do not aggregate together into dense clusters, but instead form extended assemblies. Observation over a large scale of the samples identified that the most common self-assembly configuration is in a chain-like shape, whereas a circular ring-like shape could occasionally also be formed (7 out of 135 total observed assemblies). TEM images, as shown in Figures 3(a) and 3(c), depict representative examples of the chain-like and ring-like self-assemblies, respectively. In order to understand the magnetic interaction inside each assembly, we degaussed the TEM column and utilized EH to visualize the in-plane magnetization in the vicinity of the Fe$_3$O$_4$ nanospheres. Figures 3(b) and 3(d) are maps of the magnetic induction (B) converted from the reconstructed electron holograms, illustrating the magnetization distribution of the assembled magnetite chain and ring structures at remanent state, respectively. From induction mapping, it is obvious that magnetic dipolar fields exist, regardless of assembly in the form of open chain or closed ring. In the assembly chains, Fe$_3$O$_4$ nanospheres are lined up under dipolar
interaction, although the fringing field of each dipole is unevenly distributed due to inhomogeneities of the assembly. Unlike previously reported in sub-micron scale lithography-patterned magnetic rings\(^\text{15}\) and sub-50-nm circular assembly of magnetic nanoparticles,\(^\text{10}\) where the magnetic flux-closure state is the dominant configuration, the Fe\(_3\)O\(_4\) nanosphere assembly ring does not generally show a simple magnetization state with full flux closure, instead showing a strong fringing field. One probable origin for such complicated fringing field distribution could be the irregularity of the individual particles, in which broken hollow spheres may cause branching of the induction field in 3-dimensional (3D) space. Irrespective of those complexities, the average dipole length appears to be on the order of 500 nm. According to the theory of EH,\(^\text{4}\) the magnetic contribution to the phase shift is \(\Phi_{\text{MAG}}(x) = -e\hbar \int [B_x(x, z) \, dx \, dz]\), where \(e\) is elementary charge, \(\hbar\) is reduced Planck constant, \(x\) is the incident beam direction, \(x\) is a direction in the observation plane, and \(B_x\) is the component of magnetic induction perpendicular to both \(x\) and \(z\). To build two dimensional phase maps, a corresponding relationship can be written, integrating \(B_x\) by \(dy\). By measuring the phase gradient, the integral of the projected in-plane magnetization can be obtained at any desired position. We picked several positions inside the fringing field, as labeled A–E in Figs. 3(b) and 3(d), for quantification of local magnetic field strength. This process directly gives the integrated induction field \(B\) over the beam path of regions A through E as 4.25, 4.70, 1.31, 4.72, and 1.27 T\(\cdot\)nm, respectively. These values are small when compared against the expected internal fields inside the particles, but the large length scales of these flux-closures indicate that, within the chains or rings, the individual particles nevertheless tend to have large individual moments, probably tending toward single-domain. Furthermore, the large difference among these values indicates that the directions of the nanoparticles’ magnetic moments are either distributed close to the observation plane (large consistent values, e.g., A, B, and D) or pointing to somewhat out-of-plane directions (smaller values, e.g., C and E). This further confirms the irregularity of the 3D field-distribution, which is difficult to be examined and fully understood using only one technique. Nevertheless, EH is demonstrated to be a powerful tool for observing and measuring the magnetic field of nano- and micro-structured material systems.

IV. CONCLUSIONS

In summary, Fe\(_3\)O\(_4\) nanoparticles were synthesized by a facile solvothermal method and formed in shapes of solid or hollow spheres. The nanospheres are composed of high-quality single-crystals, with average size of 150 nm. The Fe\(_3\)O\(_4\) nanospheres are self-assembled mostly into linear chains and occasionally formed circular rings. EH was used to map the in-plane magnetic induction of the assemblies, in which magnetic dipolar fields are essential to remanent magnetization configurations. Local magnetic field strength inside fringing field was quantitatively measured, indicating in-plane and out-of-plane dipole alignment at specific positions. EH technique provides a special insight into exploring and understanding the magnetic nanostructures.

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