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Focused Electron-Beam Induced Deposition, *In Situ* TEM And Off-Axis Electron Holography Investigation of Bi-Magnetic Core-Shell Nanostructures

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The demand for improved functionality in magnetoelectronic devices is resulting in the development of innovative combinations of hard and soft magnetic materials, including exchange-spring magnets. In a bi-magnetic core-shell (CS) nanostructure, exchange coupling across the CS interface facilitates cooperative magnetic switching and provides tunable magnetic properties [1, 2]. However, our current understanding of the CS exchange interaction is limited to bulk magnetic measurements and micromagnetic modelling, driving the need for local studies using transmission electron microscopy (TEM) techniques. CS nanostructures are commonly synthesized as powders or dispersions through chemical routes such as co-precipitation, but often exhibit a wide size distribution, agglomerate easily and are difficult to isolate for localized magnetic studies without inter-particle interactions. Modern scanning electron microscopes (SEMs) can incorporate systems for the injection of element-containing gases that can be used as precursors for creating magnetic nanopatterns (NPs) with feature sizes as small as 10 nm using focused electron beam induced deposition (FEBID) [3]. The deposition of reactive ferromagnetic metals such as Fe and Co can result in the formation of CS NPs through surface oxidation. Hence, we are in a timely position to synthesize isolated CS NPs using FEBID and use the TEM technique of off-axis electron holography to investigate the effect of localized magnetic exchange coupling between their metal cores and oxide shells. In the present study, we synthesize a range of CS NPs and characterize their structural, chemical and magnetic properties using a series of advanced *in situ* electron microscopy techniques.

FEBID was used to synthesis Co and Fe NPs with diameters of between ~20 and ~250 nm on the electron-transparent SiN membranes of DENSSolutions Wildfire^{TM} TEM electronic (e-) chips. $Co_2(CO)_8$ and $Fe_2(CO)$ were used as precursors for the elemental deposition of Co and Fe, with growth controlled through the systematic variation of electron beam voltage (5-15 kV) and beam current (0.34-0.69 nA). TEM imaging of the FEBID-grown structures was performed using a JEOL ARM cFEG TEM (Glasgow) or a Thermo Fisher Tecnai TEM (ER-C), with structural analysis provided by selected area electron diffraction (SAED). Electron-energy loss spectroscopy (EELS) was used to record chemical maps of elemental distributions across the CS NPs. Off-axis electron holograms were acquired in Lorentz mode on a Gatan K2 high-speed direct electron detection camera using a Thermo Fisher Titan 80-300 TEM (ER-C) equipped with an image C_S corrector and rotatable electron biprisms. Thermoremanent behavior of the NPs was studied by recording off-axis electron holograms in magnetic-field-free conditions in 100 °C intervals between 100 and 400 °C using a DENSSolutions Wildfire^{TM} heating holder and again upon cooling. The mean inner potential contribution to the phase was determined at each specimen temperature by recording holograms with the NPs magnetized in opposite directions and subtracted from subsequent phase images to construct magnetic induction maps of remanent states [4, 5].

Figure 1 shows SEM and TEM images and EELS chemical maps of FEBID-grown CS NPs, providing information about their size, chemical composition and localized structure. The SEM image in Fig. 1a shows an array of Fe NPs produced by FEBID ranging from ~20 to ~50 nm in diameter. The bright-field (BF) TEM image in Fig. 1b provides a higher magnification, localized view of an individual Fe

NP (~20 nm in diameter) recorded at 20°C, while the presence of disperse diffraction rings in the associated SAED pattern (Fig. 1b, inset) reveals that the Fe NP is near-amorphous. The EELS chemical maps show a uniform Fe distribution across the NP (Fig. 1c) and an O-rich shell (Fig. 1d), confirming the formation of an Fe / Fe-oxide CS nanostructure.

Figure 2 reveals the magnetic properties of a series of Co and Fe NPs produced by FEBID. Figure 2a shows a magnetic induction map of an Fe CS NP, with the magnetic phase contours flowing in a clockwise direction in a vortex state. Figure 2b shows a magnetic induction map of a Co CS NP, in which the downward-flowing contours could be misinterpreted as representing a uniformly magnetized state. However, as the flux loops on either side of the central magnetic core lie within the Co NP it is more likely to be a vortex state that is observed edge-on [6]. Figure 2c shows a magnetic induction map of a Co CS NP that supports a magnetic vortex at 20 °C. At 300 °C, the same Co CS NP is seen to support an 'S-shaped' domain state (Fig. 2d), suggesting a change to a different low energy magnetic configuration. This study has shown that a range of isolated Co and Fe NPs can be grown using FEBID for localized magnetic studies, with EELS chemical analysis confirming their bi-magnetic CS hetero-structure. Off-axis electron holography allows for direct imaging of their magnetic states, revealing how the low energy magnetic configurations of CS NPs can change as a function of temperature.

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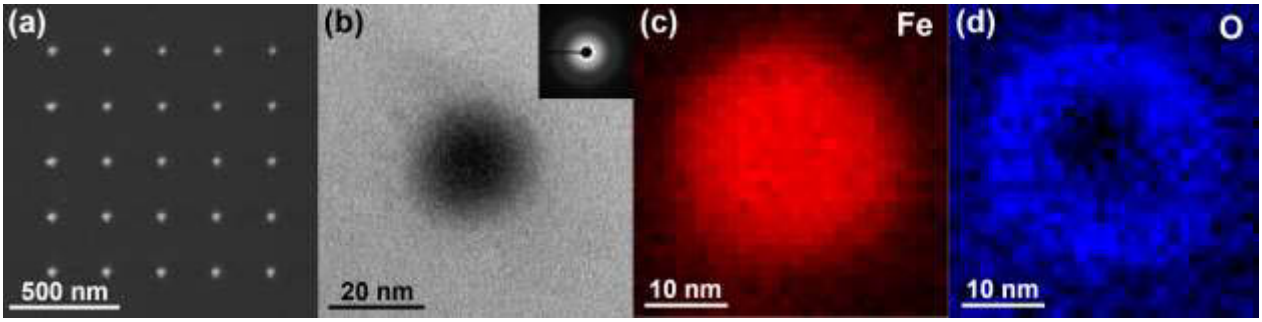

Figure 1. (a) SEM image of an array of Fe NPs produced by FEBID, ranging from ~20 to ~50 nm in diameter. (b) BF TEM image of an individual Fe NP (~20 nm in diameter) at 20°C and a corresponding SAED pattern (inset) displaying disperse diffraction rings. (c,d) EELS chemical maps showing the elemental distribution of (c) Fe; and (d) O.

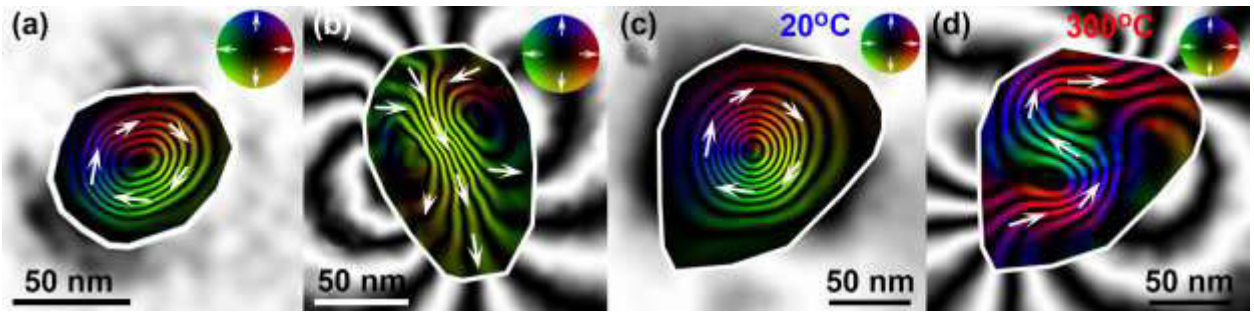

Figure 2. (a,b) Magnetic induction maps of an (a) Fe and (b) Co CS NP; with the direction of projected in-plane magnetic induction depicted in the color wheels (inset). (c,d) Magnetic induction maps of a Co / Co-oxide NP acquired at (c) 20°C and (d) 300°C, showing a change in remanent magnetic state.

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