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Synthesis, Structure, and Morphology of Magnetic Core-Shell Nanoparticles

E.C. Mattson,* E.S. Krystofiak,** P.M. Voyles,*** C.J. Hirschmugl,* M. Gajdardziska-Josifovska,* and J.A. Oliver**

*Dept. of Physics, University of Wisconsin-Milwaukee, Milwaukee, WI 53211
**Dept. of Biological Sciences, University of Wisconsin-Milwaukee, Milwaukee, WI 53211
***Dept. of Materials Science and Engineering, University of Wisconsin, Madison, WI 53706

Besides being of fundamental scientific interest, magnetic core-shell nanoparticles have significant application in cell targeting therapies when exposed to an oscillating magnetic field. Difficulties with growth of a continuous noble metal film on the terminating surfaces of an iron oxide nanoparticle hinder the controllable synthesis of these important materials. In this work, various syntheses have been correlated to the structure and morphology of the resulting materials through High Resolution Transmission Electron Microscopy (HRTEM), Selected Area Diffraction (SAD), and Infrared (IR) spectroscopy.

Magnetic iron oxide cores were synthesized in an aqueous oxygen-depleted environment by co-precipitation of $FeCl_2$ and $FeCl_3$ in an alkaline environment [1]. The nanoparticles were washed and suspended in .1M tetramethylammonium hydroxide, and size fractionated by centrifugation. The colloid was aged at least 3 days in an argon atmosphere before addition of 2.75E-3 % hydrazine in degassed dH_2O. Au shells were precipitated onto the iron oxide cores by dropwise addition of tetrachloroauric acid from a 4% stock solution [2]. Coated and uncoated NPs were deposited onto carbon-coated grids and analyzed in a Hitachi H9000 HRTEM operated at 300keV, and in a probe corrected FEI Titan STEM operated at 200keV. Other particles were dried, combined with KBr, and pressed into a disc measured in a Bruker 66V IR Spectrometer.

Characterization of the iron oxide cores by SAD found them to be consistent with the structure of magnetite (Fe_3O_4) as indexed in the pattern of (Fig. 1a). Similar rings are also present in maghemite (Fe_2O_3), but with additional weaker rings that were not observed by SAD. IR absorption spectroscopy revealed that while all preparations produced peaks consistent with Fe_3O_4, nanoparticles that demonstrated cytotoxic properties upon Au deposition also showed the IR peaks of geothite (α-FeOOH) (Fig. 1b).

HRTEM and STEM studies of the Au-coated Fe_3O_4 NPs revealed multiple faceted morphologies. A significant fraction of the particles presented a triangular morphology (Fig. 2) showing lattice fringes corresponding to the {311} and {111} interplanar spacings of Fe_3O_4 and Au, respectively. HRTEM studies of larger particles find composites of 5-6 triangular particles. Fig. 3 shows an example particle consisting of 5 triangular domains, with lattice fringes corresponding to the Fe_3O_4 {400} and Au{111} interplanar spacings. Fourier filtering was used to study the localization of Fe_3O_4 and Au, indicating that the particle is an agglomerate of 5 triangular Fe_3O_4 particles. Fig. 4a illustrates Moirè interference fringes observed in many HRTEM images of nanoparticles. These fringes are parallel to the Au{111} planes, confirming that the interference pattern is translational (Fig., 4b). The Moirè periodicity of .38 nm is consistent with the lattice mismatch between Au{111} and Fe_3O_4 {440} planes, indicating that Au{111} lies parallel to Fe_3O_4{110} at least in some of the particles. Studies

are under way to determine the orientation relationships in all morphologies of gold-magnetite particles and to explore their connection with the goethite phase detected by IR.

References:

[1] Y.S. Kang, et al., *Chem. Mater*. 8 (1996) 2209.
[2] J.L. Lyon, et al., *Nano Letters*. 4 (2004) 719
[3] This work is supported by a Scientist Development Grant (9030253N) from the American Heart Association, a UW-Madison/UW-Milwaukee intercampus research grant (133-PRJ37PH), and an MRI grant (0723002) from the National Science Foundation

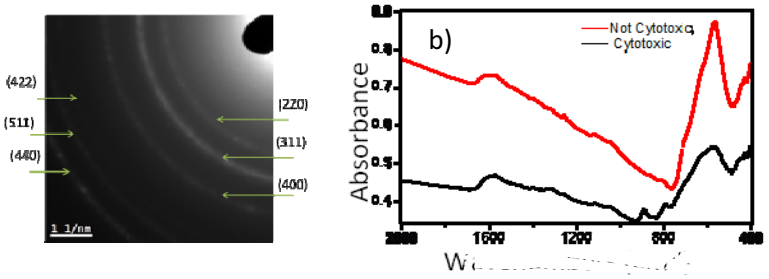

Fig. 1: SAD pattern (a) of iron oxide cores with reflections indexed to Fe_3O_4. IR spectra (b) show Fe_3O_4 (570 and 400 cm^{-1}) bands in all samples, but FeOOH (895,796 cm^{-1}) bands only in cytotoxic samples.

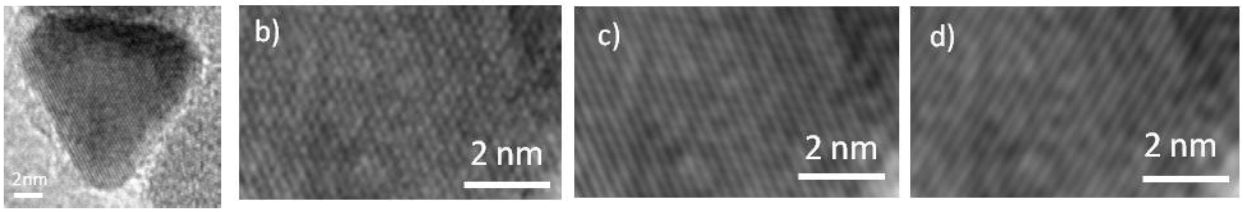

Fig. 2: HRTEM image (a) of a nanoparticle with triangular faceted morphology displays multiple lattice fringes in enlargement (b). Fourier filtering reveals two sets of Au{111} lattice fringes (c) and one set of Fe_3O_4 {311} fringes (d).

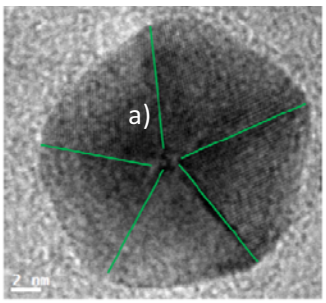

Fig. 3: a) HRTEM image of a nanoparticle composed of 5 triangular nanoparticles with Fe_3O_4 domains marked

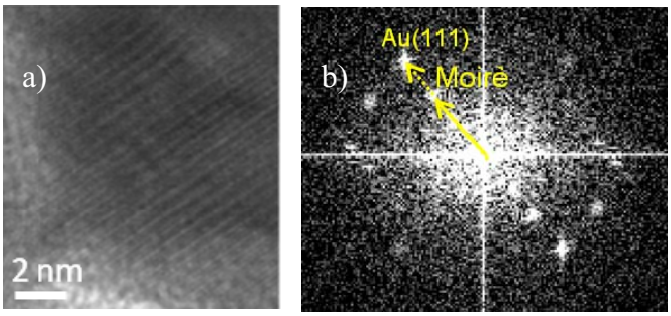

Fig. 4: a) HRTEM image of a nanoparticle showing Moirè interference fringes. b) Diffractogram indicates that fringes are parallel to Au{111}

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