

## Synthesis and Characterization of Magnetite-Gold Core-Shell Nanoparticles

E.S. Krystofiak\*, S. Rajput\*\*, R.M. Albrecht\*\*\*, M. Gajdardziska-Josifovska\*\*, J.A. Oliver\*,\*\*\*

\* Dept. of Biological Sciences, University of Wisconsin-Milwaukee, Milwaukee, WI 53211

\*\* Dept. of Physics and Laboratory for Surface Studies, University of Wisconsin-Milwaukee, Milwaukee, WI 53211

\*\*\* Dept. of Animal Sciences, University of Wisconsin, Madison, WI, 53706

Magnetic core-shell nanoparticles are of interest to multiple disciplines, including materials science, chemistry, physics, and biology. Such particles will be useful for cell targeting studies examining the effects of exposure to an oscillating magnetic field. A clear understanding of how the shell grows around the core is lacking, and as a consequence, synthesis of the particles is inconsistent. We are developing a procedure for synthesizing nanoparticles consisting of a magnetite core with a gold shell, and are studying the structure of the particles by electron microscopy.

Core-shell particles were synthesized using an aqueous oxygen-depleted system. Magnetite was produced by co-precipitation of  $\text{FeCl}_2$  and  $\text{FeCl}_3$  in an alkaline environment [1]. The nanoparticles were washed and suspended in 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  $\text{dH}_2\text{O}$ . Gold shells were precipitated onto magnetite nuclei by dropwise addition of tetrachloroauric acid from a 4% stock solution with stirring [2]. Nanoparticles were deposited onto carbon-coated grids and analyzed by TEM, SAD, SEM, and EDS using Hitachi H9000 and H600 TEMs, and an S-4800 SEM equipped with a Bruker solid state x-ray detector.

TEM and SEM analysis was used to examine the morphology of core-shell (CS) nanoparticles, colloidal gold, and uncoated magnetite. The majority of the CS particles have a rounded appearance similar to colloidal gold nanoparticles; however, a small proportion appear faceted (figure 1A-B). HR-TEM imaging at 300 keV revealed two lattice configurations: multidomains within individual nanoparticles, and single crystal domain cores within disordered shells (figure 1C). Spacings of 2.35 Å (Au 111), 2.02 Å (Au 200), and 2.48 Å ( $\text{Fe}_3\text{O}_4$  311) were observed in the CS samples.

EDS analysis, performed on CS and magnetite samples, found spectral peaks for both Au and Fe in the CS sample (figure 2A), while only the Fe peak was observed in uncoated magnetite (figure 2B). Ni and Cu peaks originate from sample grids and sample holder, respectively. Selected area diffraction (SAD) at 100 keV was performed on colloidal gold, uncoated magnetite, and CS particles. The (111), (200), and (220) Au crystal planes were used as calibration standards (figure 3A).  $\text{Fe}_3\text{O}_4$  rings of 2.99 Å, 2.53 Å, and 2.06 Å were observed and correlate to (220), (311), and (400) planes (figure 3B). The CS sample (figure 3C) showed diffraction rings from both Au and  $\text{Fe}_3\text{O}_4$  (2.32 Å from Au, 2.98 Å and 2.58 Å from  $\text{Fe}_3\text{O}_4$ ).

While CS samples contain some faceted morphologies not found in either colloidal gold or magnetite, synthesis of a true core-shell structure appears successful. HR-TEM reveals single crystal nanoparticles surrounded by a disordered shell. Elemental analysis demonstrates that both Fe and Au are present in the nanoparticles, and SAD shows the nanoparticles are crystalline in nature. Further studies will be performed to elucidate the nature of the disordered shell that surrounds the

minority faceted nanoparticles [3].

### 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 (JAO), and an MRI grant (0723002) from the National Science Foundation (MGJ).

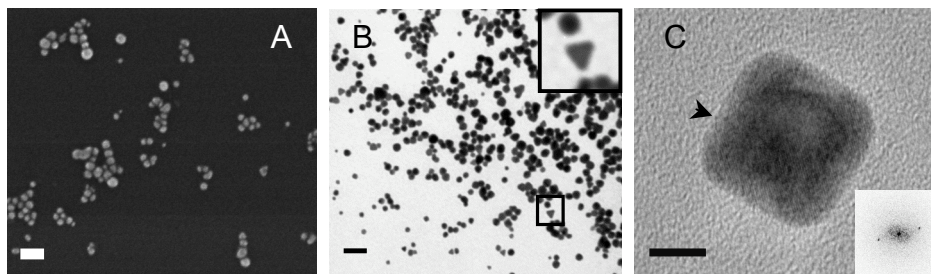


Figure 1: Morphological characteristics of core-shell (CS) nanoparticles. (A), SEM reveals three-dimensional structure of CS particles. (B), TEM shows that most CS particles are round in appearance, but a small proportion are faceted (boxed area shown in inset). (C), HR-TEM shows the lattice fringes of a faceted CS nanoparticle. Arrow indicates disordered region; inset shows FFT pattern. Scales bars are 50 nm for (A) and (B), 5 nm for (C).

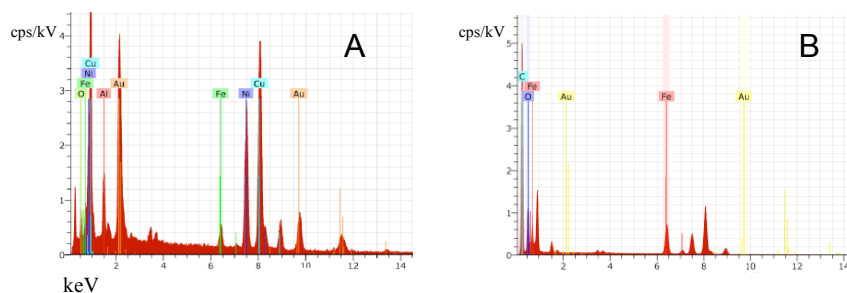


Figure 2: EDS spectra of CS particles (A) and uncoated magnetite (B). The  $K\alpha$  line of Fe is present in both CS particles and magnetite cores.  $L\alpha$  and  $M\alpha$  lines of Au are visible only in the CS sample. Colored bars indicate where elemental lines are expected.

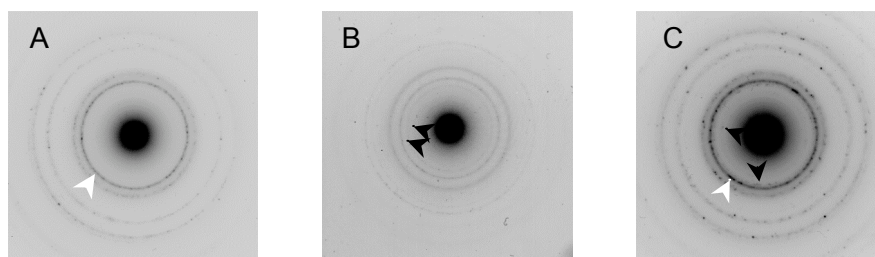


Figure 3: SAD diffraction patterns of colloidal gold, the magnetite preparation used as cores, and CS particles. The first three Au rings (A) are the (111), (200), and (220) planes (inside to out). The first three  $Fe_3O_4$  rings (B) correspond to the (220), (311), and (400) planes. The CS sample (C) has pronounced Au rings with dim  $Fe_3O_4$  rings.  $Fe_3O_4$  (220) and (311) rings, black arrows; Au (111) rings, white arrows.