Copper shells were fabricated by a displacement method around Co nanoparticles (3.2 ± 0.6 nm) at room temperature in a copper-citrate aqueous electrolyte. The nanoparticles were synthesized by a wet chemical approach using the surfactant sulfobetaine, dodecyldimethyl (3-sulfopropyl) ammonium hydroxide (98%) in tetrahydrofuran. X-ray absorption near-edge structure analysis confirmed that cobalt oxide was not present in the nanoparticles upon exposure to air, consistent with a shell formation. Additionally, the presence of the shell resulted in an increase of the blocking temperature of the core-shell nanoparticles, stabilizing the ferromagnetic behavior up to 235 K.

The iron-group nanoparticles, cobalt, iron, nickel, and nickel, are of interest due to their unusual magnetic properties, such as an enhanced coercivity compared to thin films or microcrystalline particles. Platinum alloys of Co and Fe nanoparticles have gained recent attention in high-density data storage, due to their inherent ferromagnetic behavior up to 235 K.

In an effort to control the surface chemistry of nanoparticles, the fabrication of a compact noble shell, such as gold, platinum, or silver, around the vulnerable nanoparticle, 35-38 has been demonstrated. The reported methods include a microemulsion technique where the metallic shell ions were reduced with an additional reduction agent, such as FeCo, 35-38 FeNi, 35-38 and CoNiB. 35-38 A common challenge in all these examples is the control of surface properties, because iron-group nanoparticles readily oxidize in air, which requires that the nanoparticles be stored in a protective air environment, such as N2. Cobalt oxide formation is not necessarily deleterious if the oxide shell is stabilized. For example, Co nanoparticles embedded and dispersed in a CoO matrix 35-38 result in an increase in the blocking temperature compared to uncoated Co nanoparticles.

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The absorption spectrum of a standard Si pressure. The Lemonier-type monochromator was equipped with transmission mode using ionization chambers filled with air at 1 atm energy of 1.3 GeV. The experiments were performed in standard ana State University. The storage ring was operated at an electron Microstructures and Devices synchrotron radiation source at Louisi-
al monochromator beamline at port 5A of the Center for Advanced
inserting in the sample space of the magnetometer.

The XAS experiments were performed at the XMP double crys-
tal monochromator beamline at port 5A of the Center for Advanced Microstructures and Devices synchrotron radiation source at Louisi-
ana State University. The storage ring was operated at an electron energy of 1.3 GeV. The experiments were performed in standard transmission mode using ionization chambers filled with air at 1 atm pressure. The Lemonier-type monochromator was equipped with Si(311) crystals, and the photon energy was calibrated relative to the absorption spectrum of a standard 7.5 μM Co foil, setting the first inflection point at an energy of 7709 eV. XANES spectra were collected in the −100 to +250 eV range relative to the Co K edge, with approximate step sizes of 0.5 eV and 1 s integration time per period. Samples for XAS measurement were prepared by spreading a thin layer of the dried particles uniformly over Kapton tape in air for the Co-Cu nanoparticles and in a glove box for the Co nanoparticles.

The electrochemical reaction rates were characterized on a rotat-
ing disk electrode (RDE) using linear sweep voltammetry (Solartron SI1287 and 1255B). The electrode disk area was 0.283 cm², and the rotation rate was 400 rpm. A Cu disk working electrode was used to characterize the kinetic range of the Cu reduction reaction, and a Co disk working electrode was used to characterize the anodization of Co. The counter electrode was Cu during the Cu reduction study and Pt during the Co anodization case. The applied sweep rate was 5 mV/s.

Results and Discussion

Figure 1 shows TEM images of the Co-Cu nanoparticles. As shown in Fig. 1a, the particles are discretely dispersed, having a mean diam of 3.2 nm with a standard deviation of 0.6 nm. The fringes shown in Fig. 1b have an interplanar distance of 0.18 nm. The lattice parameters of Cu and Co are 0.3615 and 0.3544 nm, respectively. Assuming a cubic structure, the measured d-spacing corresponds to a (2 0 0) face-centered cubic plane, consistent with a Cu shell. But due to the small difference in the lattice constants between Co and Cu, the measured d-spacing could also represent Co. A contrast difference, which can arise from the lattice fragments having different orientations with respect to the electron beam, has been reported as a distinguishing criterion for a core-shell structure. However, here the very small difference in atomic number Z does not make the core-shell structure distinguishable by TEM. An estimate of the Cu shell size was calculated to be 0.82 nm based on the following: average composition of the Cu content in the nanoparticles was 87.5 wt %, determined by atomic adsorption, assuming spherical particles and bulk densities. The subsequent loss in the Co radius is thus 0.78 nm.

XAS was used to verify, indirectly, the Co core protected by the Cu shell. Figure 2 shows the XANES Co K edge spectra of a standard hexagonal close-packed (hcp) Co foil, Co nanoparticles prepared in a glove box with nitrogen protection, Co-Cu nanoparticles exposed to air, Co nanoparticles exposed to air, and two cobalt oxide standards. The XANES spectrum of Co in the Co-Cu core-shell nanoparticles differs from the cobalt oxide spectra and is similar to the spectra of the air-protected Co nanoparticle and standard Co foil. The Co XANES spectrum of the Co-Cu sample exhibits a pre-edge feature at approximately 7709 eV (line A), assigned to an electron transition from 1s to a hybridized p-d orbital, and a white line at about 7724 eV (line B). The position of the absorption edge in the Co-Cu spectrum, as well as the intensity, and the energy location of the maximum white line closely resemble those of the Co nanoparticles and the standard hcp Co foil. The chemical shift of the absorption edge to higher energies (7728 eV), lower pre-edge intensity, and higher white line (lines C and D) evident in the spectra of CoO and CoO₂ were not observed in the Co-Cu sample or the N₂-protected Co nanoparticle sample. Numerous literature studies have shown that when Co nanoparticles are exposed to air they readily

![ TEM images of Co-Cu nanoparticles at (a) low and (b) high resolution, showing a 0.175 nm Cu lattice spacing.](image)

![ Co K edge XANES spectra of a hcp cobalt foil, cobalt nanoparticles, Co-Cu nanoparticles, Co nanoparticle oxidized in air, and a CoO and Co₂O₃ reference. Lines A, B, C, and D are the zero valence Co pre-edge, Co white line, and CoO and Co₂O₃ white lines, respectively.](image)
oxidize, and this is confirmed as well in the XANES spectra in Figure 2. Thus, the XANES experiments prove that the Cu shell has effectively protected the Co nanoparticle from oxidation.

The temperature dependence of the magnetization is shown in Fig. 3. The blocking temperature ($T_b$), the transition temperature between the ferromagnetic and the superparamagnetic state, is determined from the maximum in the ZFC measurements. $T_b$ is increased for the Co-Cu core-shell nanoparticles compared with the precursor Co nanoparticles. An increase of the blocking temperature due to antiferromagnetic exchange coupling has also been reported for compacted Co-CoO core-shell nanoparticles and for Co nanoparticles dispersed in a CoO matrix. In our study, the data suggest that there is little or no CoO formed, so the higher blocking temperature may be due to an increase in dipole interactions between the Co particles, as observed in Co clusters. In the FC curve, the magnetization decays uniformly as the temperature increases in both of these nanoparticle cases and can be used to evaluate particle interaction. The normalized FC magnetization curves show a difference in slope between the Co and the Co-Cu core-shell nanoparticles. The slope of the Co-Cu nanoparticles curve is lower than that of the Co nanoparticles. A smaller slope in the FC magnetization of the Co-Cu core-shell nanoparticle indicates a stronger interparticle interaction compared to Co nanoparticles, consistent with literature studies and the observed increase in the blocking temperature here.

The field dependence of magnetization is shown in Fig. 4a and b for Co and Co-Cu core-shell nanoparticles, respectively, and the magnetic parameters are summarized in Table I. At 10 K, well below the blocking temperature, a nonzero coercivity and remnant magnetization are expected; whereas, near room temperature (i.e., above the blocking temperature), coercivity and remnant magnetization are zero, indicative of the superparamagnetic state. The observed coercivity of the Co-Cu core-shell nanoparticle (−697 Oe) is slightly larger than that of the Co precursor (−656 Oe) at 10 K. The remnant magnetization increased from 0.37 emu/g for the Co nanoparticle to 0.47 emu/g for the Co-Cu core-shell nanoparticle at 10 K, where the mass used is the total sample mass. The Co mass content in the cobalt paste sample and in the Co-Cu sample is 8.4 and 4.0%, respectively. The majority of the mass in the samples consists of

| Table I. Magnetic properties of Co and Co-Cu nanoparticles (NPs). |
|-----------------|---------|--------|--------|--------|
| Sample         | $T$ (K) | $H_c$ (Oe) | $M_r$ (emu/g) | $M_s$ (emu/g) | $M_r/M_s$ |
| Co NPs         | 10      | −656.0  | 0.37    | 1.01    | 0.37     |
|                | 300     | 0       | 0       | 1.05    | 0        |
| Co-Cu NPs      | 10      | −697.0  | 0.47    | 1.53    | 0.31     |
|                | 300     | 0       | 0       | 1.06    | 0        |
The displacement reaction rate was estimated from an Evans diagram, shown in Fig. 5. The rotation rate was arbitrarily selected as an average to meet the publication costs of this article.

Louisiana State University assisted in meeting the publication costs of this article.

References


