

## Supported Superparamagnetic Pd/Co Alloy Nanoparticles Prepared from a Silica/Cyanogel Co-gel

Martina Vondrova,<sup>†</sup> Tomasz Klimczuk,<sup>†,‡</sup> V. L. Miller,<sup>†</sup> Brent W. Kirby,<sup>†</sup> Nan Yao,<sup>§</sup> R. J. Cava,<sup>†</sup> and Andrew B. Bocarsly<sup>\*,†</sup>

Department of Chemistry, Princeton University, Princeton, New Jersey 08544, Princeton Institute for Science and Technology of Materials, Princeton University, Princeton, New Jersey 08544, and Faculty of Applied Physics and Mathematics, Gdansk University of Technology, Narutowicza 11/12, 80952 Gdansk, Poland.

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Metal nanoparticles have potential applications in fields ranging from catalysis, to optics, to biosensing. The great interest in these materials stems from their unique properties due to their very small size. One such property is the superparamagnetic transition, exhibited by particles of ferromagnetic materials that are smaller than the magnetic domain size of the material. Potential applications of superparamagnetic materials in magnetic storage and recording<sup>1</sup>, magnetic force microscopy,<sup>2,3</sup> and magnetic manipulations in biological systems<sup>4</sup> have been discussed in the literature.

In this communication we report the synthesis of a composite material containing Pd/Co alloy nanoparticles embedded in silica, which exhibits the superparamagnetic transition between 50 and 75 K. This material was prepared by heating a two-phase co-gel material consisting of silica and a Pd/Co cyanogel.

Metal nanoparticles are often prepared on an inorganic support, either by the impregnation–reduction approach<sup>5,6</sup> or by sol–gel methods.<sup>7–9</sup> The inorganic support typically

plays two roles in the process: it acts to isolate small amounts of the metal precursors from each other before they are reduced to metal nanoparticles; and subsequently, the interactions of nanoparticles with the support prevent the particles from agglomerating. In addition to methods employing an inorganic substrate as a template, metal alloy nanoparticles can also be synthesized by solution methods; the polyol process, for example, has been successfully applied to the synthesis of a number of transition metal alloys and intermetallics.<sup>10–12</sup>

For some magnetic applications of nanomaterials, it is desirable to limit the magnetic interactions between particles, for example, by dispersing them in a nonmagnetic matrix.<sup>9,13,14</sup> This can be conveniently done using sol–gel methods, which typically take advantage of a template material that gels in situ, encloses the precursor materials in its pores, and allows their transformation into small particles upon reduction. This approach has been previously used to prepare, for example, CoFe<sub>2</sub>O<sub>4</sub>,<sup>9</sup> Pd/Ag,<sup>8</sup> and Pd/Co<sup>15</sup> nanoparticles in a silica matrix. However, the application of the sol–gel methods to preparation of alloy nanoparticles is somewhat precarious because these methods rely on co-reduction of two metals, often leading to heterogeneous structures rather than true alloys.

In our sol–gel method, we chose to use a cyanogel as our metal precursor because previous research has shown that these inorganic gels conveniently autoreduce at elevated temperatures to homogeneous metal alloys.<sup>16–18</sup> Cyanogels consist of coordination polymers, in which two metal centers become bridged by a cyanide ligand, typically in a reaction between a tetrachlorometalate, such as PdCl<sub>4</sub><sup>2-</sup>, and a transition metal cyanometalate, such as Co(CN)<sub>6</sub><sup>3-</sup>. Upon

\* Corresponding author e-mail: bocarsly@princeton.edu.

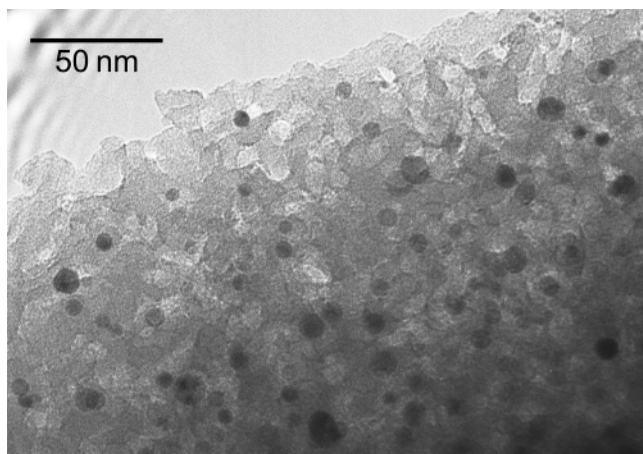
<sup>†</sup> Department of Chemistry, Princeton University.

<sup>‡</sup> Gdansk University of Technology.

<sup>§</sup> Princeton Institute for Science and Technology of Materials, Princeton University.

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**Figure 1.** HRTEM of Pd/Co particles embedded in silica prepared from a silica-cyanogel co-gel.

heating the gel above 350 °C, the cyanide groups contained within the cyanogel structure reduce the transition metal centers to metal alloys, while they are oxidized to cyanogen, (CN)<sub>2</sub>.

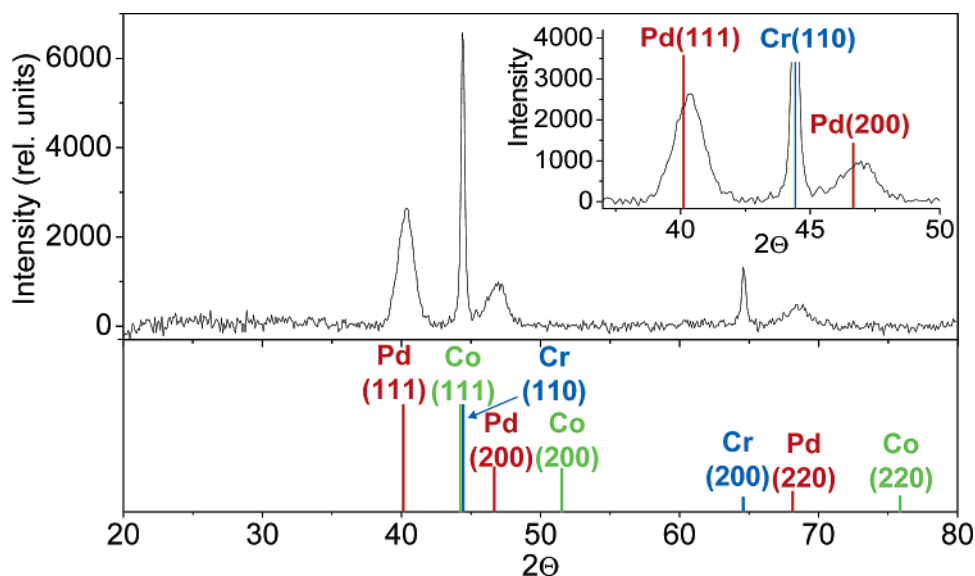
In our experiments,<sup>19</sup> silica gel was prepared from a water glass solution (SiO<sub>2</sub>/Na<sub>2</sub>O) using a modified procedure from Bhatia et al.<sup>20</sup> Aqueous solutions of Na<sub>2</sub>PdCl<sub>4</sub> and K<sub>3</sub>Co(CN)<sub>6</sub> were added to the water glass solution, and the mixture was allowed to gel. The co-gel was then aged and dried. Dried gel was heated at 600 °C under flowing argon to reduce the cyanogel phase to metal.

IR spectra of dried co-gel showed characteristic cyanogel absorption bands at 2210 and 1950 cm<sup>-1</sup>. These bands are assigned to bridging and terminal cyanide stretches, respectively. The slight shift toward higher frequency as compared to pure Pd/Co cyanogel<sup>17,18</sup> can be explained by the influence of the silica matrix on the cyanide groups' environment. The appearance of the bridging cyanide confirms that the polymerization reaction between PdCl<sub>4</sub><sup>2-</sup> and Co(CN)<sub>6</sub><sup>3-</sup> inside the pores of silica had occurred. Upon heating at 600 °C, the cyanide absorption bands disappeared from the IR spectrum.

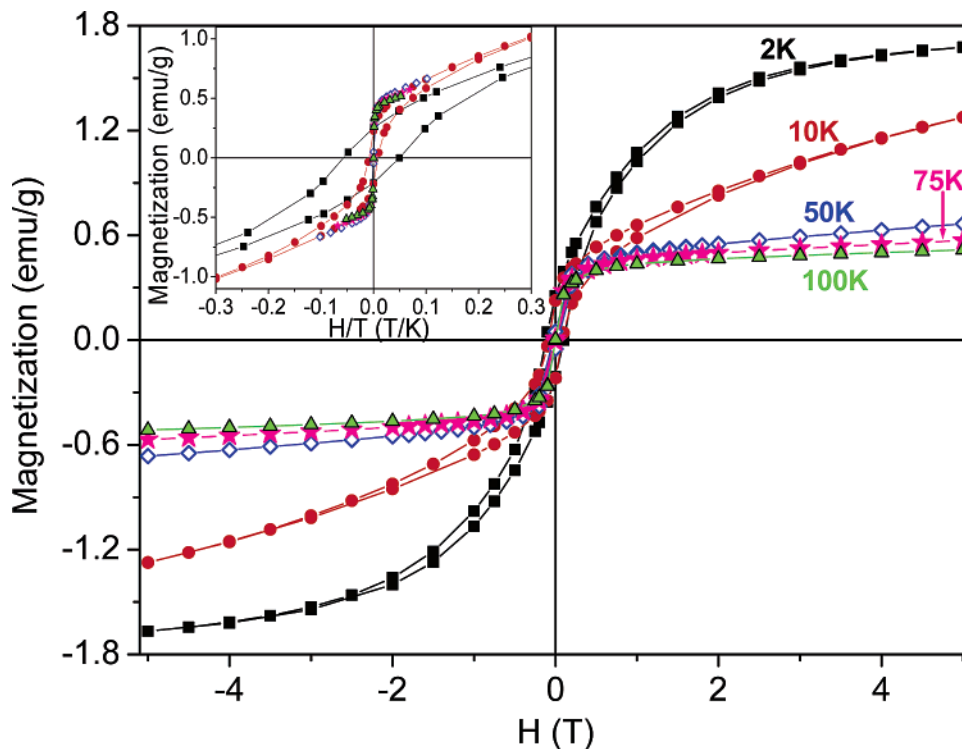
TEM images of the composite material prepared by heating the co-gel (Figure 1) showed particles 3–12 nm in diameter embedded in a matrix that was somewhat transparent to the electron beam. Statistical analysis based on 100 particles yielded an average particle size of 7 (± 2) nm. The analysis of the diffraction pattern from the particles confirmed the FCC structure of the particles expected for a Pd/Co alloy. Energy-dispersive X-ray (EDX) analysis performed with a small electron probe using the TEM detected both Pd and Co in the particles and no Pd or Co in the matrix.

The X-ray powder diffraction (XRD) pattern of the thermally reduced Pd/Co on silica showed very broad (111), (200), and (220) peaks slightly shifted toward higher angles from the positions of the (111), (200), and (220) peaks in pure Pd (Figure 2), indicating inclusion of Co in the Pd lattice. The percent composition of the particles estimated from the position of the peaks by linear interpolation between lattice parameters of pure Pd and pure FCC Co is approximately 90 (± 5)% Pd. The same percent composition was obtained by comparing the powder diffraction results with the experimentally determined dependence of the lattice parameter on composition in Pd–Co alloys found in the literature.<sup>21</sup> The Pd:Co ratio determined by EDX is consistent with the XRD data. The average particle size calculated from the breadth of the peaks using the Scherrer formula<sup>22</sup> is 7 nm, consistent with the TEM images. Work on achieving better size monodispersity and control over the alloy composition is currently in progress.

Magnetization curves measured at 2, 10, 50, 75, and 100 K of Pd/Co nanoparticles embedded in silica are shown in Figure 3. At 2, 10, and 50 K there is a hysteresis loop indicating ferromagnetic behavior. At 2 K the coercivity is about 1.2 kOe, but the loop narrows as temperature increases. At 75 K the hysteresis is no longer present, indicating that particles of all sizes have undergone the superparamagnetic transition (the superparamagnetic transition temperature increases with particle size). This suggests that the superparamagnetic blocking temperature of the largest particles



**Figure 2.** X-ray powder diffraction pattern of the Pd/Co alloy nanoparticles/silica composite with internal Cr standard (upper panel) and calculated positions of peaks for Pd,  $\alpha$ -Co, and Cr. The inset displays an expanded view of the (111) and (200) peaks of the Pd/Co alloy nanoparticles showing the shift toward higher angles from pure Pd. The background due to the silica matrix was subtracted from the spectrum.



**Figure 3.** Magnetization curves at 2 K (squares), 10 K (circles), 50 K (diamonds), 75 K (stars), and 100 K (triangles) of Pd/Co nanoparticles embedded in silica. The inset shows the same curves plotted vs  $H/T$ . Note the overlap of the 50, 75, and 100 K  $M$  vs  $H/T$  curves, indicative of superparamagnetic behavior.

in the sample is below 75 K. The inset shows the magnetization curves at different temperatures plotted versus  $H/T$ . According to the theory of superparamagnetism,<sup>23,24</sup> in a sample of truly monodispersed particles the plots of  $M$  versus  $H/T$  at different temperatures superimpose above the blocking temperature. The good overlap of the curves at 50, 75, and 100 K is consistent with the superparamagnetic response. The saturation magnetization at 2 K tends to the value 1.8 emu/g. According to the metal-to-matrix ratio estimated

from the elemental analysis by SEM/EDX, this value of magnetization at 2 K corresponds to approximately 3800 emu/mol. This value is somewhat larger than the magnetic moment reported for the bulk Pd–Co alloy (90% Pd) at 5K (0.5 Bohr magnetons  $\approx$  2800 emu/mol).<sup>25</sup> This difference is within the error range of the estimation of the metal:matrix ratio by EDX.

In summary, we have prepared a co-gel of silica and a Pd/Co cyanogel coordination polymer. Upon heating at 600 °C, this material transformed into a silica composite material with embedded Pd/Co alloy nanoparticles with an average diameter of 7 nm. Magnetic measurements showed the superparamagnetic transition of the material below 75 K. Considering the versatility of the cyanogel systems, this method could be extended to preparation of a wide variety of supported transition metal alloy nanoparticles including Pt/Co, Pd/Fe, or Pt/Fe particles with superparamagnetic transition.

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- (19) Six grams of  $\text{Na}_2\text{SiO}_3$  solution (28%  $\text{SiO}_2$ ) were dissolved in 10 mL of deionized water. To this solution was added 25 g of acidic cation-exchanged resin (Amberlite R-120(plus)) with stirring to bring the pH of the solution down to  $\sim 4$ . The resin was then removed by filtration. Two milliliters of 0.2 M  $\text{Na}_2\text{PdCl}_4$  and 1 mL of 0.2 M  $\text{K}_3\text{Co}(\text{CN})_6$  were added to the solution with stirring. Addition of 0.9 mL of  $\text{Na}_2\text{SiO}_3$  solution brought the pH to  $\sim 7$  causing gelation. The co-gel was aged for 4 days to allow all the precursors to fully react. It was then washed, filtered, and then dried at 70 °C overnight. Dried gel was heated at 600 °C for 1 h under flowing argon to reduce the cyanogel phase to metal and sinter the silica.
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