

## Higher Order Construction of Molecule-Based Magnets

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The chemical synthesis and fabrication of inorganic materials with higher order organization is currently of great interest.<sup>1</sup> A key strategy in this endeavor is to use sacrificial organic templates with extended structures that contain organized interstitial spaces, which can be subsequently in-filled to produce patterned inorganic replicas. A range of micromoulding systems have been used, including foams of emulsion droplets,<sup>2</sup> polymer gels,<sup>3</sup> bacterial superstructures,<sup>4</sup> and colloidal crystals,<sup>5</sup> in association with reaction solutions or dispersions of inorganic nanoparticles, to prepare ordered inorganic structures with pore sizes in the micrometer range. In particular, colloidal crystals of polymer or silica spheres have been extensively investigated as a facile route to a wide range of inorganic materials and metals with inverse opal structures.<sup>6</sup> However, little attention has been paid so far to the higher order construction of molecule-based inorganic materials such as transition metal coordination polymers, even though the synthesis and properties of these materials are of significant interest to a wide range of research areas. Superlattices of ferrous hexacyanoferrate (Prussian blue) cubic nanoparticles have been produced by photoreduction of  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$  in the presence of  $[\text{Fe}(\text{CN})_6]^{3-}$  ions confined within the nanoscale water droplets of reverse microemulsions,<sup>7</sup> but to the best of our knowledge there are no reports on the

preparation of molecule-based magnet materials with ordered porous microstructures.

In this paper, we show that inverse opals of cobalt hexacyanoferrate ( $\text{M}^I_x\text{Co}_4[\text{Fe}(\text{CN})_6]_y$ ,  $\text{M}^I =$  alkali cation,  $x$  and  $y = 4$  for the stoichiometric compound) can be produced by several iterations of a simple reaction cycle that results in the in-filling of the interstitial spaces of colloidal crystals prepared from monodisperse spheres of polystyrene or silica.<sup>8</sup> Synthesis of cobalt hexacyanoferrate inside the colloidal crystals was achieved by alternately immersing the opals in 0.1 M aqueous solutions of cobalt(II) chloride and potassium ferricyanide. Infiltration was allowed to proceed for 30 min in each solution. Between each soaking, excess reactant was carefully removed by quickly washing the opal with double-distilled water. Four iterations of this impregnation cycle were usually sufficient to fill the voids with the dark red coordination polymer. Inverse opals were prepared by either dissolving the polystyrene microspheres with acetone or the silica colloid with a 5 wt % solution of buffered HF, over a period of up to 12 h. The solutions were then removed and the resulting inverse opals washed several times with acetone or double-distilled water and slowly dried under vacuum.

Scanning electron microscopy indicated that the inverse replicas consisted of a well-ordered periodic array of interconnected spherical voids that were ca. 100 nm in width (Figure 1a). The voids were surrounded by a continuous framework of the coordination polymer that contained 25-nm-wide perforations associated with sphere-to-sphere contacts in the colloidal crystal templates. Corresponding transmission electron microscopy (TEM) images of fractured samples viewed in various projections (Figure 1b,c) confirmed the presence of an intact three-dimensional inverse opal framework with both tetrahedral and octahedral interconnections.

Electron diffraction analysis of the fractured replicas gave powder patterns with reflections at 0.49, 0.32, 0.25, 0.20, and 0.16 nm, corresponding to the  $\{200\}$ ,  $\{220\}$ ,  $\{400\}$ ,  $\{420\}$ , and  $\{440\}$  of a well-ordered cubic structure of  $\text{K}_x\text{Co}_4[\text{Fe}(\text{CN})_6]_y$  with unit cell parameter  $a = 1.0$  nm. Energy-dispersive X-ray analysis (EDXA) confirmed the presence of cobalt, iron, and potassium and a sulfur peak due to residual sulfonate groups from the surface of the polystyrene spheres (Figure 2). Similarly, a small silicon peak was detected in silica-templated inverse opals. FTIR spectroscopy showed two absorption bands of equal intensity: these included a sharp band at 2157  $\text{cm}^{-1}$  due to the cyanide stretching vibration in the  $\text{Fe}^{\text{III}}-\text{CN}-\text{Co}^{\text{II}}$  environment and a broad peak that was convoluted into two bands at  $\approx 2120$  and 2096  $\text{cm}^{-1}$  corresponding to  $\text{Fe}^{\text{II}}-\text{CN}-\text{Co}^{\text{III}}$  and  $\text{Fe}^{\text{II}}-\text{CN}-\text{Co}^{\text{II}}$

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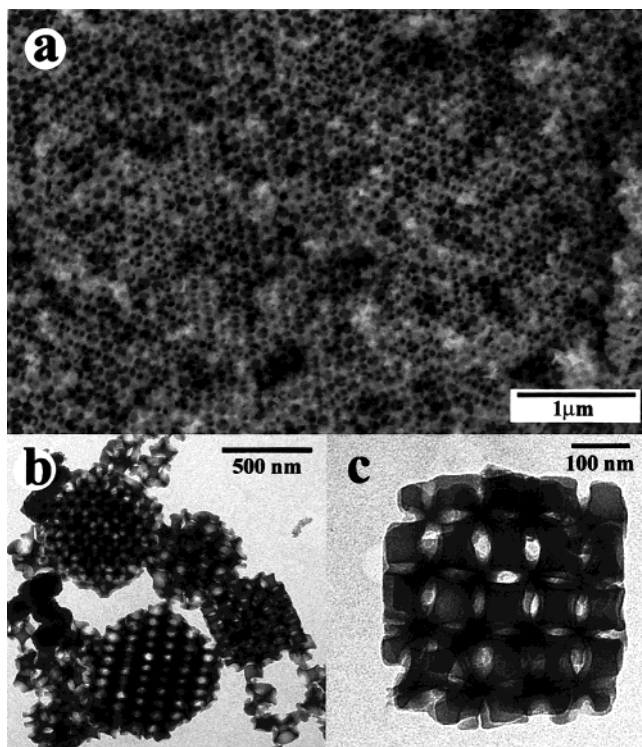
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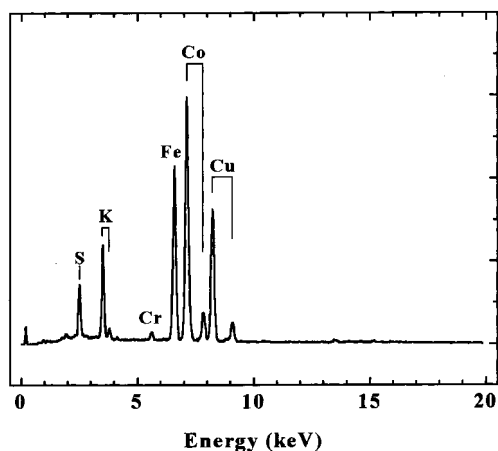
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(8) Polymer opals were formed by slow evaporation of an aqueous suspension of 140-nm-diameter polystyrene spheres at room temperature to produce colloidal crystals approximately  $3 \times 3 \times 1$  mm in dimension. The surface of the hydrophobic latex spheres was treated by immersion in concentrated sulfuric acid for 40 min, followed by repeated washing with double-distilled water until neutral pH to produce a hydrophilic opal. Silica opals were prepared from colloidal suspensions of 130-nm silica spheres according to Stöber (Stöber, W.; Fink, A.; Bohn, E. *J. Colloid Interface Sci.* **1968**, *26*, 62). The suspensions were left to settle naturally over 3 months to form  $10 \times 3 \times 0.3$  mm opal monoliths that were used without further treatment.

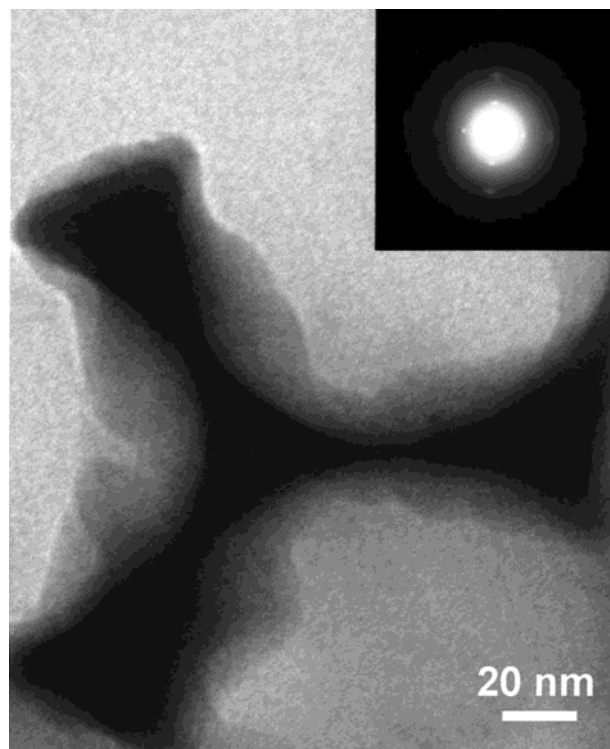


**Figure 1.** (a) SEM image showing an inverse opal of cobalt hexacyanoferrate prepared from a colloidal crystal of polystyrene microspheres. (b) and (c) TEM images of fractured samples of cobalt hexacyanoferrate inverse opals produced using a silica colloidal crystal template.



**Figure 2.** EDXA spectrum of cobalt hexacyanoferrate inverse opal. Chromium and copper peaks are from the sample grid.

pairs, respectively.<sup>9</sup> As only  $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$  ions were introduced into the synthesis mixture,  $\approx 50\%$  of these was therefore reduced to  $\text{Fe}^{\text{II}}$  centers by light-induced charge transfer. Interestingly, the corresponding infrared spectrum of a sample of bulk cobalt hexacyanoferrate that was prepared and kept under the same conditions as the inverse opal counterpart showed identical absorption bands, except that the cyanide stretch corresponding to the  $\text{Fe}(\text{II})\text{--CN--Co}(\text{III})$  pair at  $2121\text{ cm}^{-1}$  was significantly increased in intensity. Further studies are required to determine the factors



**Figure 3.** High-magnification image showing continuous wall structure of crystalline cobalt hexacyanoferrate. Inset: selected area electron diffraction pattern showing cubic reciprocal lattice of  $\{h00\}$  reflections.

responsible for the lower level of  $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$  reduction associated with the inverse opal form of the coordination polymer.

Higher magnification TEM images showed that the framework consisted of 5 to 10 nm-thick walls with smooth surfaces and few defects (Figure 3), indicating a high level of fidelity in the replication process. In general, the walls had a homogeneous texture, suggesting that they were constructed from a single domain of crystalline  $\text{K}_x\text{Co}_4[\text{Fe}(\text{CN})_6]_y$  rather than a polycrystalline mosaic of nanoparticles. Although lattice images could not be readily obtained without incurring significant beam damage, selected area electron diffraction on individual walls or small fragments gave single-crystal patterns of cubic cobalt hexacyanoferrate (Figure 3, inset). The results suggest that single crystals of the molecule-based magnet are initially nucleated within the interstitial spaces during the first stage of the coprecipitation procedure and that these nanocrystals grow in preference to the formation of new nuclei during further additions of the reactants. However, although the walls were crystallographically continuous at the nanoscale, the polycrystalline electron diffraction patterns obtained from larger fragments indicated an absence of long-range coherence between the nucleation centers.

Our results indicate that good quality inverse opals of  $\text{K}_x\text{Co}_4[\text{Fe}(\text{CN})_6]_y$  can be readily prepared using either polystyrene or silica colloidal crystal templates. The higher order construction of such materials might be useful for improving the optical properties of molecule-based magnets. For example, nonstoichiometric cobalt hexacyanoferrate is known to exhibit an increase in magnetization when irradiated by red light (660 nm),

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which can be partially reverted by exposure to blue light (450 nm).<sup>10</sup> Photoswitching of the magnetization is however limited in the bulk solid because low temperatures are required (<20 K) and switching times are large (several minutes).<sup>10</sup> In addition, only  $\approx 50\%$  of the Fe(II)–CN–Co(III) diamagnetic pairs are switchable to paramagnetic Fe(III)–CN–Co(II) bridges because of lattice strain associated with the concomitant increase in bond lengths so that electron transfer occurs predominantly in the vicinity of hexacyanoferrate vacancies or at the surface of the crystals.<sup>11</sup> Thus, in principle, inverse opals of  $K_xCo_4[Fe(CN)_6]_y$  might address this limitation because of the large surface-to-volume ratio associated with the continuous porous framework.

We also note that the photoinduced magnetization of cobalt hexacyanoferrate is limited in natural light by photobleaching associated with the blue region of the

visible spectrum.<sup>11</sup> Because the transmission spectrum of the opal structure can be tuned by selecting the size of the colloidal spheres—for example, in our studies a crystal of the 130-nm silica beads showed a stop band at 375 nm (data not shown)—and by modifying the gap by coating the spheres with a dye<sup>12</sup>—in our case the cobalt hexacyanoferrate absorbs in the range 350–600 nm—the gap of the corresponding inverse opal could be tailored to filter out the blue components of natural light while allowing red light to propagate, thereby maximizing the remanent magnetization. Although further advances are required to determine whether the optical properties and high porosity associated with the inverse opal microstructure can be exploited to improve the performance of molecule-based magnets such as  $K_xCo_4[Fe(CN)_6]_y$ , it should be relatively straightforward to develop this archetypal system for the higher order construction of a wide range of inorganic coordination polymers and organometallic materials with useful physical properties. This would significantly increase the scope of template methods being currently investigated in fields such as organized matter chemistry.

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