One-pot Borohydride Synthesis of Magnetically Modified Lepidocrocite

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The one-pot borohydride treatment of a $Fe(NO_3)_3/CoCl_2$ aqueous solution results in an inorganic magnetic nanocomposite γ-FeOOH/Co where the properties of the layered support are combined with those of the cobalt nanoparticles.

The polymorphs of iron(III) oxyhydroxide (FeOOH) have interesting structural properties and important applications as pigments, catalysts and precursors of magnetic materials to name a few.[1] Despite the lack of ion-exchange properties, iron oxyhydroxides still exhibit a wide chemistry as a result of their sizeable amount of unsaturated coordination sites. They are usually prepared by oxidative precipitation of aqueous ferrous salt solutions in the presence of structural and morphological directing agents.[2] A well-studied member of this family is mineral lepidocrocite (γ-FeOOH). Lepidocrocite is a nonmagnetic layered solid composed of stacked iron oxyhydroxide sheets that are held together by hydrogen bonding via hydroxy groups. Each sheet is built of double chains of [FeO(OH)] octahedral interlinked by sharing opposite edges. Its particle morphology may be layered-like, elongated, or platy.[2,3]

Recently, the design of magnetic nanocomposites based on layered solids has drawn particular attention because of the combined properties of the layered support and of the magnetic nanoparticles. In fact, such magnetic nanocomposites are promising for low cost industrial, technological and environmental applications.[4–6] To this end, the present work describes a facile route for the synthesis of lepidocrocite magnetically modified with cobalt nanoparticles based on the borohydride treatment of a $Fe(NO_3)_3/CoCl_2$ aqueous solution. Borohydride is an effective reducing agent of transition metal ions and its action is strongly influenced by the metal oxidation state, counterions, solvent, concentration, and temperature.[7] Accordingly, a variety of products can be foreseen by the borohydride method including the magnetic nanocomposite of the present study.

In a typical procedure, 0.41 g of $Fe(NO_3)_3 \cdot 9H_2O$ and 0.24 g of $CoCl_2 \cdot 6H_2O$ (molar ratio of Fe/Co $\approx$1:1) were dissolved in 10-mL of H_2O followed by the direct addition of 0.2 g of high grade $NaBH_4$ specimens ($NaBH_4$ pellets). After thoroughly mixing the reactants the mixture was allowed to stir for 20–25 min and the resulting magnetic precipitate was magnetically separated and rinsed twice with water, once with acetone and air-dried. During the reaction course the pH of the dispersion was $\approx$8. Finally, the dried solid was treated with 10 mL of water containing 0.5 g of NaCl and heated for 45 min in a steam bath. The as-treated solid was washed well with water, acetone and air-dried to afford a strongly magnetic black powder. Addition of concd HNO_3 to the solid liberates brown nitrogen oxide gases indicating the presence of metal nanoparticles in the sample. The composite lacks of ion-exchange properties. Elemental analysis (XRF) gave 33% Fe, 45% Co and 2% B.

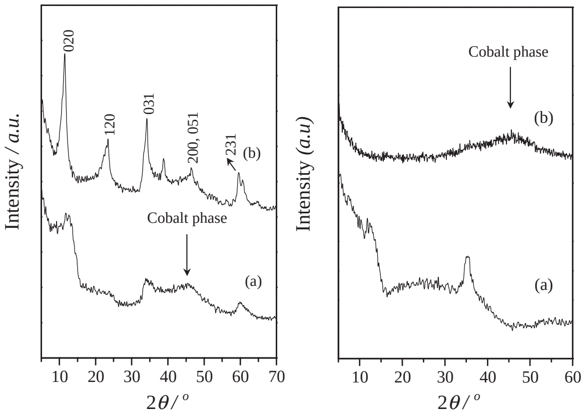

Figure 1. Left: XRD patterns of the magnetic nanocomposite before (a) and after (b) treatment with NaCl solution. Right: Blank experiment with $Fe(NO_3)_3 \cdot 9H_2O$ (a) and $CoCl_2 \cdot 6H_2O$ (b).

Figure 1, left, shows the XRD patterns of the magnetic solid before and after treatment with NaCl solution. Before treatment the solid shows poor crystallinity with a broad reflection at $\approx 45^\circ$ assigned to the formation of amorphous, probably boron-containing cobalt nanoparticles. In line with this observation, a blank experiment in the absence of $Fe(NO_3)_3 \cdot 9H_2O$ gave amorphous cobalt nanoparticles (Figure 1, right). Accordingly, the magnetic properties of the composite mainly arise from the cobalt magnetic phase. Note that no maghemite phase (γ-Fe_2O_3), a magnetic iron oxide, was detected by the XRD pattern. After the NaCl treatment the solid becomes crystalline preserving its strong magnetic properties. The XRD pattern as well as the temperature-depended Mössbauer spectra (vide infra) of the final product is quite characteristic of lepidocrocite.[8] The effect of chloride ions on the selective formation of lepidocrocite is known in the literature and probably explains the effect of the sodium chloride treatment on the crystallinity of the product.[2] The NaCl treatment affects only the crystalinity of the composite and not its magnetic properties that remain unchanged before and after treatment. Also note that simple aqueous treatment of the composite does not improve its crystallinity. On the other hand, treatment of $Fe(NO_3)_3 \cdot 9H_2O$ itself with borohydride and subsequently with NaCl solution as described above afforded poorly crystalline lepidocrocite as an nonmagnetic orange powder (Figure 1, right) (the formation of lepidocrocite was supported by Mössbauer spectroscopy, vide infra). More specifically, addition of $NaBH_4$ to the aqueous iron(III) nitrate solution initially gave a black precipitate that was gradually converted to a green and finally to an orange solid. Accordingly, lepidocrocite is most likely formed by the initial borohydride reduction of trivalent iron to metallic iron nanoparticles (black), followed by air oxidation to $Fe(OH)_2$ (green) and a final air oxidation to lepidocrocite. In presence of cobalt, both the magnetic phase and layered solid formation take place simultaneously. Nevertheless it is not clear whether a Fe–Co metal alloy or a Fe/Co metal mixture is the initial product prior transformation to the nanocomposite. Since the material lacks of ion exchange properties—a fact that would signal the formation of cobalt–iron layered double hydroxides—and it is strongly magnetic, we can safely conclude that the divalent cobalt is quantitatively reduced to the corresponding me-

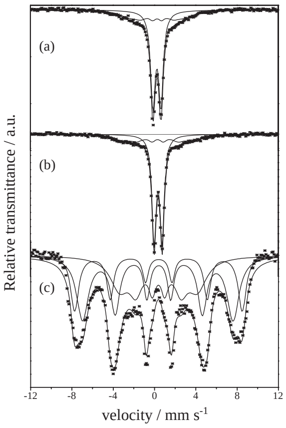

Figure 2. Mössbauer spectra of the composite [(a): RT, (b): LN, (c): LHe].

tallic phase without substituting the trivalent iron centers of the oxyhydroxide matrix.

It should be mentioned that increasing the iron content at the expense of cobalt in the final product, i.e., Fe/Co ≈2:1 molar ratio, leads to highly crystalline lepidocrocite, that however, possesses poor magnetic properties. On the contrary, increment of the cobalt content at the expense of iron, i.e., Fe/Co ≈1:2 molar ratio, leads to a strongly magnetic solid of poor crystallinity. Therefore, the molar ratio of ≈1:1 appears to be the optimum condition for achieving both good crystallinity and magnetic properties. Still, the method is influenced by the nature of the counterions and the grain size of the added $NaBH_4$. For example, the reduction of $FeCl_3$ or $FeCl_2$ by borohydride solutions leads to amorphous Fe–B magnetic particles,[7] while reduction of the pair $FeCl_3/CoCl_2$ results in an amorphous magnetic solid (most likely an Fe–Co alloy). When fine powder of $NaBH_4$ (instead of pellets) was added to the $Fe(NO_3)_3/CoCl_2$ aqueous solution we received a poorly crystalline solid probably as a result of the rapid decomposition of the $NaBH_4$. The rapid decomposition can be avoided by conducting the reaction at 3–4 °C. It is also worth mentioning the fact that replacement of the cobalt salt by $AgNO_3$ followed by treatment as above leads to XRD-detectable γ-Fe_2O_3/Ag nanocomposites of various compositions in which the corresponding magnetic and electric properties are combined together. Thus, it becomes clear that the present method is promising for the preparation of a library of inorganic nanocomposites with valuable and controllable properties.

Figure 2 presents the Mössbauer spectra of the magnetic nanocomposite. While both the spectra at room temperature (RT) and liquid nitrogen (LN) are practically composed of a paramagnetic doublet with the same quadrupole splitting ($Q = 0.80\,\mathrm{mm\,s^{-1}}$) and isomer shifts ($\delta$) of 0.36 and $0.46\,\mathrm{mm\,s^{-1}}$, indicative of trivalent iron, the liquid helium (LHe) spectrum becomes magnetically ordered giving a broad sextet with $\delta = 0.48\,\mathrm{mm\,s^{-1}}$ and hyperfine field $H = 480\,\mathrm{kOe}$. These temperature-depended changes and parameters are consistent with lepidocrocite.[9] In contrast to lepidocrocite, α-FeOOH (goethite), β-FeOOH (akaganeite) and $Fe(OH)_3$ become magnetically ordered at much higher temperatures, i.e., RT or LN.[9] Concerning the blank iron oxyhydroxide phase obtained in the absence of cobalt, this gave a paramagnetic doublet at RT ($\delta = 0.35\,\mathrm{mm\,s^{-1}}$, $Q = 0.70\,\mathrm{mm\,s^{-1}}$), a paramagnetic doublet at LN ($\delta = 0.48\,\mathrm{mm\ s^{-1}}$, $Q = 0.70\,\mathrm{mm\,s^{-1}}$) and a magnetic sextet at LHe with $\delta = 0.49\,\mathrm{mm\,s^{-1}}$ and $H = 500\,\mathrm{kOe}$, thus providing evidence for the formation of lepidocrocite.[9]

A TEM study of the composite reveals that the embedded magnetic nanoparticles are spherical in shape with a size ranging from 5 to 8 nm (Figure 3A). The magnetization results at RT, Figure 3B, show a remaining magnetization of $12\,\mathrm{emu\,g^{-1}}$, saturation magnetization of $27\,\mathrm{emu\,g^{-1}}$ and coercivity of 500 Oe. These properties arise from the magnetic cobalt nanoparticles that probably interact magnetically with the layered matrix to provide the enhanced magnetic properties in the composite. Note that lepidocrocite is macroscopically nonmagnetic and the cobalt nanospheres of 8 nm lack of coersivity.[10] Similarly, powdered fcc type Co–Pt alloy nanoparticles with comparable size and spherical morphology as for the cobalt nanoparticles of this study posses a saturation magnetization of $25\,\mathrm{emu\,g^{-1}}$ and no remaining magnetization.[11] Therefore, such enhanced magnetic properties make the composite fairly attractive for low cost and effective applications in environment, magnetic materials and catalytic synthesis of carbon nanotubes.[12]

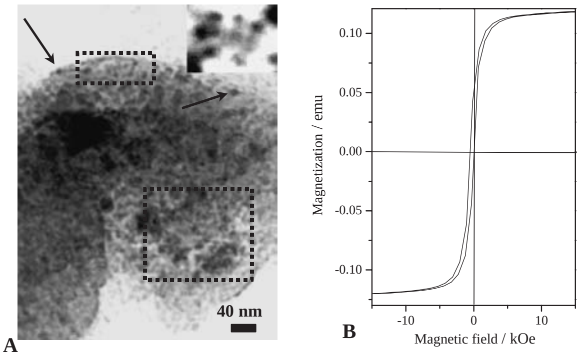

Figure 3. **A** TEM micrograph of the magnetic nanocomposite (the doted squares, arrows and inset denote cobalt nanoparticles). **B** Magnetization versus applied field curve at room temperature for the composite (mass = 4.1 mg).

On the basis of these results, the magnetic nanocomposite can be rationalized as layered lepidocrocite decorated on the external surface by cobalt nanoparticles. The Co nanoparticles are strongly adhered on lepidocrocite (no phase separation is observed upon sonication in water) indicating grafting of Co nanoparticles through interaction of the hydroxy groups of the support with the boron component of the nanoparticles at their interface.

In summary, we have presented a facile route for the synthesis of magnetically modified lepidocrocite based on the action of $NaBH_4$ on a solution of $Fe(NO_3)_3/CoCl_2$.

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