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Sonochemical Synthesis of Nanosized Hollow Hematite

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Hollow inorganic materials are of great interest, in part because of their diverse applications for drug delivery, catalysis, photonic crystals, etc.[1] Various preparation methods have been developed to fabricate hollow inorganic materials[2,3] and even hollow single crystals;[4] most commonly these synthetic methods exploit the use of silica nanospheres as a sacrificial template material. While silica colloids are commercially available in various sizes, silica template removal is time-consuming, and the use of the highly aggressive and toxic hydrofluoric acid is unavoidable. Here, we report a sonochemical fabrication of crystalline hollow hematite (α-Fe_2O_3) using carbon nanoparticles as a spontaneously removable template for nanosized hollow core formation.

Ultrasound has found an important niche in the preparation of inorganic materials, including amorphous metals and metal oxides, nanostructured layered materials with high catalytic activity, and semiconductor quantum dots.[4,5] During the irradiation of liquids with ultrasound, the extreme but transient local conditions caused by acoustic cavitation ($\sim$5000 K, $\sim$500 bar)[6] can not only decompose organometallic precursors to generate metal atoms but can also facilitate the uniform deposition of the nanosized inorganic particles onto another surface or template.[4,7]

Nanosized hollow iron oxide was prepared by irradiating a mixture of carbon nanoparticles (0.1 g) and iron pentacarbonyl (0.5 mL) in 40 mL of hexadecane with a high-intensity ultrasound horn (Sonics & Materials, model VCX-750, 1 cm^2 Ti horn at 20 kHz and 50 W/cm^2 at 20 °C for 3 h under argon flow) (Figure S1 in Supporting Information (SI)). Spherical carbon nanoparticles (4−12 nm diameter, Figures S2 and S3 in SI) were prepared from the carbonization of polypyrrole nanoparticles as previously reported with some modification.[8] The initial product of Fe/carbon composite was quickly washed with pentane and filtered under air to remove hexadecane and unreacted $Fe(CO)_5$. As soon as the Fe/carbon composite was dried, the composite rapidly oxidized with release of heat, turning color from black to red. (CAUTION: On larger scale, this autoignition might prove hazardous.) After a few minutes, the resulting red-colored product was thoroughly washed again with pentane.

The as-obtained product was investigated by transmission electron microscopy (TEM). The TEM image (Figure 1a) shows iron oxide with nanosized hollow cores. The hollow structure is more clearly visible with a dark-field image as shown in Figure 1b, and selected-area electron diffraction (SAED) pattern reveals the crystalline nature of the hollow iron oxide (Figures S3 and S4 in SI). Energy dispersive X-ray spectroscopy (EDS) analysis and electron energy loss spectroscopy (EELS) performed in nanoprobe mode confirm the formation of hollow iron oxide (Figure S5 in SI). The hollow iron oxide was also examined by scanning transmission electron microscopy (STEM) with EDS line analysis across a single hollow iron oxide sphere. The Fe K line decreases from the outer wall in toward the center of a particle, confirming the presence of the inner hollow core (Figure S6 in SI).

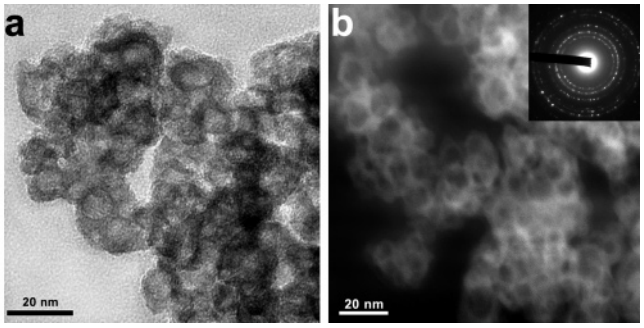

Figure 1. (a) Bright-field TEM image and (b) dark-field TEM image (inset: SAED pattern) of nanosized hollow iron oxide.

Figure 2 parts a and b show powder X-ray diffraction (XRD) pattern and Raman spectrum of the nanosized hollow iron oxide. The resolved diffraction peaks match the standard α-Fe_2O_3 sample perfectly (JCPDS 33-0664), and no characteristic peaks of impurities were observed. The Raman spectrum of the hollow iron oxide also matches that of typical hematite (α-Fe_2O_3),[9] including the unusual two-magnon scattering (i.e., a collective spin transition) at 1320 cm^{-1}. Mössbauer spectra (Figure S7 in SI) confirm the presence of hematite as the only iron species.

The as-produced hollow hematite was annealed at 450 °C for 2 h under air to completely remove any organic residues. TEM observation and EDS analysis reveal that the hollow hematite still maintains its morphology and composition after the heat-treatment. The SAED pattern indicates improved crystallinity of the hollow hematite after annealing. Consistent with the improved crystallinity, the XRD pattern and Raman spectrum are more sharply defined (Figure 2c,d).

As a control experiment, we sonicated iron pentacarbonyl in hexadecane without the carbon nanoparticles under the same reaction conditions. A TEM examination of the as-prepared product (Figure S8 in SI) shows agglomerated nanoparticles of $\sim$6 nm, as noted before.[5b] In contrast to the hollow iron oxide synthesized in the presence of the carbon template, XRD analysis reveals that the product is amorphous iron oxide, and Raman spectrum of the amorphous iron oxide is featureless, consistent with the XRD analysis (Figure S9 in SI).

Hematite, which has relevance to corrosion, pigments, catalysis, and even sensors, is the most thermodynamically stable phase of iron oxide.[10] In addition, hematite has been investigated as a photoanode for water splitting because of its ability to absorb a large part of the solar spectrum with its band gap of 2.2 eV.[11] Bulk hematite is weakly ferromagnetic at 298 K with a Néel temperature of 950 K and undergoes a "spin-flop" (Morin) transition at 263 K, in which the magnetic moments change orientation.[12] Nanoparticles, however, often exhibit unusual magnetic behaviors different from that of bulk samples, owing to finite size effects.[13] Figure 3 shows magnetization curves of the hollow hematite measured at 5 and

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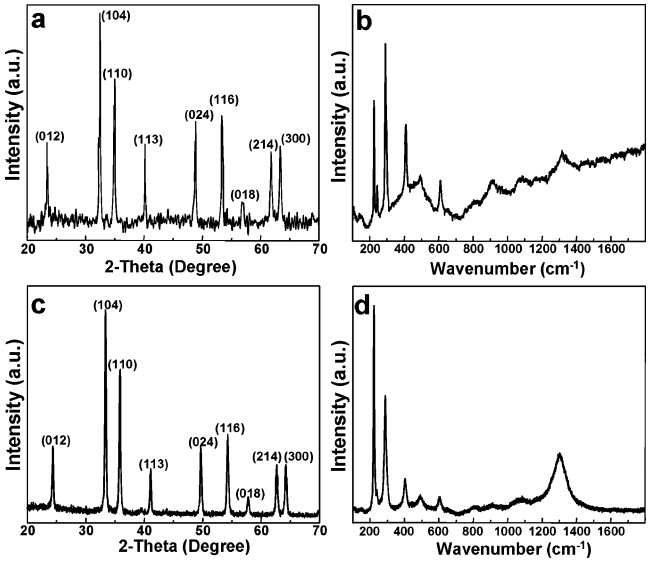

Figure 2. XRD patterns and Raman spectra of nanosized hollow iron oxide, before (a and b, respectively) and after (c and d, respectively) heat treatment at 450 °C for 2 h under air.

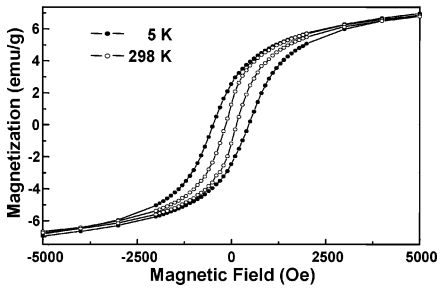

Figure 3. Magnetization curves showing hysteresis loops for nanosized hollow iron oxide measured at 5 and 298 K.

298 K, which show ferromagnetic hysteresis loops. Such magnetic irreversibility was also confirmed by zero-field cooling/field cooling (ZFC/FC) measurements (Figure S10 in SI). In contrast to bulk hematite, our hollow hematite is weakly ferromagnetic down to 5 K (which may reflect small amounts of impurities or finite size effects).

The mechanism of the hollow hematite formation utilizes in situ combustion of the carbon nanoparticles. Polymer and carbon templates have been previously used as alternative templates for the preparation of hollow materials and are normally removed from an initial composite by either decomposition through calcination or dissolution by exposure to solvents.[2a,c] We speculate that in our case, amorphous iron nanoparticles produced from sonochemical decomposition of $Fe(CO)_5$ form shells around the pre-existing carbon nanoparticles. Upon exposure to oxygen, the heat released from rapid oxidation of the high-surface-area iron shells ignites the carbon particles. The combustion of the nanosized carbon particles generates enough heat to crystallize the iron oxide shells, converting them to α-Fe_2O_3 with remnant hollow cores. In fact, a similar synthetic approach to the preparation of maghemite (γ-Fe_2O_3) was previously reported[14] by air exposure of Fe(0) particles produced by irradiating aqueous Fe^{2+} with γ-rays.

In conclusion, a facile and novel method for sonochemical preparation of nanosized hollow iron oxide using carbon nanoparticles as a template has been demonstrated. The hollow iron oxide is the thermodynamically stable crystalline hematite (α-Fe_2O_3) and shows weak ferromagnetism down to 5 K. Without the use of carbon template, only agglomerated amorphous iron oxide was obtained, demonstrating the dual roles of the carbon nanoparticles: template and fuel for combustion. We believe that this procedure will be easily extended to prepare other hollow inorganic materials.

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Supporting Information Available: Further characterization of nanosized hollow hematite and characterization of amorphous iron oxide synthesized without carbon template. This material is available free of charge via the Internet at http://pubs.acs.org.

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