Sonochemical Synthesis and Characterization of Nanocrystalline Paramelaconite in Polyaniline Matrix

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A simple method for the fabrication of nanocrystalline Cu_4O_3 in polyaniline is reported. An aqueous solution of copper(II) acetate and aniline (1:10 mole ratio) is irradiated by ultrasound to produce nanophased Cu_4O_3 embedded in a polyaniline matrix. The as-prepared Cu_4O_3–polyaniline is characterized by X-ray diffraction (XRD), thermogravimetric analysis (TGA), and transmission electron microscopy (TEM). The mechanism for the fabrication of Cu_4O_3–polyaniline is proposed and discussed. This method is general and works also for the production of nanocrystalline Fe_3O_4 and Cu_2O embedded in polyaniline. This technique is an easy route for the production of other metal oxides embedded in polyaniline as well.

Introduction

The discovery of the superconducting mixed-valence copper oxides and the possible role of magnetic interactions facilitating the very high T_c has intensified interest in the binary oxides. Cu_2O was one of the original "electronic materials", and CuO has the remarkable property of having a large but almost constant paramagnetic susceptibility at low temperatures.[1] The magnetic properties of CuO are currently the subject of intense theoretical and experimental study.[2−4] Paramelaconite (Cu_4O_3) was discovered as a new mineral in the famous Copper Queen mine located at Bisbee, AZ, during the late 1870s. Koenig[5] first determined the composition and crystal class. Earlier, some unsuccessful attempts were made to prepare the Cu_4O_3. The methods tried for its synthesis were as follows: (a) controlled reduction of CuO by reducing gases and decomposition in a vacuum;[6,9] (b) controlled oxidation of Cu_2O.[9] Long and Petford−Long[6] showed that microscopic quantities of Cu_4O_3 are produced on decomposition of CuO in the beam of an electron microscope. By this method it is obviously not possible to produce sufficient quantities for the measurement of its properties. More recently Morgan[7] et al. prepared Cu_4O_3, which is a mixture of Cu_4O_3, Cu_2O, and CuO. Mansour[8] also observed Cu_4O_3 along with Cu_2O and CuO, when copper(II) acetate was decomposed thermally. Recently Li and co-workers[9] observed the Cu_4O_3 phase by sputtering the CuO thin films. Most recently Tejada-Rosales[10] and co-workers prepared a paramelaconite ($Ag_2Cu_2O_3$) by simple chemical method at room temperature.

Recently sonochemical processing has proven to be a useful technique for generating novel materials with unusual properties.[11] The chemical effects of ultrasound arise from acoustic cavitation, i.e., the formation, growth, and implosive collapse of bubbles in a liquid. The implosive collapse of the bubble generates localized hot spots through adiabatic compression or shock wave formation within the gas phase of the collapsing bubble. The conditions formed in these hot spots have been experimentally determined, with transient temperatures of ~5000 K, pressures of 1800 atm, and cooling rates in excess of 10^8 K/s. The extreme conditions attained during bubble collapse have been exploited to prepare amorphous metals,[12] carbides,[13] oxides,[14] composites,[15] and nanocrystaline materials.[15] The difference between these two classes can be understood on the basis of the existence of two regions of sonochemical reactivity, as postulated by Suslick et al., the inside part of the collapsing bubble and the interface between the bubble and the liquid.[17] In the sonication of volatile

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precursors such as transition metal carbonyls, a gas-phase reaction takes place inside the collapsing bubble and the amorphous product is a result of the high cooling rates ($>10^{10}$ K/s). For a nonvolatile precursor a liquid-phase reaction occurs in the thin liquid layer immediately surrounding the collapsing cavity.[18]

In this manuscript we report the sonochemical synthesis and the characterization of Cu_4O_3 nanoparticles embedded in a polyaniline matrix.

Experimental Section

The experimental procedure for the preparation of Cu_4O_3 nanoparticles embedded in polyaniline matrix is as follows: Copper(II) acetate monohydrate (Aldrich Chemicals) and aniline (Aldrich) were taken in 1:10 mole ratio in 100 mL of doubly distilled water. The mixture was deoxygenated by bubbling argon through the mixture for 25 min and then irradiated under argon flow at 1.5 atm and at 10 °C with a high-intensity ultrasonic probe (Sonics and Materials, VC-600, 20 kHz, Ti horn, 100 W cm^{-2}). After 3 h of irradiation the resulting black powder was recovered by centrifugation, washed repeatedly with absolute ethanol, and dried in an inert glovebox (O_2, <2 ppm). It was then vacuum-dried at room temperature overnight and characterized. The X-ray diffraction (XRD) measurements were carried out using a Bruker, D8 model. Elemental analyses were carried out using a Eager 200 CHN analyzer. EDAX measurements were carried out on a JEOL JSM-840, scanning electron microscope. Transmission electron microscopy (TEM) examinations of the sample were carried out with a JEOL-JEM 100SX microscope. The powdered sample was dispersed in ethanol by sonication and dropped on a conventional carbon-coated grid. FT-IR spectra (KBr pellets) were recorded on a Nicolet Impact 410 infrared spectrophotometer. The TGA measurements were carried out under nitrogen on a Mettler Toledo TGA/SDTA 851 instrument at a heating rate of 10 °C/min.

Results and Discussion

Cu_4O_3–polyaniline composite was prepared by ultrasound irradiation of aqueous solution containing copper(II) acetate and aniline in 1:10 mole ratio. When we changed the concentration of copper(II) acetate and aniline to a 1:2 mole ratio in 100 mL of water, we obtained the nanocrystalline Cu_2O–polyaniline composite material, whereas 1 g of copper(II) acetate in 100 mL of aniline (without water) leads to the formation of amorphous copper–polyaniline composite. A detailed study of Cu_2O–polyaniline and copper–polyaniline composite materials is in progress. Figure 1 depicts the XRD patterns of (a) Cu_4O_3 calculated patterns (JCPDS card no: 83-1665), (b) as-prepared Cu_4O_3–polyaniline composite material, (c) as-prepared Cu_4O_3–polyaniline material heated at 350 °C for 6 h under argon flow (sample B), and (d) as-prepared Cu_4O_3–polyaniline composite material heated at 500 °C for 6 h under argon flow (sample C). Figure 1b clearly indicates that the as-prepared material is crystalline and all the diffraction lines are assigned to Cu_4O_3 on the basis of JCPDS card no. 83-1665. We cannot detect any major diffraction lines related to Cu_2O or CuO. Figure 1c indicates that when heated at 350 °C for 6 h under argon flow, the as-prepared material becomes a mixture of crystalline Cu_2O and Cu. The diffraction lines were assigned to Cu_2O and metallic Cu on the basis of JCPDS cards no. 35-1091 and no. 04-0836, respectively. Li[9] and coworkers also observed the formation of Cu_2O when Cu_4O_3 was annealed at 340 °C in a vacuum. Figure 1d indicates that when heated at 500 °C for 6 h under argon flow, the as-prepared material becomes crystalline and all the diffraction lines are assigned to metallic Cu on the basis of JCPDS card no. 04-0836. The particle sizes, calculated by using the Debye–Scherrer formula,[19] are 8 and 15 nm for as-prepared material and sample C, respectively. Figure 2a depicts the TEM picture of as-prepared material and shows that the Cu_4O_3 particles are coated with polyaniline. The selected area electron diffraction (SAED) pattern of annular regions shows that the material is crystalline and the lattice spacing of Cu_4O_3 match very well the XRD results. Figure 2b depicts the TEM picture of sample C and shows the relatively well-separated metallic Cu particles. The particle sizes measured from TEM pictures are 5–10 and 12–20 nm for as-prepared Cu_4O_3–polyaniline and sample C, respectively.

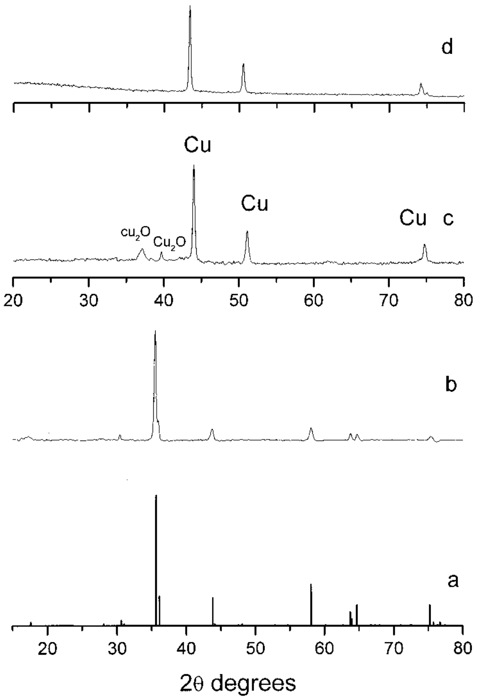

Figure 1. X-ray diffraction pattern of (a) Cu_4O_3 calculated patterns (JCPDS card no. 83-1665), (b) as-prepared Cu_4O_3–polyaniline composite material, (c) as-prepared Cu_4O_3–polyaniline heated at 350 °C for 6 h under argon flow, and (d) as-prepared Cu_4O_3–polyaniline heated at 500 °C for 6 h under argon flow.

FT-IR measurements of as-prepared composite material show the characteristic peaks of polyaniline at ~1590 and 1497 cm^{-1}, which represents the C=C stretching vibrations of quinoid and benzenoid rings, respectively.[20–21] We also observe the peak at ~1299 cm^{-1}, which is attributed to C–N stretching of the

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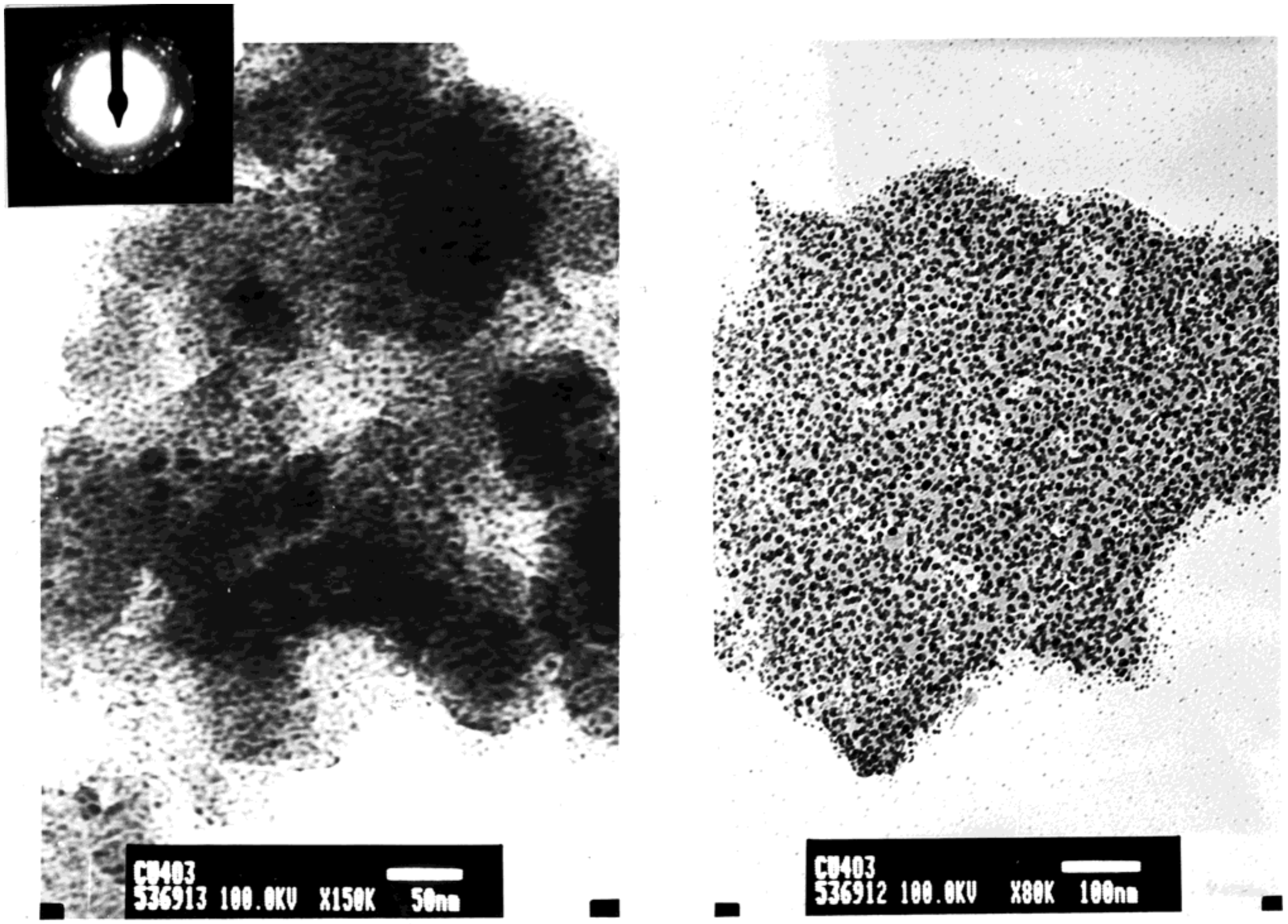

(a) (b)

Figure 2. (a) Transmission electron micrograph of the as-prepared Cu_4O_3-polyaniline. Inset: electron diffraction of the as-prepared Cu_4O_3-polyaniline. (b) As-prepared Cu_4O_3-polyaniline heated at 500 °C for 6 h under argon flow.

benzenoid units. Furthermore, the peak intensity of the N=Q=N absorption at ~1160 cm^{-1} (Q refers to the quinoid ring) is considerably smaller than C–N stretching of the benzenoid units at ~1299 cm$-^{1}$. Instead of multiple peaks at 1160 cm^{-1}, as in the case of partially crystalline polyaniline, we observe a single peak, suggesting the amorphous nature of the polyaniline. This is the consistent with the XRD and TEM results. C, H, and N analysis and energy-dispersive X-ray spectroscopy (EDS) showed that the as-prepared Cu_4O_3-polyaniline powder contains about 60% of Cu_4O_3 and 40% of polyaniline.

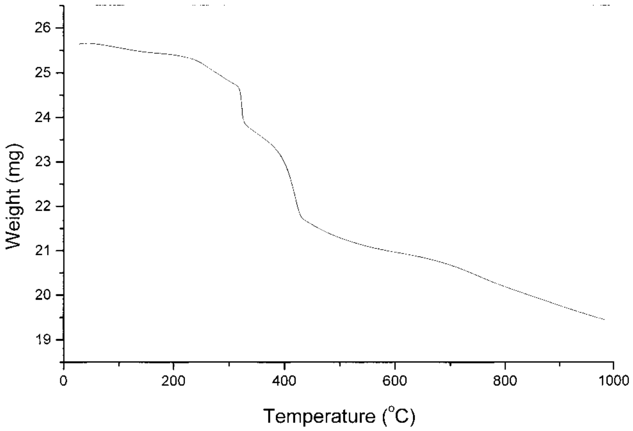

Figure 3. TGA spectra of as-prepared Cu_4O_3-polyaniline.

We have carried out TGA measurements to assess the thermal stability of the as-prepared Cu_4O_3-polyaniline composite. The results of the TGA measurement are shown in Figure 3. There are two major weight losses for the as-prepared Cu_4O_3-polyaniline powder. The first weight loss at ~320 °C indicates a structural decomposition of the polyaniline and Cu_4O_3. The chemically synthesized polyaniline has been reported as stable up to ~400 °C.[22] The reason for the lowering of the decomposition temperature could be due to the perturbation of Cu_4O_3, which affects the three-dimensional structure of the polyaniline. This perturbation weakens the van der Waals interaction between the polymer chains, thus affecting the stability of the polymer, which is reflected in the lowering the decomposition temperature. Morgan[7] et al. also observe the weight loss for the crude Cu_4O_3 at 300 °C in helium atmosphere which was leading to the formation of Cu_2O. The second weight loss at ~415 °C is associated with the further decomposition of Cu_2O to Cu and decomposition of cross-linked polyaniline, which is continued to further weight loss

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at higher temperatures. These results are in good agreement with XRD results.

Mechanism for the Sonochemical Fabrication of Nanocrystalline Cu_4O_3 Particles Embedded in Polyaniline Matrix. The chemical reactions reported to be driven by intense ultrasonic waves that are strong enough to produce cavitation are as follows: oxidation, reduction, dissolution, decomposition, polymerization, and hydrolysis.[23−26] These reactions can occur in three different regions[27,28] surrounding the collapsing bubble in an aqueous media. They are as follows: (a) the inner environment (a gas-phase reaction) of the collapsing bubble, where elevated temperatures (several thousands of degrees) and high pressures (hundreds of atmospheres) are produced, causing the pyrolysis of water into H and OH radicals; (b) the interfacial liquid region between the cavitation bubbles and bulk solution (the temperature in this region is lower than that of the interior of the bubbles, and the reaction is a liquid-phase reaction; however, the temperature is still high enough to rupture chemical bonds); and (c) the bulk of the solution, which is at ambient temperatures and where the reaction between reactant molecules and surviving OH or H can still take place.

We propose for the formation of Cu_4O_3 a two-step mechanism. In the first step we suggest the formation of CuO and that of Cu_2O in the second step. The reaction steps for the formation of Cu_4O_{3-}polyaniline are as follows:

$$Cu^{2+}(aq) + H_2O(l) \xrightarrow{)))))} CuO(s) + 2H^{+}(aq) \qquad (1)$$

$$CuO + aniline \rightarrow Cu_2O + polyaniline \qquad (2)$$

$$2CuO + Cu_2O \rightarrow Cu_4O_3 \qquad (3)$$

To substantiate the reaction mechanism, we have carried out the sonication of copper(II) acetate in water and found that CuO is formed through the sonohydrolysis mechanism (reaction 1). The pH of the solution (reaction 1) was measured before and after the reaction. A decrease in the pH from 5.7 before to 4.9 after the reaction occurred indicates the generation of H^+ ions during the sonication. The CuO formed functions as an oxidant to initiate the polymerization of aniline,[29] resulting in the formation of polyaniline and its reduction to Cu_2O. High-energy conditions are created during ultrasonic irradiation of powders in liquids.[30] Acoustic cavitation in liquids generates implosive bubble collapse, microjets, and associated shock waves. The shock waves so generated can cause small particles to collide into one another with great force, producing an interparticles melt. The products CuO and Cu_2O recombine to form Cu_4O_3. The above reactions 1−3 take place in the interfacial region. However, to confirm this mechanism, we need to do some more studies, which are in progress.

Conclusions

Nanocrystalline Cu_4O_3 particles embedded in polyaniline have been prepared from copper(II) acetate and aniline in water by the sonochemical method. Using this method, we have also prepared Fe_3O_4 and Cu_2O in polyaniline. This sonochemical method can be used for obtaining novel metal oxides in a polyaniline matrix.

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