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Sonochemical synthesis of amorphous Cu and nanocrystalline Cu_2O embedded in a polyaniline matrix

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Composite materials containing amorphous Cu nanoparticles and nanocrystalline Cu_2O embedded in polyaniline matrices have been prepared by a sonochemical method. These composite materials were obtained from the sonication of copper(II) acetate when aniline or 1% v/v aniline–water was used as solvent. Mechanisms for the formation of these products are proposed and discussed. The physical and thermal properties of the as-prepared composite materials are presented. A band gap of 2.61 eV is estimated from optical measurements for the as-prepared Cu_2O in polyaniline.

1 Introduction

The use of a polymer matrix as an environment for *in situ* nanoparticle growth synergistically combines the properties of both the host polymer matrix and the discrete nanoparticles formed therein. Nanoparticles of metals and metal oxides embedded in polymer matrices have attracted increasing interest because of the unique properties displayed by these materials. Due to the nanometer size of these particles, their physicochemical characteristics differ significantly from those of molecular and bulk materials.[1,2] Such composite materials are expected to have novel electrical, optical, magnetic, catalytic, and mechanical properties.[3–7] Many techniques have been exploited to prepare the metal– or metal oxide–polymer nanocomposites.[8–14] Most recently copper–polymer composite materials were prepared by Haung and Yang[15] and Lyons and co-workers[16] by two different methods: one by *in situ* reduction within a Cu^{2+} poly(itaconic acid-*co*-acrylic acid) complex, and the other by thermal decomposition of a copper formate–poly(2-vinylpyridine) complex, respectively. Copper, cobalt, or nickel particles embedded in polyaniline matrices were prepared by Deschamps *et al.*[17] by the polyol process in which reduction of a precursor and polymerization are achieved in one step at 180 °C. Recently, Matijevic and co-workers[18] reported the preparation of uniform spherical CuO particles coated with polyaniline by mixing CuO powder, aniline, and poly(vinyl alcohol) (a stabilizing agent) in ethanolic solution in a sealed reaction vessel and heating at 100 °C for 48 h. Casella *et al.*[19] prepared an electrode composed of copper microparticles dispersed in a polyaniline film by an electrochemical method. Casella claims that the microparticles of copper entrapped within the polymer skeleton exhibit powerful catalytic activity towards the electro-oxidation of scarcely electroactive compounds such as carbohydrates and amino acids. This electrode can be used as an amperometric sensor for carbohydrates and amino acids.

The application of high-intensity ultrasound radiation in polymer chemistry has been an active area of research.[20–24] The main advantages of ultrasound polymerization are the absence of external chemical initiators, the low temperature range in which the reaction takes place, and the possibility of bulk polymerization.

The propagation of ultrasound waves through a fluid causes the formation of cavitation bubbles.[25] The collapse of these bubbles, described as an adiabatic implosion in the hot-spot theory, is the origin of extreme local conditions: high temperature (5000 K) and high pressure (1000 atm).[25] The cooling rates obtained following the collapse are greater than 10^{10} K s^{-1}.[26,27] These high cooling rates have been utilized by Suslick and co-workers in the sonication of iron pentacarbonyl as a neat liquid or in solution[26,27] to prepare amorphous iron nanoparticles. We prepared amorphous Ni[28] and amorphous Cr_2O_3 and Mn_2O_3,[29] all with nanometer-sized particles.

Polymer synthesis using ultrasound has been reported previously.[30,31] Kruus and co-workers studied the polymerization of nitrobenzene[32] and methylmethacrylate[33,34] as well as other monomers.[34] We have successfully prepared metal–polymer composite materials[35,36] using ultrasound radiation.

In the present investigation we have combined the two sonochemical methods — polymerization of aniline and creation of amorphous Cu nanoparticles and nanocrystalline Cu_2O particles — to obtain the composites of both amorphous Cu nanoparticles and nanocrystalline Cu_2O with polyaniline. The characterization and properties of these composite materials is reported.

2 Experimental

The experimental procedure used for the preparation of the amorphous Cu–polyaniline and nanocrystalline Cu_2O–polyaniline composites is as follows: 1 g of copper(II) acetate monohydrate (Aldrich chemicals) in 100 mL of aniline (Aldrich chemicals) or 1 g of copper(II) acetate in 100 mL of 1% v/v aniline–deoxygenated doubly distilled water were irradiated with a high-intensity ultrasonic horn (Ti-horn, 20 kHz, 100 W cm^{-2}) under 1.5 atm of argon at 10 °C for 3 h. The products obtained were washed thoroughly with absolute ethanol in an inert glove box ($O_2 < 2$ ppm) and vacuum dried at room temperature overnight.

The XRD measurements were carried out using a Bruker, D8, instrument. Transmission electron microscopy (TEM) examinations of the samples were carried out with a JEOL-JEM 100SX microscope. The powdered samples were dispersed in ethanol by sonication and dropped onto a conventional carbon-coated copper grid. FT-IR spectra were recorded on a

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Nicolet Impact 410 infrared spectrophotometer from KBr pellets. The TGA measurements were carried out under nitrogen on a Mettler Toleso TGA/SDTA 851 instrument at a heating rate of 10 °C min^{-1}. Absorption spectra were recorded on a Hewlett-Packard 8453 UV-visible spectrophotometer. The solutions were prepared from 5 mg of as-prepared powdered samples dispersed in 100 mL of ethanol by sonication. No precipitate was observed. Diffuse reflection spectroscopy (DRS) measurements were recorded on a Varian Cary-500 spectrophotometer equipped with an integrated sphere. Spectra were recorded at room temperature.

3 Results and discussion

The sonication of Cu(II) acetate in the presence of aniline leads to the formation of amorphous copper nanoparticles embedded in polyaniline. In contrast, the sonication of copper(II) acetate in an aqueous solution of aniline produces nanocrystalline Cu_2O particles embedded in polyaniline. FT-IR spectra of the as-prepared composite materials are shown in Fig. 1. The characteristic peaks of polyaniline at ~1590 cm^{-1} and 1497 cm^{-1}, which represent the C=C stretching vibrations of quinoid and benzenoid rings, respectively,[37,38] are detected. We also observe a peak at ~1299 cm^{-1}, which is attributed to C–N stretching of the 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. Instead of multiple peaks at 1160 cm^{-1}, as in the case of partially crystalline polyaniline, we observe a single peak, implying an amorphous nature for the polyaniline. This is consistent with the XRD and TEM results. In Fig. 1(b) we also observe a major peak at ~625 cm^{-1}, assigned to Cu_2O.[39]

Fig. 2 depicts the powder XRD patterns of: (a) as-prepared Cu–polyaniline composite, (b) as-prepared Cu–polyaniline composite heated at 300 °C for 6 h under a flow of pure nitrogen, and (c) as-prepared Cu_2O–polyaniline composite. Fig. 2(a) clearly indicates that the as-prepared Cu–polyaniline composite is amorphous in nature, no trace of a crystalline phase was detected. Figs. 2(b) and (c) indicate that the composite materials are crystalline with structures matching those of metallic copper and copper(I) oxide, JCPDS card nos. 4-836 and 34-1354, respectively. The XRD study demonstrates the amorphous nature of the as-prepared Cu–polyaniline and, on the other hand, the crystallinity of the as-prepared Cu_2O–polyaniline. The particle sizes, calculated by using the Debye–Scherrer formula,[40] are 8 nm and 20 nm for as-prepared Cu_2O–polyaniline and heated Cu–polyaniline composite materials, respectively.

In Fig. 3 we present the TEM pictures of: (a) the as-prepared Cu–polyaniline composite material, and (b) the as-prepared Cu_2O–polyaniline composite material. Figs. 3(a) and (b), which present the two as-prepared composite materials, show the excellent dispersion of Cu and Cu_2O, respectively, in the polyaniline matrix. Fig. 3(a) does not provide any evidence for the crystalline nature of the copper particles whereas Fig. 3(b) clearly shows that the product of the aqueous aniline reaction is a crystalline Cu_2O product coated with polyaniline. The selected area electron diffraction (SAED) patterns of annular regions of as-prepared Cu_2O–polyaniline show that the composite material contains crystalline particles and that the lattice spacing matches that of Cu_2O, whereas a diffuse ring pattern is detected for the as-prepared Cu–polyaniline indicating its amorphous nature. These results also match the XRD results quite closely. The particle sizes of Cu and Cu_2O in the polyaniline are about 4–10 nm and 5–13 nm, respectively. The sizes are in reasonable agreement with the XRD results for Cu_2O–polyaniline.

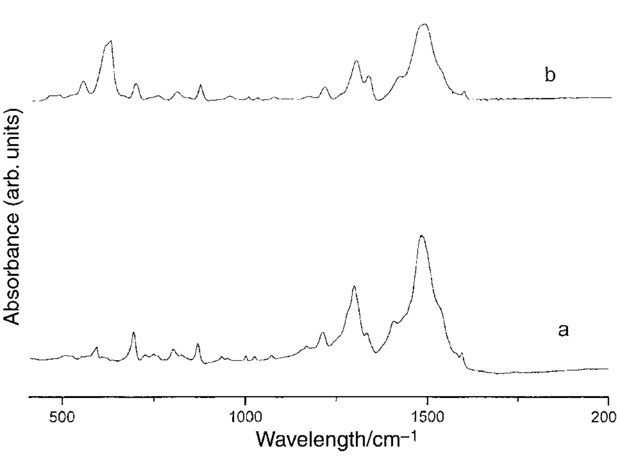

Fig. 1 FT-IR spectrum of (a) as-prepared Cu–polyaniline and (b) as-prepared Cu_2O–polyaniline composites.

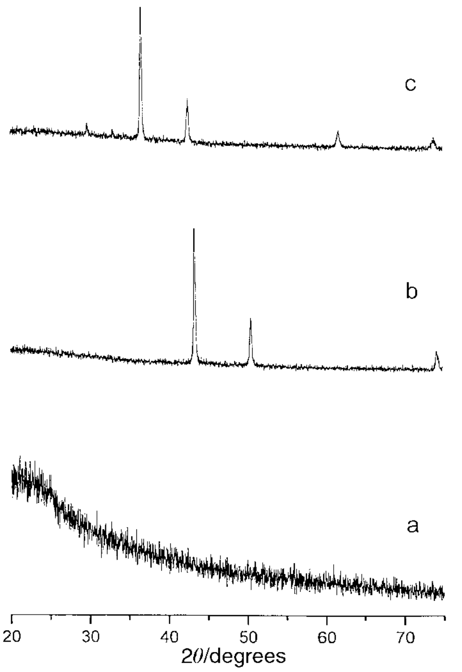

Fig. 2 Powder X-ray diffraction patterns of (a) as-prepared Cu–polyaniline composite (b) composite material (a) after heating at 300 °C for 6 h under a flow of pure nitrogen and (c) as-prepared Cu_2O–polyaniline composite.

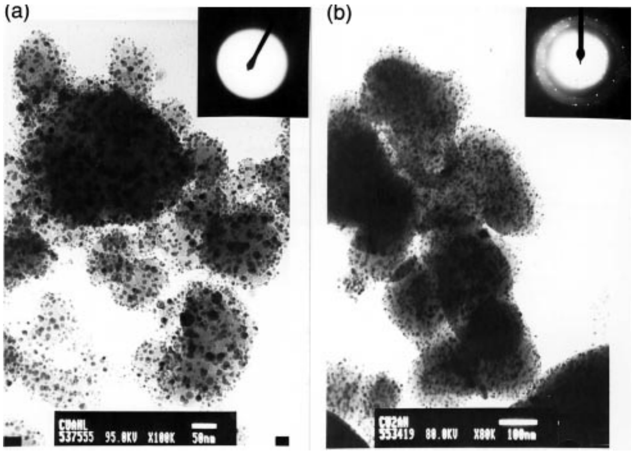

Fig. 3 Transmission electron micrographs of (a) as-prepared Cu–polyaniline. Inset: electron diffraction of the as-prepared Cu–polyaniline, and (b) as-prepared Cu_2O–polyaniline. Inset: electron diffraction of the as-prepared Cu_2O–polyaniline.

We have carried out TGA measurements to determine the

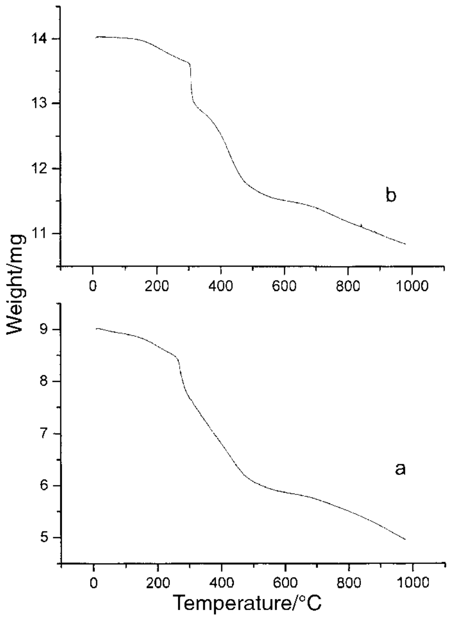

Fig. 4 TGA curves for (a) as-prepared Cu–polyaniline and (b) as-prepared Cu_2O–polyaniline.

thermal stability of the as-prepared composite materials. Fig. 4 depicts the TGA curves of: (a) as-prepared Cu–polyaniline composite and (b) as-prepared Cu_2O–polyaniline composite. Chemically synthesized polyaniline is stable up to 400 °C,[41] while the as-prepared composites of Cu–polyaniline and Cu_2O–polyaniline are stable only up to temperatures of 285 °C and 308 °C, respectively. The reason for this could be that the perturbation of the Cu and Cu_2O affects the three-dimensional structure of the polymer. 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 of the decomposition temperature.

Fig. 5 displays the absorption spectrum of the as-prepared Cu–polyaniline composite dispersed in ethanol. It shows only one broad peak, at ~520 nm, which is attributed to polyaniline.[38,42] We have not observed an absorption peak at 570 nm due to the plasma oscillation characteristic of the Cu surface. The absorption spectra of colloidal copper particles of various sizes have been described and simulated.[41,43] It has been shown that the progressive appearance of the 570 nm plasmon peak occurs with an increase in size of the copper clusters and that the copper particles with a diameter below 4 nm exhibit a strong broadening of the plasmon band. Since copper particles obtained in this work have an average particle size larger than 4 nm, the lack of a plasmon peak could not result from the broadening of the band due to the size effect. On the other hand, it has been demonstrated that the plasmon absorption band of metals such as Ag and Cu is very strongly influenced by chemical modification of the surface.[44,45] In our case, strong coating of polyaniline on amorphous copper may be the reason why we do not observe the 570 nm plasmon peak for the copper particles; however a detailed investigation is needed to confirm this possibility.

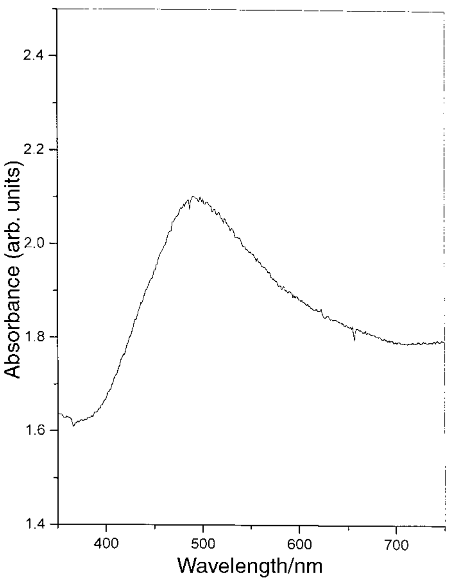

Fig. 5 Absorption spectrum of as-prepared Cu–polyaniline dispersed in ethanol.

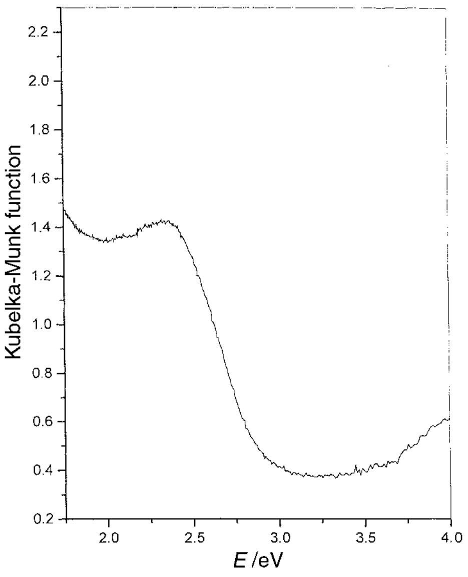

Fig. 6 Kubelka–Munk remission function *versus* eV of Cu_2O–polyaniline.

We have measured the optical diffusion reflection spectra of the Cu_2O–polyaniline powder in order to resolve the excitonic or interband (valence–conduction band) transitions of Cu_2O, which allow us to calculate the band gap. Fig. 6 depicts the optical diffuse reflection spectrum of the Cu_2O–polyaniline powder. The optical band gap E_g was estimated from the DRS spectra. The spectrum in Fig. 6 shows a plot of the Kubelka–Munk remission function[46,47] (converted from the diffuse reflection values using the spectrophotometer software) *vs.* energy. >From the spectrum, we calculate the band gap of the Cu_2O–polyaniline composite to be 2.61 eV. The value of the band gap energy is larger than that of the reported value for the bulk Cu_2O (2.17 eV).[48] Generally, the optical properties of nano-sized particles are very different from those of bulk materials. The increase in the band gap may be indicative of the size quantization, which is usually observed for nanoparticles.[49,50]

Mechanism for the formation of amorphous copper nanoparticles or nanocrystalline copper(I) oxide particles embedded in polyaniline

The chemical reactions reported to be driven by intense ultrasonic waves that are strong enough to produce cavitation are: oxidation, reduction, dissolution, decomposition, and hydrolysis.[23,51–53] Other reactions, such as polymerization, have also been reported to be induced by ultrasound. These reactions can occur in three different regions[54,55] surrounding the collapse of a bubble in aqueous media. These are: (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 $H^\bullet$ and $OH^\bullet$ radicals; (b) the interfacial

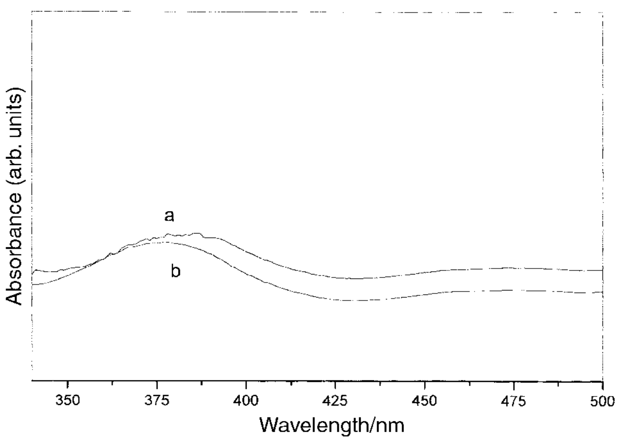

Fig. 7 Absorption spectra of (a) 1 g of copper(II) acetate in 100 mL of aniline and (b) 1 g of copper(II) acetate in 1% v/v aniline–water immediately prior to sonication.

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. The third region, (c), is the bulk of the solution, which is at ambient temperatures and this is where the reaction between reactant molecules and surviving OH• or H• radicals can still take place. To understand the mechanism better, we have carried out UV-Visible measurements for both the reaction mixtures just before the sonication (see Fig. 7). The absorption peaks observed at 380 nm for both the reaction mixtures are assigned to the copper(II) complex of aniline.[38] The small increase in the absorbance of the Cu(II)–aniline complex compared to the Cu(II)–aniline–water complex may be due to increasing the ratio of aniline to copper(II). Similar results were observed earlier.[38] On the basis of UV-Visible results we are proposing that the first stage of the reaction mechanism involves the formation of the copper complex of aniline (reaction 1). In our case, among the three possible sonochemical regions mentioned above [(a), (b) and (c)], it appears that the sonochemical reaction occurs within the interfacial region. The copper complex of aniline is ionic, and its vapor pressure is low so that the complex vapor does not exist in region (a). The temperature generated during the collapse of a gas-filled cavity is higher in the case of low vapor pressure solvents.[54] The vapor pressure of aniline is lower than that of 1% aniline–water, hence the temperature at the interfacial region of interest is also higher in the case of aniline than in 1% aniline–water, yielding amorphous materials as a result of the very high quenching rates experienced by the products. Therefore we obtain the amorphous Cu embedded in polyaniline when aniline is used as solvent. In the present case it is reasonable to assume that the reaction may not take place in region (c). The reason for this could be that the ambient temperatures and very low concentrations of H_2O_2 may not be sufficient to yield the products.

The likely reaction steps for the formation of amorphous Cu–polyaniline are as follows:

$$C_6H_5NH_2 + Cu^{2+} \rightarrow C_6H_5NH_2\cdots Cu^{2+} \qquad (1)$$

$$C_6H_5NH_2\cdots Cu^{2+} \rightarrow (\text{-}C_6H5NH\text{-})_n + Cu \qquad (2)$$

$$H_2O \xrightarrow{)))))} H^{\cdot} + OH^{\cdot} \qquad (3)$$

$$2H^{\cdot}/2OH^{\cdot} \rightarrow H_2/H_2O_2/H_2O \qquad (4)$$

$$Cu^0 + H_2O_2 \rightarrow Cu_2O + H_2O \qquad (5)$$

We obtained the nanocrystalline Cu_2O embedded in polyaniline when 1% aniline–water was used as solvent. A possible pathway for the formation of Cu_2O could be due to the partial oxidation of Cu^0 by the secondary species formed by the recombination of the H• and OH• radicals. In the absence of any additives or scavengers the H• and OH• radicals readily recombine to give the products as shown in eqn. (4).[56]

4 Conclusions

Uniformly dispersed amorphous nanoparticles of copper and nanocrystalline Cu_2O particles embedded in a polyaniline matrix have been obtained by means of ultrasound irradiation. This technique can also be applied to the preparation of different metals or metal oxides embedded in polyaniline matrices.

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