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Ultrasound-Assisted Synthesis of CuO Nanorods in a Neat Room-Temperature Ionic Liquid

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CuO nanorods were prepared via ultrasound-assisted synthesis in the room temperature ionic liquid (RTIL) 1-butyl-3-methylimidazoliumbis(trifluoromethylsulfonyl)imide [C_4mim]-[Tf_2N] as a reaction medium. The structure and morphology of CuO nanorods were characterized with X-ray powder diffraction (XRD), transmission electron microscopy (TEM), energy-dispersive X-ray analysis (EDX), X-ray photoelectron spectroscopy (XPS), vibrational and UV/Vis absorption spectroscopy. The synthesized CuO nanocrystals are of rod like shape with lengths from 30 to 100 nm and diameters of about 10 nm. Quantum size effects were observed as the bandgap of the CuO nanorods was determined to 2.41 eV from UV/Vis absorption measurements, which is significantly larger than the bulk value.

Introduction

Ionic liquids (ILs) are an unconventional class of solvents, which are actually molten salts at relatively low temperatures (room temperature and below), consisting entirely of ions. By the respective cation-anion combination many of their physical and chemical properties can be tuned. Compared to widely used volatile organic compounds (VOCs), most ionic liquids have practically no measurable vapour pressure and possess a comparatively high chemical stability at high temperatures. In addition, ionic liquids offer many other advantageous properties, such as a wide electrochemical stability window and good conductivities, low toxicity, and unusual capabilities to dissolve solutes. Because of that they are obtaining growing attention as alternative and sometimes green solvents in the field of organic synthesis, catalysis, separation and synthesis of inorganic materials.[1–5] Nanocrystals of metal oxides are of widespread interest because of their properties, which deviate from those of the bulk material, such as large surface area-to-volume ratio, increased chemical reactivity, special electronic properties and exceptional optical properties.[6–8] Compared to other transition metal oxides the preparation of copper monoxide at the nanoscale has received astonishingly little attention. However, CuO is a *p*-type semiconductor with a narrow bandgap, the size of the band-gap being highly dependent on the morphology and the particle size of the material.[9] CuO has become important for high-temperature superconductors and antiferromagnetic semiconductors.[10] Other applications include gas sensors,[11] magnetic storage media,[12] solar cells,[13] and as a heterogeneous catalyst.[14] Nanoparticles of CuO have been made by various synthetic routes, amongst them low-temperature solid-state synthesis,[15] thermal decomposition,[16] sol-gel methods,[17] microwave irradiation,[18] a co-implantation technique,[19] hydrothermal[20] and electrochemical routes.[21] Meanwhile, the mechanism of formation via $Cu(OH)_2$ has been established quite well.[22] CuO nanoplatelets have been obtained from a mixture of water and the ionic liquid ([C_4mim]Cl) upon heating the reagents in an autoclave at 140 °C for 20 h.[23] In the past years, sonochemical has developed into a powerful method for the preparation of nanoparticles[24] and has been used for the preparation of CuO nanoparticles.[25] The sonochemical preparation of nanocrystalline CuO in PVA [poly(vinylalcohol)] and the effect of PVA on the growth of CuO has been investigated extensively.[25b] When a liquid is subjected to ultrasound bubbles are formed, which grow and implode. This leads locally to extremely high temperatures, pressures and cooling rates.[26] Recently, by combining advantages of both room-temperature ionic liquids (RTILs) and ultrasound synthesis we have developed an easy way to access ZnO nanorods.[27] Here we report a highly selective, facile, seedless and template-free (besides the ionic liquid itself) route for the production of CuO nanorods from copper(II) acetate hydrate by ultrasound-assisted synthesis in the RTIL [C_4mim][Tf_2N].

Results and Discussion

Figure 1 gives the X-ray diffraction (XRD) pattern of the synthesized CuO nanorods. All reflection

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peaks can be indexed to monoclinic CuO (JCPDS card no. 45-0937). No peaks of crystalline impurities can be detected.

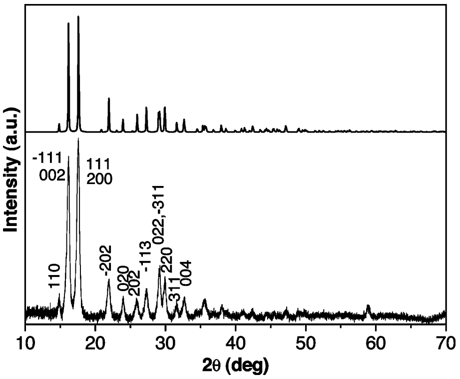

Figure 1. XRD pattern of the synthesized CuO nanoparticles (bottom), pattern simulated from single-crystal data (top).

TEM images of a typical CuO sample are shown in Figure 2 (top). The TEM images reveal that the reaction product consist of rodlike particles with 10 nm in diameter and 30–100 nm in length. The selected area electron diffraction (SAED) pattern in Figure 2, bottom, shows that the particles are well crystallized and the diffraction rings can be indexed to the reflections of monoclinic CuO.

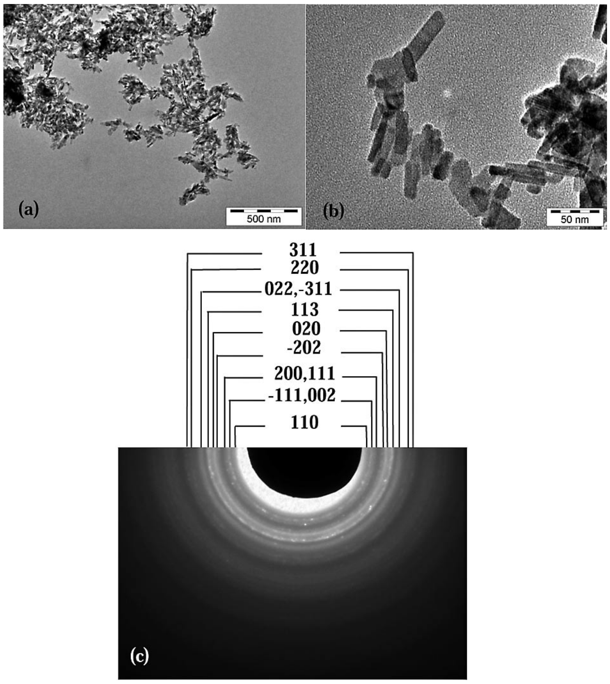

Figure 2. TEM (top) and selected area electron diffraction pattern (bottom) of the as-prepared CuO nanoparticles.

The EDX spectrum of CuO nanorods (Figure 3) indicates that the sample contains only Cu and O. The presence of Au and C signals arises from the TEM grid.

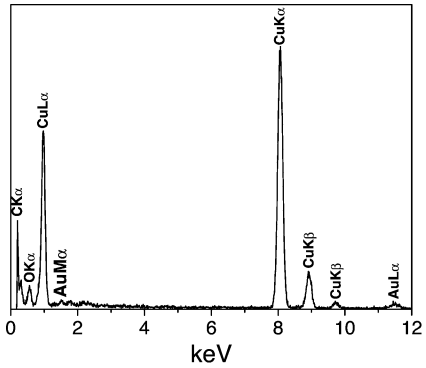

Figure 3. EDX spectrum of CuO nanorods.

The results of XPS (X-ray photon electron spectroscopy) measurements on a representative CuO nanorod sample are shown in Figure 4. The binding energies in the XPS spectra are calibrated against the C1s signal (284.8 eV). This can be done, as the sample holder is coated with carbon. The strong peak at about 934.1 eV is attributed to $Cu2p_{3/2}$ (Figure 4, right). The O1s signal (Figure 4, left) at about 530.5 eV is related to lattice oxygen in the CuO. The $Cu2p_{3/2}$ level in bulk CuO is observed at 933.6 eV, the O1s signal at 529.6 eV.[28] No obvious peaks for other elements or impurities can be observed confirming the EDX and XRD results.

Figure 5 shows the IR spectrum of the as-prepared CuO nanorods. The CuO nanorod sample shows absorption maxima at 420, 484 and 597 cm^{-1} which are due to Cu–O stretching modes.[29,23] The peak at 1080 cm^{-1} belongs to overtones.For bulk CuO these frequencies are found at 444, 515 and 586 cm^{-1}.[30] The blue-shift of the vibrational frequencies can be attributed to the small size of the prepared nanorods as observed previously for other samples.[31]

The optical absorption properties of CuO nanorods have been studied in order to estimate the bandgap of the obtained material. Figure 6 shows the UV/Vis absorption spectrum of CuO nanorods dispersed in absolute ethanol. The spectrum shows a broad absorption peak at about 380 nm. By equating E_g with the wavelength at which the absorption is half of the excitonic peak[32] the bandgap of the CuO nanorods is estimated to be 2.41 eV. This value is significantly larger than the reported value for the bulk material (E_g = 1.21 eV)[33] which is indicative of quantum size effects.[34] The bandgap of CuO with various morphology and particle sizes has been determined. Values such as 2.36 eV for CuO rodlike,[20] 2.43 eV for CuO spherical nanoparticles,[18] and 3.02 eV for CuO nanoplatelets[37] have been reported, all of them larger than the bulk value.

Nitrogen adsorption-desorption measurements of the products were performed to determine the specific surface area of the CuO nanorods. The data were analyzed according to the Brunauer–Emmet–Teller (BET) equation. A comparison with the value of bulk CuO (4.07 m^2/g)[36] shows that the resulting specific surface area of a typical CuO nanorod sample is astonishingly high with 61.4 m^2/g.

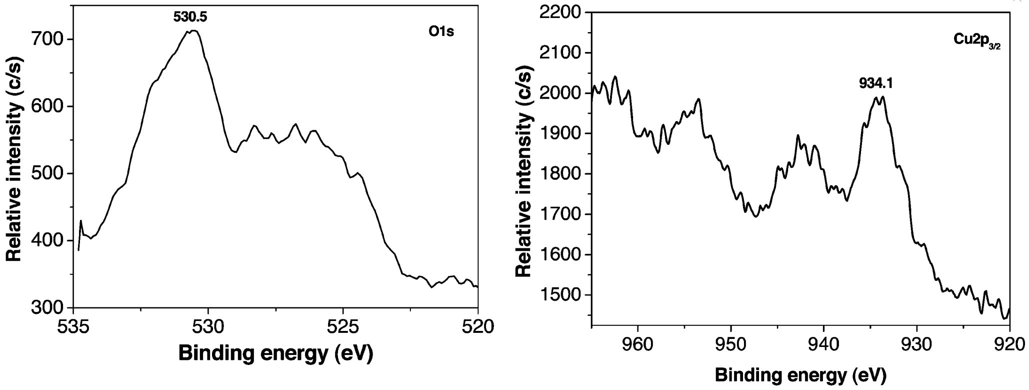

Figure 4. XPS spectrum of CuO nanorods. O_{1s} region (left), Cu_{2p} region (right).

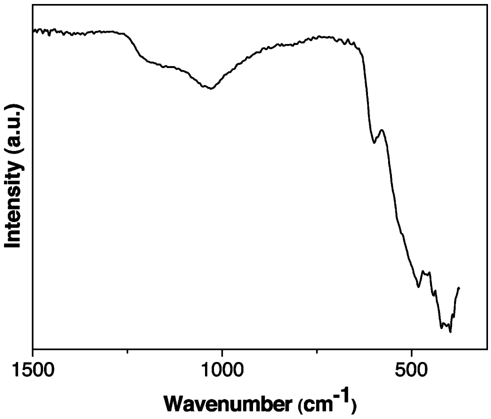

Figure 5. IR spectrum of the CuO nanorods.

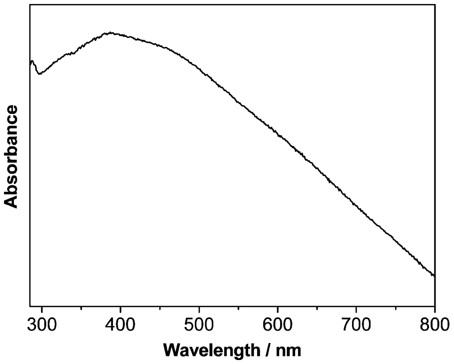

Figure 6. UV/Vis spectrum of the CuO nanorods.

Conclusions

In conclusion, CuO nanorods have been prepared by an ultrasound-assisted synthesis route at room temperature using an ionic liquid as solvent without employing further organic solvents or water. This method is simple, effective, mild, templateless (aside form the reaction medium itself), and surfactant-free. The as-obtained product is characterized by an uniform particle morphology and particle size, has a high surface area and at the same time a noticeable enlarged band-gap. As demonstrated by this successful example, the reported synthesis method may also be extended to prepare other oxidic nanomaterials.

Experimental Section

General: All reagents employed were commercially available and directly used without further purification. [C_4mim][Tf_2N] was synthesized according to the literature.[35] The synthesis of CuO nanoparticles has been carried out as follows: 100 mg of finely powdered sodium hydroxide (98% purity, from J. T. Baker) was added to a mixture of 200 mg of $Cu(CH_3COO)_2\cdot H_2O$ (98%, from Aldrich) in 1 mL [C_4mim][Tf_2N]. The reaction mixture was then irradiated in a glass tube sealed with a screw cap in an ultrasound bath (USC200T, VWR International, frequency 45 kHz, power 60 W) at room temperature in ambient air for 24 h. The products obtained were washed thoroughly with distilled water and finally with absolute ethanol, then dried in a drying oven at 90 °C for 4 h.

XRD measurements were carried out on a Huber G670 diffractometer (Huber, Rimsting, Germany) with with Mo-K_α radiation (λ = 0.07107 nm). Transmission electron microscopy (TEM) images, selected area electron diffraction patterns (SAED), and were obtained by using a Hitachi H-8100 working at 200 kV. The CuO samples for TEM measurements were prepared by suspending the dried sample in ethanol by treating it in an ultrasonic bath for 15 min. A drop of this slurry was deposited on a carbon film supported on a gold grid. The X-ray photoelectron spectra (XPS) were collected on a Leybold RH 63 setup. The UV/Vis absorption spectra were recorded with a Cary 50 scanning photospectrometer. Vibrational spectra were measured on a Bruker-Alpha IR spectrometer equipped with a diamond ATR unit. The nitrogen adsorption isotherme was measured at a Quantachrome Autosorb-1 MP surface analyzer.

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