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

Tarek Alammar,[a] Alexander Birkner,[b] and Anja-Verena Mudring*,[a]

Keywords: Copper oxide / Ionic liquids / Inorganic materials synthesis / Nanoparticles

CuO nanorods were prepared via ultrasound-assisted synthesis in the room temperature ionic liquid (RTIL) 1-butyl-3-methylimidazoliumbis(trifluoromethylsulfonyl)imide \([\text{C}_4\text{mim}]-[\text{Tf}_2\text{N}]\) 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\(_4\)mim][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(vinyl-alcohol)] 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 \([\text{C}_4\text{mim}][\text{Tf}_2\text{N}]\).

Results and Discussion

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

---

[a] Anorganische Chemie I – Festkörperchemie und Materialien, Fakultät für Chemie und Biochemie, Ruhr-Universität Bochum, 44780 Bochum, Germany
Fax: +49-234-32-14951
E-mail: anja.mudring@rub.de
[b] Physikalische Chemie I, Fakultät für Chemie und Biochemie, Ruhr-Universität Bochum, 44780 Bochum, Germany