



One-step synthesis of nanocrystalline ZnO via cryomilling

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ARTICLE INFO

Article history:

Received 17 May 2012

Received in revised form 14 October 2012

Accepted 20 October 2012

Available online 27 October 2012

Keywords:

Nanoparticle

ZnO

Cryomilling

Semiconductor

Nitrogen

ABSTRACT

In this work, the ZnO spherical nanoparticles with a diameter in the range of 10–30 nm have been prepared via mechanochemical oxidation of metallic Zn powders treated in a vibratory ball mill in the presence of air and liquid nitrogen. The as-prepared nanocrystals were characterized by XRD, HR-TEM, FTIR, XPS, and UV–vis spectroscopy. The results show that metallic zinc powder is completely converted to nanocrystalline ZnO within 48 h of cryomilling. The XPS analysis confirms the presence of incorporated nitrogen as well as Zn(OH)₂ and carbonate species formed on the reactive structurally-disordered surface shell of the as-prepared nanoparticles. Compared with the pure ZnO, the light absorption by the as-prepared ZnO nanocrystals was shifted to longer wavelengths.

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1. Introduction

Wide band gap semiconductors are extensively studied due to their potential applications in optoelectronic and microelectronic devices. Zinc oxide (ZnO) is one of the most important semiconductors with a wide and direct band gap of 3.37 eV at room temperature, high transparency (>80%) in the visible wavelength region and high binding excitation energy of 60 meV [1]. Especially ZnO in a nanocrystalline state has attracted great interest because of its unique and fascinating applications in antireflection coatings, transparent electrodes in solar cells, UV light emitters, electron luminescent devices, diode lasers, photodetectors, varistors, piezoelectric devices, spin-electronics, surface acoustic wave propagators, antibacterial agents, photonic materials and gas sensing [2–4].

Among the many types of nanocrystalline materials' preparation techniques, the nonconventional mechanochemical synthesis has been recognized as a powerful route to novel, high-performance and low-cost nanomaterials. Great efforts have been devoted to mechanochemical synthesis of pure and doped ZnO nanocrystals. Zandi et al. [5] synthesized nanocrystalline ZnO by milling of zinc acetate and citric acid followed by calcination. In order to avoid high temperature treatment, Ozcan et al. [6] used reactive wet ball milling of metallic zinc powder in distilled water. On the other hand, Glushenkov et al. [7] performed reactive ball milling of zinc powder under oxygen overpressure. In contrast

to the pure nanocrystalline ZnO, doping by non-metal elements can exhibit improved electrical, optical and catalytic properties [8]. N-doped ZnO nanocrystals were prepared by co-milling of the ZnO and urea mixture, followed by calcination at 400 °C [9]. Although all of these mechanochemical processes led to the formation of nanocrystalline ZnO, the involvement of cryomilling can result in more uniform particle/crystallite size distribution [10].

In the present work, we report on the easy to handle one-step mechanosynthesis of ZnO nanopowders by high-energy cryomilling of metallic Zn in the presence of atmospheric air and liquid nitrogen. To the best of our knowledge, the heterogeneous mechanochemical reaction, involving all three aggregation states [solid (Zn), liquid (N₂), gas (O₂)] and leading to nanocrystalline ZnO, has not been reported yet. Note that cryomilling technique used in the present work possesses several advantages in comparison to a conventional room-temperature ball milling, including relatively high strain rates, large cumulative strains, uniform particle size distribution and the relatively low level of milling energy [10–14]. Moreover, the milling time required to reach the final grain size was found to be significantly shorter for cryomilling than that for the conventional milling performed at ambient temperature, which was attributed to the suppression of the recovery effect at cryogenic temperatures [11–14].

2. Experimental

A 5 g of Zn powder (–400 mesh) was milled for various times (up to 48 h) in a Pulverisette 0 vibratory ball mill (Fritsch, Germany) at a frequency of 350 Hz. A grinding chamber (150 cm³ in volume) and a ball

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(50 mm in diameter) made of stainless steel were used. The ball-to-powder weight ratio was 20:1. Milling experiments were performed in the presence of atmospheric oxygen and liquid nitrogen in open milling chamber; in every 20 min, 100 ml of liquid nitrogen was added to the milled powder.

The X-ray diffraction (XRD) patterns were collected using a Phillips PW 1820 (Netherlands) diffractometer with Cu K_{α} radiation. XRD data were analyzed using the STOE software utilizing the JCPDS PDF database. The FTIR and UV spectra were recorded using an Avatar 330 spectrophotometer (Thermo-Nicolet, USA) and an UV/VIS spectrometer HeXos GAMMA (ThermoSpectronic, USA), respectively.

The morphology of the as-synthesized powders and the sizes of individual crystallites were studied using a high-resolution transmission electron microscope (HR-TEM) of the type Jeol JEM-2100 F (Japan). Prior to HR-TEM investigations, powders were crushed in mortar, dispersed in ethanol and fixed on copper supported carbon film.

X-ray photoelectron spectroscopic (XPS) measurements were performed on an ESCALAB-MkII (VG Scientific, UK) electron spectrometer with non-monochromatized Al K_{α} radiation (excitation energy $h\nu = 1486.6$ eV), operating at 10 kV and 20 mA. The residual pressure inside the analysis chamber was below 5×10^{-9} Torr. The binding energies (BE) were calibrated by taking carbon C 1s peak (285 eV) as reference. The accuracy for the estimation of BE was ± 0.1 eV.

3. Results and discussion

The high-energy milling of the Zn powder in the presence of atmospheric oxygen and liquid nitrogen initiates a heterogeneous mechanochemical reaction leading to the oxidation of metallic zinc powder (see Fig. 1). After 48 h of milling, the diffraction peaks corresponding to metallic Zn (JCPDS 4-831) disappeared completely, indicating the full conversion of the mechanochemical oxidation reaction. In the final stage of the mechanochemical processing, all XRD peaks detected above background can be attributed to the zincite phase of ZnO (JCPDS 36-1451).

The relatively broad shape of diffraction peaks belonging to the mechano-synthesized zincite phase reflects its nanoscale nature. The average crystallite size of the nanomaterial, calculated from the XRD data, was found to be 14.6 nm. This correlates with the particle size estimated by HR-TEM (see Fig. 2). As it is shown in Fig. 2b, the mechano-synthesized nanoparticles are nearly spherical with a relatively narrow size distribution in the range of 10–30 nm. Additionally, HR-TEM revealed a nonuniform structure of mechano-synthesized nanoparticles, consisting of an ordered core surrounded by a disordered surface shell region (Fig. 2a and b). The selected area electron diffraction (SEAD) pattern, shown in Fig. 2c, depicts well-defined rings for nanocrystalline zincite phase.

The FT-IR spectrum of the mechano-synthesized nanomaterial is shown in Fig. 3. The peaks at 500 cm^{-1} and 450 cm^{-1} are characteristic for stretching vibrations of Zn–O bonds in ZnO [15]. In contrast, no peaks belonging to the Zn–O bond were observed in Zn powder before cryomilling (figure not shown). Thus we consider that possible surface oxidation of Zn starting powder as well as metallic Zn residue in the final product is irrelevant and under the detection limit of XRD and FTIR spectroscopy, respectively. The broad absorption peaks at 3427 cm^{-1} and 1638 cm^{-1} can be attributed to the characteristic absorption of hydroxyl groups. Stretching vibrations of adsorbed CO_3^{2-} and of created species of $(\text{HCO}_3)^-$ are seen at 1410 cm^{-1} and 1370 cm^{-1} , respectively. It is difficult to estimate the asymmetric vibrations of CO_3^{2-} and $(\text{HCO}_3)^-$ in the range of $1600\text{--}1640\text{ cm}^{-1}$ due to their overlapping with the vibration modes of hydroxyl groups. Note that carbon dioxide may also be present in the disordered surface shell of nanoparticles as CO_3^{2-} ions and CO_2 molecules and can be removed from ZnO by subsequent annealing [16].

A wide survey scan of XPS spectrum of the mechano-synthesized material taken in the range 0–1150 eV is shown in Fig. 4a. The higher

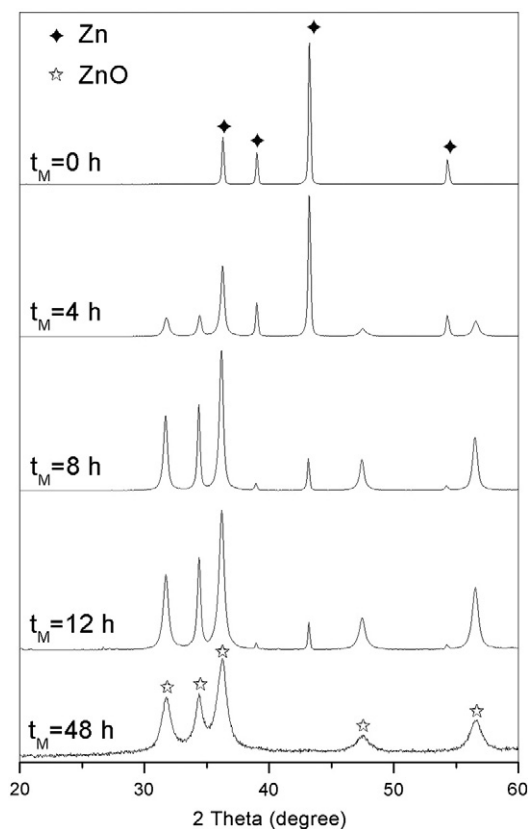


Fig. 1. XRD patterns illustrating the mechanochemical oxidation of metallic zinc powder during its high-energy cryomilling in the presence of atmospheric air and liquid nitrogen. The milling times (t_M) are shown in the figure.

resolution scanning XPS spectrum of the material, presented in Fig. 4b, shows two peaks at binding energies of 1021.9 and 1044.8 eV, which can be identified as Zn $2p_{3/2}$ and Zn $2p_{1/2}$ lines for ZnO, respectively, indicating that Zn is in the 2+ state [17–20]. The O 1s photoelectron spectrum of the sample can be fitted into four peaks (Fig. 4c). In accordance with previous work published on this topic, the peak located at 530.3 eV belongs to the lattice oxygen (Zn–O bonding) in ZnO [21–24]. The peak at 531.4 eV can be ascribed to the OH^- group presented in $\text{Zn}(\text{OH})_2$ [23,25] and $(\text{HCO}_3)^-$, respectively. Note that these phases could be formed by absorbing atmospheric moisture [26]. The peak at 532.2 eV can be ascribed to the presence of CO_3^{2-} , which could be formed by trapping the gaseous carbon on the highly reactive surface of activated nanoparticles during the sample exposure and handling in air. The peak at 533.2 eV can be ascribed to the presence of adsorbed water on the surface of mechano-synthesized nanoparticles [24,26]. To confirm the formation of CO_3^{2-} on the surface of as-prepared sample, the high resolution XPS spectrum of C 1s was fitted into three peaks (see Fig. 4d). The peak located at 285 eV, usually used as a reference line, belongs to the adventitious carbon. The peak located at 286.8 eV corresponds to the C–O bond and peak located at 289.9 eV can be ascribed to the CO_3^{2-} group [27]. To confirm the possible presence of nitrogen in the structure of ZnO, the higher resolution scanning spectrum of N 1s was also measured (Fig. 4e). The presence of nitrogen signals at the binding energy of about 400 eV can be seen in the spectrum, though the peak intensity is very small. The N 1s peak has a characteristic asymmetry for doped oxides suggesting a complex chemical state of nitrogen [24]. It should be emphasized that it is difficult to determine the bond character of nitrogen ions in the mechano-synthesized material because of controversial interpretation of the values for Zn–N bonding in the literature. However, the measured BE value in the present case is very close to the values published by other authors [21,28–30].

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