



Trade Science Inc.

Materials Science

An Indian Journal

Full Paper

MSAIJ, 4(2), 2008 [100-103]

Synthesis and characterization of porous sphere-like ZnO with dendrite nanocrystals from layered inorganic-organic nanocomposite on titanium substrate

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Received: 9th February, 2007 ; Accepted: 14th February, 2007

ABSTRACT

With the present of CTAB (cetyltrimethylammonium bromide, $\text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_3)_3\text{Br}^-$) surfactant, porous sphere-like ZnO inorganic-organic nanocomposites have been prepared by self-assembly at room temperature on the titanium substrate. After high temperature oxidation, all the organic were removed and the porous sphere-like ZnO dendrite nanocrystals were obtained. The resultant products have been characterized by X-ray powder diffraction (XRD), field emission scanning electron microscopy (FE-SEM), and transmission electron microscopy (TEM). The XRD pattern shows that the as-synthesized porous sphere-like is multilayered inorganic-organic nanocomposite, and the sample calcined at 500°C for 2h has a hexagonal wurtzite crystal structure. FE-SEM and TEM images demonstrate that porous sphere-like ZnO dendrite nanocrystals are formed. A possible formation mechanism is preliminary proposed for the formation of the novel nanostructure.

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KEYWORDS

Nnanocomposites;
Multilayer structure;
ZnO dendrite nanocrystal;
Surfactant.

INTRODUCTION

Semiconductor nanostructures are gaining increasing technical importance for classic areas of application such as catalysts, passive electronic components, or ceramic materials^[1]. Nanostructured metal oxide semiconductors are also widely used in industrial applications as catalysts, ceramic, pigments and so on. ZnO is a promising luminescent material and used for various applications such as vacuum fluorescent dis-

plays due to its wide band-gap (3.37eV), large exciton binding energy (60meV), non-linear optical property and room temperature ultraviolet emission^[2]. As a large-band gap semiconductor and luminescence materials, nanostructured ZnO (nanoparticles, nanowires, nanobelts, and nanotube) have been widely studied^[3-6] and prepared with various routes, including solvothermal, hydrothermal, self-assembly and a template assisted sol-gel process at a relatively low concentration of zinc^[7]. Designing the morphology of ZnO

into the hierarchical nanostructures is now focus of current research for improving the physical and chemical performance in devices^[8], the examination of the factors governing their growth, and the discovery of new properties^[9]. The effects of organic molecular on the morphology control of inorganic materials in the process of biomineralization have long been realized. Nowadays, these effects have been utilized to prepare inorganic materials with desired morphologies in different systems^[10]. The flowerlike single-crystal ZnO nanostructures by the CTAB-assisted hydrothermal process at low temperature (120°C) was reported^[11]. In this paper, we report a new method to obtain porous sphere-like ZnO with dendrite nanocrystals on Ti substrates by the CTAB-assisted growth, which can be easily employed in the coating of complex geometries. The structures and morphology of the materials were characterized by X-ray diffraction analysis(XRD), filed emission scanning electron microscopy (FE-SEM), and transmission electron microscopy(TEM).

EXPERIMENTAL

All the chemical reagents used in the experiments were obtained from commercial sources as guaranteed-grade reagents and used without further purification. The purity of CTAB is 98% and of the inorganic precursors are not less than 98% respectively.

The titanium plate had the following composition (in mass percent): Fe 0.0015, Si 0.0010, C 0.0005, N 0.0003, H 0.00015, O 0.0015, with the balance being Ti. The plates were polished metallographically with SiC emery paper to remove the oxide surface layer. The final polishing was performed with no. 800 paper and the final thickness of the polished plates was ca. 1 mm. The plates were ultrasonically washed in acetone for ca. 10 min and rinsed in deionized water for 1 min. Subsequently, the plates were aged in deionized water at room temperature. The plates were taken out after one day and rinsed in deionized water for 1 min and then dried at 60°C for one day. The mixed solution was based on the use of the cationic surfactant (CTAB) and the simple chemical materials (hydrous zinc chlorides and NH₄OH) as inorganic precursors. The mixing solution was based on as follows: (1) CTAB were mixed with the distilled deionized water with stirring until a

homogenous solution was obtained; (2) NH₄OH (25wt.% solution) were mixed with the distilled deionized water and then added into the CTAB solution with stirring; (3) when the mixing solution became homogenous, a Zn²⁺ solution of 1.36g ZnCl₂ diluted with 25ml distilled deionized water was introduced, producing a white slurry. The molar ratio of CTAB:ZnCl₂:NH₄OH:H₂O was 1.5:1.0:5.3:561. Subsequently, one plate was placed in the mixed solution with white slurry at room temperature for up to 15 days to induce coating formation.

Powder X-ray diffraction (XRD) data were carried out with a Rigaku D/max-RB diffractometer with Cu K α radiation($\lambda=1.5418\text{\AA}$). The sample was scanned from 1.2°C to 10°C and 20°C to 80°C (2 θ) in steps of 0.02°C. Field emission scanning electron microscopy (FE-SEM) photograph was obtained by JSM-6301F. The samples for SEM were prepared by dispersing the final powders in the conductive glue; this dispersing was then sprayed with carbon. The transmission electron micrographs (TEM) were made with on the Hitachi-800 transmission electron microscope operated at 200KV. The samples for TEM were prepared by dispersing the final powders in distilled deionized water; this dispersing was then dropped on carbon-copper grids.

RESULTS AND DISCUSSION

The XRD patterns of the as-synthesized and calcined products are presented in figure 1. The pattern of zinc oxide assembled with CTAB contains only a series

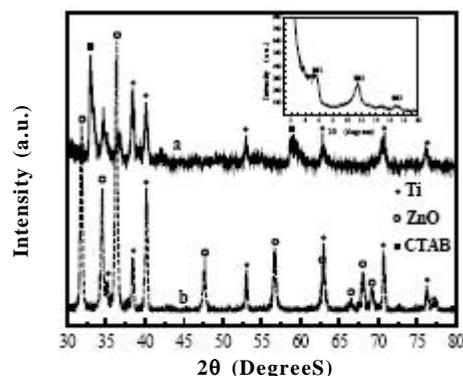


Figure 1: XRD patterns of the results products at the small-angle (inset) and wide-angle diffraction peaks of as-synthesized (a) and calcined at 500°C for 2h (b)

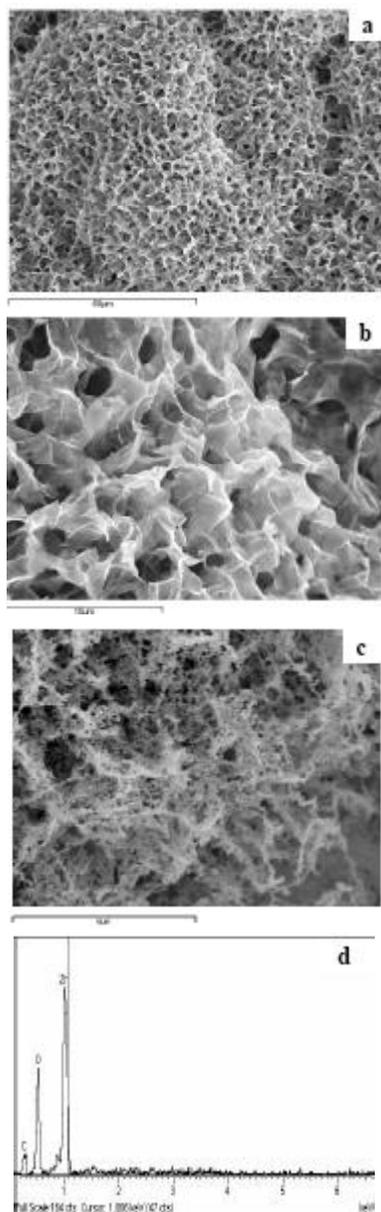


Figure 2: SEM images of the porous sphere-like ZnO nanolayered structures from (a) and (b) as-synthesized sample, and (c) sintered sample. (d) is energy dispersive spectroscopy (EDS) of calcined sample

of low angle peaks (Figure 1 inset). These equidistant diffraction peaks have been recognized to arise from an ordered nanolayered structure. The peaks are attributed to the 00l rational reflections, characteristic of lamellar nanostructure. On the basis of the XRD results, the inter-layer distance of the Zn-L mesolamellar structure is determined to be 15.81 Å, 7.7 Å, and 5.28 Å, respectively. XRD pattern is presented for product calcined at 500°C for 2h as shown in figure 1b. Wide-

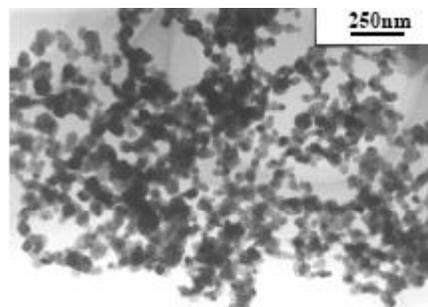


Figure 3: TEM image of ZnO dendrite nanocrystalline

angle X-ray diffraction studies of as-synthesized sample clearly shows the broad peaks that can be indexed according to their corresponding crystalline oxide phases. The data indicate that the inorganic products may consist of nanocrystalline oxide domains. The resulting material is highly crystalline after their calcinations because the diffraction peaks are higher and narrower. The materials exhibits reflections of comparable integral intensity in the region 2θ 20-80° that are characteristic of hexagonal wurtzite structure (JCPDS card 36-1451). Comparing figure 1a and figure 1b, the surfactant CTAB has been removed.

The morphologies of the as-synthesized and calcined samples on titanium substrate were characterized by field emission electron microscopy (FE-SEM). Typical examples are shown in figure 2. Figure 2 shows the FE-SEM image of porous sphere-like ZnO. The typical porous sphere-like ZnO structures consisted of the ZnO-CTAB inorganic-organic composite with large numbers of irregularly distributing macropores ranging from 300 to 600nm, as shown in figure 2a. High magnification image reveal that the sphere composite is made up of sheetlike structures (Figure 2b). The addition of CTAB caused the formation of sponge like shapes. Remarkably a hierarchical organisation of the surface morphology was built up in this self-assembly process. Whereas hemispherical features existed on a micrometer scale (Figure 2a), also explicit structuring was observed in the sub-micrometer regime (Figure 2b). The SEM image of the calcined sample is also shown in figure 2c. From the SEM observations, the ZnO nanocrystalline contains numerous dendrites, and almost all of them show same morphology. The oxidation of the lamellar structure in air produced wurtzite ZnO dendrites. The EDS result (Figure 3d) demonstrates only

elements Zn and O contained in the sample. Hence the calcined sample is hexagonal wurtzite ZnO.

Figure 3 illustrates the representative TEM micrograph of typical ZnO dendrite. The fine particles are more or less spherical in shape and each particle is found to be an aggregate of very small crystallites. It is obvious that ZnO dendrites are crystalline with ca. 20-50nm particle size in TEM image.

Based on the investigation of the crystallization process of ZnO in alkali medium, the growth of hexagonal wurtzite structured ZnO is related to both its intrinsic crystal structure and external factors such as temperature, solution pH and substrates^[12,13]. The different morphologies can be formed by the different concentration of the hydroxyl groups on different substrates.

After the old oxide surface layer is removed through polishing, a fresh oxide layer, which is too thin to be detected by XRD, will quickly form on the Ti plate. When the oxidized titanium plates are aged in the water, the surface reactions will take place. According to the potential-pH (i.e., E-pH diagram) for the Ti-H₂O corrosion system, the passive TiO₂ layer is stable in pure water^[14]. Therefore, the titanium plate surface oxidation will continue to thicken the oxide layer, and at the same time the oxide layer will induce dissociative decomposition of water molecules, resulting in a covering of hydroxyl groups, including half acidic (doubly coordinated) and half mainly basic (singly coordinated) hydroxyls, termed TiOH and Ti-OH groups, respectively^[15,16]. The existence of hydroxyl groups changes the ligands of Zn²⁺ ions in growth unit^[17]. The similar porous spherical morphology was observed in previous investigation^[13,18]. This particular morphology resembles the multiple roughness structure of self-cleaning surfaces, which can be found for example in the water repellent leaves of *Colocasia esculenta* or *Nelumbo nucifera*^[19,20].

Further work will be carried out to give a more detailed explanation on the growth mechanism.

CONCLUSION

A porous sphere-like ZnO with dendrite nanocrystals can be generated by a simple template method. The porous sphere-like ZnO are assembled by many lamellar dendrites. The results investigated by XRD,

FE-SEM, and TEM indicated that these nanostructured ZnO have fine hexagonal wurtzite crystal structure. The formation mechanism of ZnO nanostructure in our synthesis process has been proposed based on the synthesis process. Further investigation of the formation mechanism, the properties and the applications of this kind of nanostructure are being performed.

ACKNOWLEDGMENT

This work was supported by National Natural Science Foundation of China (No.50662006), and the Natural Science Foundation of Yunnan Province, China (No.2006E0013M). Authors thank X.H.Chen and Y. J. Yan for their help in the TEM and SEM experiments in Tsinghua University.

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