Materials Science in Semiconductor Processing 76 (2018) 7–13

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

Large-scale synthesis of ZnO nanostructures by pulse electrochemical method and their photocatalytic properties

Anna Ulyankina[a,*], Igor Leontyev[b], Marina Avramenko[b], Denis Zhigunov[c], Nina Smirnova[a]

[a] Platov South-Russian State Polytechnic University (NPI), Novocherkassk Prosveschenia 132, 346428, Russia
[b] Southern Federal University, Rostov-on-Don Zorge 5, 344090, Russia
[c] Faculty of Physics, M.V. Lomonosov Moscow State University, Moscow Leninskie Gory 1, 119991, Russia

ARTICLE INFO

Keywords:
ZnO
Nanocrystalline materials
Semiconductors
Pulse alternating current
Electrochemical synthesis
Photocatalytic activity

ABSTRACT

In this paper, we report a simple environment-friendly and large-scale approach to synthesis of highly crystalline zinc oxide nanostructures using pulse alternating current (PAC). The morphological results demonstrate flower-like architectures of nanoparticle-based and nanorod-based zinc oxide (ZnO-NPs and ZnO-NRs) obtained in KCl and NaCl as electrolytes. The photocatalytic activity of the obtained materials was performed in methylene blue dye degradation reaction under UV light irradiation. A high efficiency of ~ 90% within 60 min with excellent rate constant ($k = 0.0386\ min^{-1}$) was observed in the presence of ZnO-NPs synthesized in 2 M KCl which is attributed to the larger specific surface area ($27\ m^2\ g^{-1}$), total pore volume and more defective structure.

1. Introduction

Synthetic organic dyes are used in the textile, paper, food, plastic, and other industries. The discharge of dye-containing effluents into the water resources can lead to very serious environmental problems. Up to now, various physical and chemical treatment methods have been investigated to remove organic dyes [1]. Among them photocatalysis technique has been developed as a new alternative over the last years due to the possibility to degrade organic pollutants without the production of undesirable byproducts. Different metal semiconductor materials such as TiO_2 [2–4], Fe_2O_3 [5], CdS [6] and ZnS [7] are used as photocatalysts. Zinc oxide is extensively investigated as a promising candidate for organic pollution degradation due to its low-cost, non-toxicity, excellent chemical and mechanical stability [8]. A lot of papers are devoted to decay of organic dyes such as methylene blue (MB), Rhodamine B and methyl orange under UV/visible irradiation in the presence of ZnO-based nanomaterials [9–12]. Special attention is focused to promote the photocatalytic activity of ZnO by controlling the size and shape of particles, concentration of oxygen and zinc-related defects, and surface area [13–16]. Nowadays, numerous methods including hydrothermal, sol-gel process, precipitation and thermal decomposition have been explored to prepare nano-ZnO with diverse microstructure and dimensions [17,18]. However, the solution of fabrication problems including sophisticated techniques, toxic reagents and high resource consumption attracts significant attention of researchers [19,20]. Moreover, in the most of solution-based growth methods morphology of ZnO are designed by adding different surfactants which can affect the purity of the synthesized nanomaterials [21,22]. Thereby, it is necessary to develop a simple, large-scale and low-cost way to obtain ZnO nanostructures for photocatalytic application.

The one-step electrochemical route based on electrochemical oxidation of zinc electrodes under pulse alternating current (PAC) is a suitable method, having advantages of being simple, environment-friendly and convenient, which provides preparation of large quantities of nano-ZnO powders in the absence of templates or surfactants. This approach was successfully used for synthesis of metal oxides such as NiO [23] and SnO_2 [24]. The possibility to control the size and morphology of CuO_x particles obtained by PAC synthesis using different current densities was shown in our previous work [25].

In this paper we report on synthesis, characterization and photocatalytic activity of nano-ZnO prepared by means of zinc electrochemical oxidation using PAC. The effect of type of electrolyte on the morphological, structural and optical properties of ZnO was evaluated. Photocatalytic activity was studied using MB degradation under UV irradiation.

2. Experimental

Analytical-grade sodium chloride (NaCl), potassium chloride (KCl) and methylene blue ($C_{16}H_{18}ClN_3S_2{\cdot}3H_2O$) were purchased from Alfa Aesar (Germany). The electrodes were prepared from Zn foil purchased

* Corresponding author.
E-mail address: anya-barbashova@yandex.ru (A. Ulyankina).

https://doi.org/10.1016/j.mssp.2017.12.011
Received 24 August 2017; Received in revised form 16 November 2017; Accepted 18 December 2017

from Sigma Aldrich (USA).

For the synthesis of nano-ZnO, two zinc electrodes (S = 4 cm^2) were placed in an electrochemical reactor with 2 M NaCl or KCl aqueous solution as an electrolyte. The electrodes were connected to *ac* source operating at 50 Hz. We used an asymmetric pulse alternating current with a ratio of anodic to cathodic current densities j_a:j_k = 1:2 (j = 1.2:2.4 A cm^{-2}). Under PAC the Zn electrode was oxidized with a formation of ZnO. After synthesis, the obtained white sediment was washed with deionized water and finally dried at 80 °C. The samples obtained in KCl and NaCl were denoted by ZnO-NPs and ZnO-NRs, respectively.

The XRD investigations were performed with the Swiss-Norwegian beam lines at the European Synchrotron Radiation Facility (SNBL ESRF) at λ = 0.7121 Å using a 2-D Pilatus2M (Dectris) image-plate detector. A NIST powder LaB_6 (NISTSRM660a) was used for calibration of the wavelength, sample-to-detector distance, detector tilts and resolution of the setup. All two-dimensional (2D) XRD images were integrated to one-dimensional (1D) patterns using SNBL ToolBox software [26]. The diffraction powder patterns data were analyzed using FullProf software.

Samples morphology was studied using Hitachi transmission electron microscope (TEM) HT 7700. Target-oriented approach was utilized for the optimization of the analytic measurements [27]. Before measurements the samples were mounted on a 3 mm copper grid and fixed in a grid holder. Images were acquired in bright-field TEM mode at 100 kV accelerating voltage.

The elemental contents of the products were investigated using energy dispersive x-ray analysis (Zeiss EVO 40 with X Flash 1106 EDX detector). The Raman spectra were recorded with Renishaw spectrometer.

The Brunauer–Emmett–Teller (BET) method based on nitrogen adsorption/desorption with a Quantachrome Nova 1200 e was used to determine the specific surface area and pore size distribution.

The absorption spectra of the samples were obtained using UV–visible spectroscopy (UV-1800 Shimadzu, Japan). Photoluminescence (PL) spectra were measured at room temperature under an excitation of a He-Cd laser operated at 325 nm and collected using a single-grating 500 mm focal length spectrometer equipped with an air-cooled CCD (Hamamatsu).

The photocatalytic experiments were carried out using the as-prepared nano-ZnO in MB degradation reaction. Test solution was prepared by dispersing 0.02 g of the sample into MB solution (10 ppm). The suspension was stirred in the dark during 1 h to reach adsorption-desorption equilibrium of MB molecules on nano-ZnO. Then the mixture was exposed to UV-light irradiation with a mercury lamp. The tested dye solution was periodically withdraw and analyzed by collecting the adsorption spectra using UV–vis spectroscopy (Shimadzu UV-1800, Japan).

The C/C_0 ratio was utilized to represent the degradation efficiency, where C_o and C are the initial concentration and the concentration at time t, respectively.

3. Results and discussion

The ZnO formation rate was calculated to be 917.5 and 943.75 mg cm^{-2} h^{-1} for ZnO-NPs and ZnO-NRs, respectively. The synthesis can be easily upscaled. For the present work amounts of ca. 4 g per hour were routinely synthesized.

Transmission electron microscopy (TEM) was employed to determine the morphology and size of the nano-ZnO. TEM images of the samples demonstrate the flower-like architectures of the as-synthesized zinc oxides. It can be seen that the sample prepared in 2 M KCl as an electrolyte consists of small particles about 30–50 nm in size (Fig. 1(a,b)). The sample prepared in 2 M NaCl is composed of the nanorods with the average size in the range of 30–90 nm (Fig. 1(d,e)).

The selected area electron diffractions (SAED) of ZnO-NPs and ZnO-NRs are shown in Fig. 1(c) and (f), respectively. The diffraction rings indicate that the obtained samples are polycrystalline nature of ZnO [28].

The XRD patterns and Rietveld refinement plots of synthesized ZnO samples are presented in Fig. 2. The vertical bars show the peaks associated with hexagonal wurtzite structure of ZnO (space group is *P63mc*). For estimation of the nanoparticles size, unit cell parameters and particle shape (i.e., average shape of the crystallites) in the synthesized materials we employed the Rietveld refinement technique using linear combination of spherical harmonics for Laue class 6/mmm. The background was determined by 2θ -6 coefficients polynome function. Analysis of the results presented in the Table 1 indicates that: (i) ZnO nanoparticles synthesizing in both electrolyte are extended along the direction (001) wherein the ratio D_{100}/ D_{001} is almost independent of the type of electrolyte; (ii) the average particle size of ZnO nanoparticles synthesized in KCl is less than that synthesized in NaCl both along the (001) and (100) directions. The values of the unit cell parameters and the average volume nanoparticles size along the (100) and (001) directions are presented in Table 1. It should be noted that the obtained unit cell parameters for prepared samples are larger than the unit cell parameters of both poly- and nanocrystalline pure ZnO [29,30]. This could be attributed to the replacement of small O^{2-} ions (0.14 nm) with large Cl^- ions (0.18 nm) that induce the expansion of the crystal lattice [31].

EDX spectra confirm the incorporation of chlorine in nano-ZnO as shown in Fig. 3. In addition to the signals from oxygen and zinc, a weak peak at 2.63 keV was observed and assigned to chlorine. The Cl content is found to be 0.73% and 0.76% for ZnO-NPs and ZnO-NRs, respectively.

Raman spectra of ZnO-NPs and ZnO-NRs turned out to be almost indistinguishable from each other (see Fig. 4(a)) and highly typical of wurzite-type ZnO [32,33]. Twenty bands are observed in the range 50–1200 cm^{-1} (Fig. 4(b)). The lines at 99, 380, 414, 438, 572 and 585 cm^{-1} comprise the first-order Raman spectrum of ZnO. It consists of two modes of E_2 symmetry (at 99 and 438 cm^{-1}), transversal optical modes of A_1 and E_1 symmetry (at 380 and 414 cm^{-1}, respectively) and longitudinal optical modes of A_1 and E_1 symmetry (at 572 and 585 cm^{-1}, correspondingly). The lines at 200, 285, 332, 483, 534, 653, 695, 975, 1075, 1110 and 1147 cm^{-1} can be assigned to the second-order combinations of silent (at 285 cm^{-1}), optical (at 332 and 1075 cm^{-1}), optical and acoustic modes (at 653 and 695 cm^{-1}) and different overtones (at 200, 483, 534, 975, 1110 and 1147 cm^{-1}) [32]. Low-frequency features similar to the rest of obtained lines (at 64, 78 and 130 cm^{-1}) are reported to be observed in case of ZnO nanoparticles [34].

An important factor in tailoring the photochemistry of nanomaterial is its surface area. In the present study, N_2 adsorption-desorption isotherms were recorded for all samples. DFT method for pore size distribution (inset) was carried out as shown in Fig. 5. These isotherms show type IV curves accompanied by a type H3 hysteresis loop. The pore size distribution reveals the presence of mesoporous structure. The pore sizes of nano-ZnO are not uniform due to the arrangement of solid ZnO particles. The BET surface areas for ZnO-NPs and ZnO-NRs were found to be 27 m^2 g^{-1} and 12 m^2 g^{-1}, respectively. It is known, that the increased surface area leads to the creation of more active sites for dye molecules absorption, which enhances the photocatalytic activity [35].

Optical properties of the nano-ZnO were revealed by UV–vis spectra and photoluminescence spectroscopy at room temperature, as shown in Fig. 6(a) and (b), respectively. All the samples exhibit a single and well-defined absorption band from ultraviolet to the visible area with the maximum peaks at 368 and 365 nm for ZnO-NPs and ZnO-NRs, respectively, which are characteristics peak of wurtzite hexagonal ZnO phase (Fig. 6a). Based on the maximum absorption wavelength, the band gap values of nano-ZnO were estimated according to the following equation (1) [14]: