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Photocatalytic Oxidation of Paracetamol and Chloramphenicol by ZnO Nanowires

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This study is focused on ZnO nanowires, synthesized by chemical bath deposition method and spin-coating technique. The dimensions of nanowires growth (diameter and height) are controlled by adjusting of zinc nitrate and methenamine concentrations in the precursor.

The crystallite size, surface morphology and photocatalytic efficiency are determined by X-ray diffraction, scanning electron microscopy and UV-vis spectroscopy. The ZnO nanowires, grown on glass substrate have average diameter of 100–150 nm and height of approximately 3–3.5 μm. The nanocrystallites size is of 70 nm. The photocatalytic action of ZnO nanowires is checked in photodegradation of two pharmaceutical drugs, *Paracetamol* (PCA) and *Chloramphenicol* (CA), in aqueous solutions under UV-light irradiation. The experimental results show that the films exhibit better photocatalytic activity in the degradation of CA, compared to that of PCA.

Keywords: Photocatalysis, ZnO nanowires, UV, Paracetamol, Chloramphenicol

INTRODUCTION

One-dimensional (1D) semiconductor nanostructures such as nanowires, nanorods, nanofibres, nanobelts and nanotubes are of a great interest in both academic research and industrial applications because of their potential as building blocks for other structures [1]. 1D nanostructures are useful materials for investigating the dependence of electrical and thermal transport or mechanical properties on dimensionality and size reduction (or quantum confinement) [2]. They also play an important role as both interconnects and functional units in the fabrication of electronic, optoelectronic, electrochemical and electromechanical nanodevices [3]. Among the one-dimensional (1D) nanostructures, zinc oxide (ZnO) nanowire is one of the most attractive nanomaterials for nanotechnology in modern research [4]. ZnO is a semiconductor material with direct wide band gap energy (3.37 eV) and a large exciton binding energy (60 meV) at room temperature [5]. ZnO is also biocompatible and biodegradable for medical and environmental applications [6].

ZnO nanowires are attractive candidates for many applications such as UV lasers [7], light-emitting diodes [8], solar cells [9], nanogenerators [10], gas sensors [11], photodetectors [12] and photocatalysts [13]. Among these applications, ZnO nanowires are being increasingly used as photocatalysts to inactivate bacteria and viruses for the degradation of environmental pollutants such as dyes, pesticides, pharmaceutical products and volatile organic compounds under appropriate light irradiation [14, 15].

There are many fabrication methods for 1D ZnO nanostructures, such as the vapor phase transport deposition, pulsed laser ablation, chemical vapor deposition, electro deposition and thermal evaporation [16-20]. Most of these methods are not suitable for controllable synthesis. Moreover, the complex processes, sophisticated equipment and economically prohibitive high temperatures are also required. Compared with those methods, chemical bath deposition method (CBD) can be controlled easily, and no sophisticated equipments are required. The most important advantage is that the experiment can be carried out under low temperature. Temperature is an important thermodynamic factor that plays a key role in controlling the growth rate and aspect ratio of ZnO 1D nanostructure [21]. It is well known that the properties of ZnO are dependent on preparation parameters such as growth temperature, precursor concentration and time.

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In this paper we investigate the photocatalytic efficiency of low-temperature grown well-aligned ZnO nanowires. The films are deposited on glass substrates by spin coating technique and chemical deposition growth. Then their structure and morphology are investigated. The decolorization kinetics of two pharmaceutical drugs – *Paracetamol* (PCA) and *Chloramphenicol* (CA) are studied in aqueous solutions.

EXPERIMENTAL

Materials

Zinc acetate dihydrate, 2 methoxyethanol, zinc nitrate hexahydrate (>99.9%) and commercial ZnO powder were from Fluka. Methenamine (>99.9%) were from Reidel de Haen. The pharmaceutical drugs – Paracetamol ($C_8H_9NO_2$, Actavis) and Chloramphenicol ($C_{11}H_{12}Cl_2N_2O_5$, Actavis) were used as model contaminants in the photocatalytic experiments. All chemicals were of analytical reagent grade and without further purification. The glass plates (50x50x20 mm) used as substrates were subsequently cleaned with acetone, ethanol and distilled water for 20 min, respectively. Then, the substrates were dried in an oven for several minutes. Finally the thin films were thoroughly cooled to room temperature, washed with water and dried in air.

Preparation and characterization of ZnO nanowires

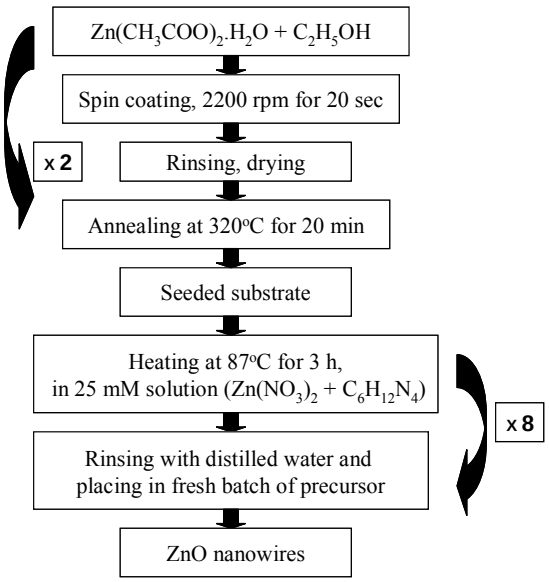

Fig. 1. Synthesis procedure of ZnO nanowires, coated onto glass substrates by wet chemical method.

ZnO nanowires used in the experiment were grown on the glass slides by wet chemical method (Fig. 1). The procedure consists of two steps [22]: (1) modification of the substrates with a thin layer of densely and uniformly dispersed ZnO by spin coating, and (2) hydrothermal growth of ZnO nanowires in aqueous solution. Zinc acetate dihydrate was dissolved in pure ethanol with concentration of 5 mM. Commercial ZnO powder was suspended in pure ethanol to form 25 wt% suspension. The resulting solution of zinc acetate was coated on glass by spin coating with rate 900 rpm for 10 sec and then at 2200 rpm for 20 sec (one cycle). The substrates were coated by four cycles and rinsed with water. The substrates were dried at room temperature and annealed at 320 °C for 20 min. The above procedure was repeated twice. The seeded substrates were placed in 25 mM aqueous solution of zinc nitrate hexahydrate and methenamine and heated up in a closed vial at 87 °C for 3 h. Then the samples were removed from the solution, rinsed with distilled water and placed in a new batch of precursor solution. The growth process was repeated eight times and finally the samples were dried in air. Figure 2 shows schematic illustration of preparation scheme for ZnO nanowires on glass substrate.

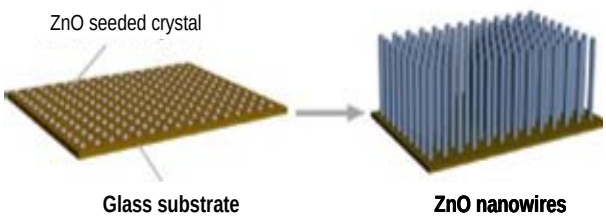

Fig. 2. Schematic illustration of the growth process of the ZnO nanowires on glass substrate.

The morphology and crystallite size of ZnO nanowire films were characterized using Scanning Electron Microscopy (SEM) and X-ray diffraction (XRD).

The SEM images were obtained by scanning electron microscope (JSM-5510 JEOL) operated at 10 kV of acceleration voltage. The investigated samples were coated with thin film of gold by fine coater (JFC-1200 JEOL) before observation.

The XRD spectra were recorded at room temperature by powder diffractometer (Siemens D500 with CuKα radiation within 2θ range 25-75 deg at a step of 0.05 deg 2θ and counting time 2 s/step).

Photocatalytic measurements

The photocatalytic efficiency of ZnO nanowires was investigated and compared in photo oxidation of *Paracetamol* and *Chloramphenicol* from aqueous solutions. The measurements were

conducted in glass reactor, equipped with magnetic stirrer and UV lamp (Sylvania BLB, 315-400 nm of emission range, 18 W). The distance between the sample and the lamp was 15 cm. The light power density of the sample position was 0,66 mW/cm^2 as measured with research radiometer (Ealing Electro-optics, Inc.).

The volume of PCA and CA solutions was 150 ml with initial concentration of 15 and 8 ppm respectively. The decolorization processes of the pharmaceutical drugs was measured by UV-vis absorbance spectroscopy (spectrophotometer Evolution 300 Thermo Scientific, wavelength range from 200 to 400 nm) after aliquot sampling at regular time intervals. Each aliquot sample was returned back to the reaction reactor immediately after the spectrophotometrical measurement. All photocatalytic tests were performed at a constant stirring rate of 500 rpm and at room temperature (23±2°C).

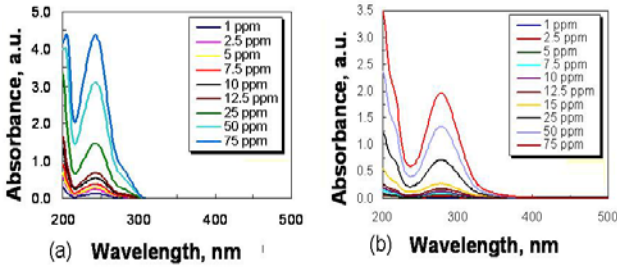

Fig. 3. Absorbance spectrum of PCA (a) and (b) CA in water solutions. The initial concentrations are 15 and 8 ppm.

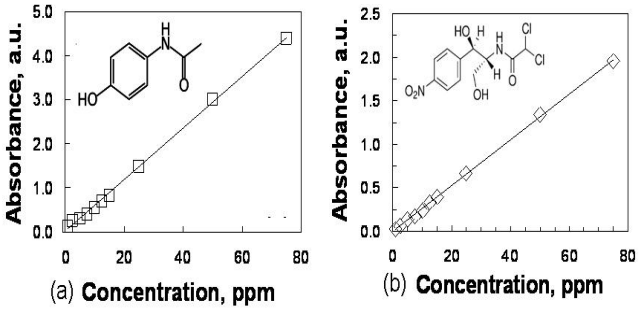

Fig. 4. Change in the absorbance maxima of PCA and CA at wavelength 243 and 278 nm versus the drugs concentration.

Paracetamol and *Chloramphenicol* exhibit one maximum of absorbance at 243 and 278 nm, respectively. The absorption spectra are measured at various concentrations of the pollutants (Fig. 3 and 4).

The photocatalytic efficiency of decomposition D (%) of PCA and CA were calculated using the equation:

$$D\%=(C_0-C_t)/C_0.100 \quad (1)$$

where C_0 represents the initial concentration, C_t represents the drugs concentration after t min of photocatalysis.

RESULTS AND DISCUSSION

Structure characterization

The morphology of ZnO nanowires with hexagonal crystal structure and density, alignment and size is shown in Fig. 5. The films obtained by wet chemical method (shown on Fig. 1) are with density about 3 μm. The diameter of nanowires is 100-150 nm and length 3-3.5 μm. The nanowires grow perpendicular to the glass substrate. This is due to the two stage preparation method (seeding and growing process separately).

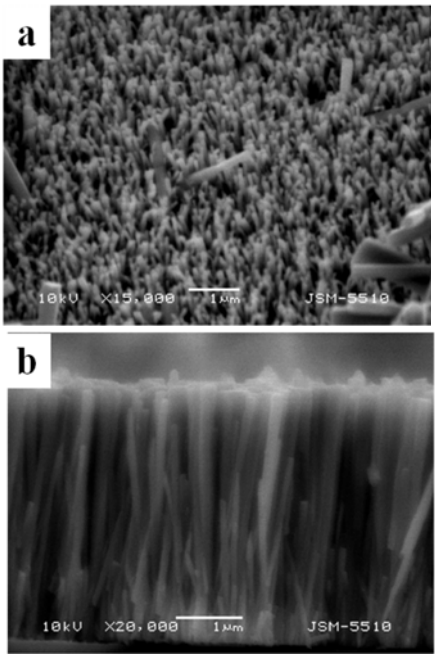

Fig. 5. SEM images of ZnO nanowires grown on glass substrate (a) plain view and (b) cross-section.

XRD patterns are taken to examine the crystal structure of ZnO nanowires. Figure 6 shows the typical XRD patterns of the well-ordered ZnO nanowires grown on glass substrate. The sample gives XRD spectra indicating the nanowires are of high crystallinity. The three characteristic peaks clearly proof the existence of ZnO, which correspond to different crystallographic orientations of the crystal lattice of wurtzite (from left to right) (100) - at (2θ = 31.76°); (002) - at (2θ = 34.39°)

and (101) - at 2θ = 36.24°. The most intense peak is in charge of the crystallographic orientation (002).

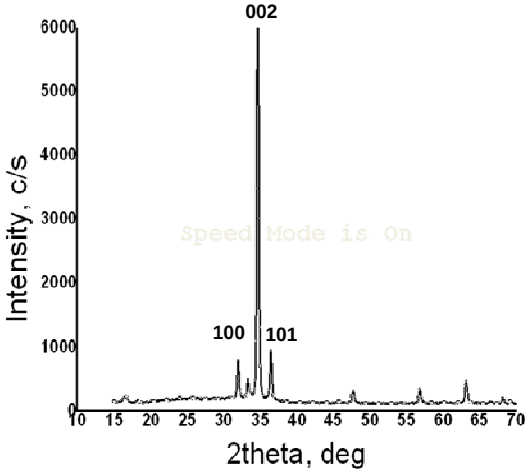

Fig. 6. XRD spectra of ZnO nanowires.

This means that the crystal growth of the resulting nanowires of zinc oxide is z-axis, i.e. nanowires, and the other axis is negligible. The average size of crystallites is 70 nm as calculated by the Scherrer equation.

Photocatalytic activity

The decomposition of model pharmaceutical products, *Paracetamol* (analgesic) and *Chloramphenicol* (antibiotic), in aqueous solutions are investigated using ZnO nanowires under UV-light illumination. The initial concentrations of PCA and CA are 15 and 8 ppm.

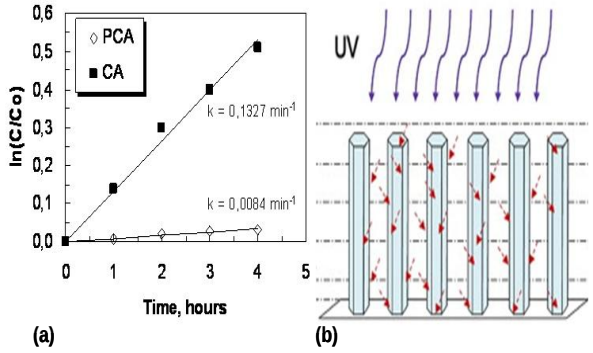

Fig. 7. Photodegradation kinetic of PCA and CA in the presence of ZnO nanowires (a) and (b) schematic illustration of photocatalytic action ZnO nanowires under UV-light illumination.

The reaction kinetics is revealed by plotting the natural logarithm of concentration ratio, $\ln(C/C_o)$, versus the irradiation time, *t*. Straight lines are obtained, indicating that the reaction is of pseudo first-order expressed by $\ln(C/Co) = -kt$. The slope of logarithmic scale linear fits represents the rate constant of photocatalysis k. As seen from Fig. 7, the ZnO nanowires exhibit higher photocatalytic efficiency (k = 0.1327 min^{-1}) in the degradation of CA compared to of PCA (k = 0.0084 min^{-1}). The degradation of drugs is calculated using equation 1 and the results are presented in Figure 8.

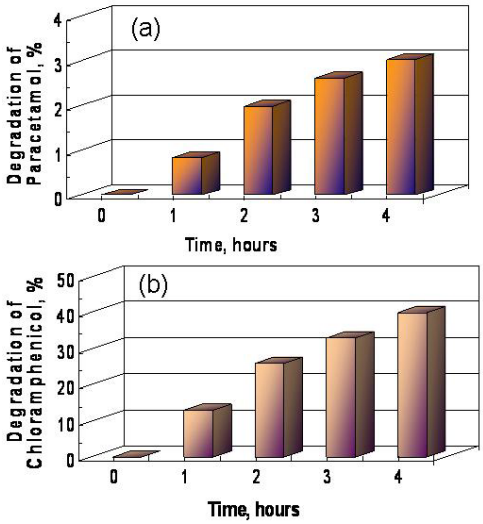

Fig. 8. Photocatalytic activity regarding the degradation of PCA and CA by ZnO nanowires for 4 hours UV illumination.

Figure 8 compares the photocatalytic activity of ZnO nanowires with respect to the degradation of pharmaceutical products under UV-light illumination. Nanostructure films have the higher decolorization percentage of *Chloramphenicol* (36.08% for four hours) compared to *Paracetamol* (3% for four hours).

CONCLUSIONS

ZnO nanowires with hexagonal structure are successfully prepared on glass substrates by chemical bath deposition technique. The optimal method for synthesis of ZnO nanowires with high density and uniformity and aligned along the z-axis is a seed deposition by spin coating on glass substrates. This synthesis route has a good reproducibility. The as-obtained ZnO nanowires are used for photocatalytic degradation of the pharmaceutical drugs – *Paracetamol* and *Chloramphenicol*. The experimental results show that the films have higher activity and faster decolorization *Chloramphenicol* in comparison with *Paracetamol*. This is confirmed by the values of the rate constants and degree of degradation.

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ФОТОКАТАЛИТИЧНО ОКИСЛЕНИЕ НА ПАРАЦЕТАМОЛ И ХЛОРАМФЕНИКОЛ ЧРЕЗ ZnO НАНОЖИЧКИ

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(Резюме)

Това изследване е фокусирано върху наножички от ZnO, синтезирани чрез метода за химично отлагане и техника за нанасяне. Размерът за растежа на наножичките (диаметър и височина) се контролира посредством концентрациите на цинков нитрат и метенамин в прекурсорът.

Размерът на кристалитите, повърхностната морфология и фотокаталитичната ефективност са установени чрез Рентгенова дифракция, сканираща електронна микроскопия и УВ-вис спектроскопия. Наножичките от ZnO, израснали върху стъклена подложка имат среден диаметър 100 – 150 nm и височина около 3 – 3.5 μm. Размерът на нанокристалитите е 70 nm. Фотокаталитичната активност на ZnO наножички е установена чрез фотокаталитичното разграждане на две фармацевтични лекарства, Парацетамол (PCA) и Хлорамфеникол (CA), във водни разтвори при облъчване с УВ светлина. Експерименталните резултати показват, че филмите проявяват по-добра фотокаталитична активност при разграждане на CA, в сравнение с PCA