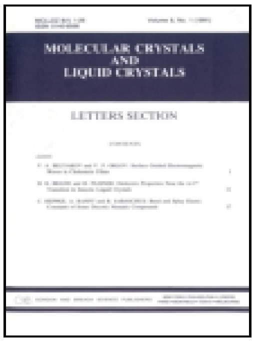

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Photodegradation of Endocrine Disrupting Chemicals by ZnO Nanorod Arrays

YANGSI LIU* AND WEI GAO

Department of Chemical and Materials Engineering, The University of Auckland, Auckland, New Zealand

ZnO nanorod arrays (NRAs) were synthesized via magnetron sputtering and a low temperature aqueous solution growth in a short period time. The morphology and crystal structure were characterized by scanning electron microscopy (SEM), and X-ray diffraction (XRD). The ZnO NRAs were applied to conduct photo degradation of endocrine disrupting chemicals (EDCs) such as estrone (E1), 17β-estradiol (E2), 17α-ethinylestradiol (EE2), and bisphenol A (BPA). The results indicate that ZnO NRAs exhibited different performances in dealing with various EDCs but do not have selectivity for a multicomponent mixture.

Keywords ZnO; nanorod arrays; photocatalysis; endocrine disrupting chemicals

Introduction

Waste water treatment and reuse are critical issues for many countries and areas where water resources are scarce. Organic pollutants known as endocrine disrupting compounds (EDCs) may survive conventional water treatment process, resulting in residual concentrations in drinking water. These chemicals have been detected in the environment worldwide with the potential to elicit negative effects on the endocrine systems of human beings and wildlife. Their resistance to physical and biological treatment, even in their trace levels in water, makes them difficult to remove completely [1–3].

ZnO photocatalysis is a newly developed advanced oxidation process (AOP), which can be conveniently applied for complete destruction of EDCs [4]. ZnO showed much higher photocatalytic efficiency than the widely used TiO_2 in many cases [5, 6]. Its nanostructure can be easily produced as thin films or in immobilized states, which are convenient for water treatment applications [4, 7–11].

ZnO nanorods arrays can be synthesized via magnetron sputtering and hydrothermal techniques and they were applied to photocatalytic degradation of four typical EDCs. They are estrone (E1), 17β-estradiol (E2), 17α-ethinylestradiol (EE2) and bisphenol A (BPA). The molecular structures of these phenolic compounds are shown in Fig. 1. Female steroid hormones, such as estrone (E1) and 17β-estradiol (E2), are the main natural estrogens [12]. 17β-estradiol (E2) is a potent endogenous estrogen produced primarily within the

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*Address correspondence to Yangsi Liu, Department of Chemical and Materials Engineering, The University of Auckland, Private Bag 92019, Auckland 1142, New Zealand. Tel.: +64 9 3737599 ext. 89840; Fax: +64 9 3737463. E-mail: yliu403@aucklanduni.ac.nz

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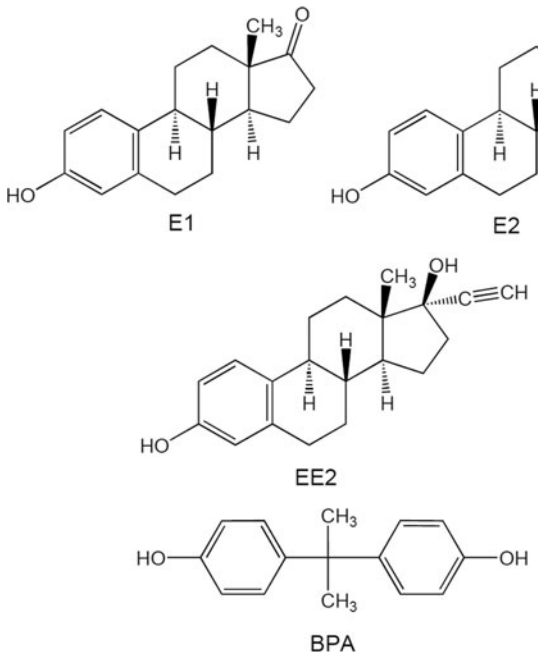

Figure 1. Molecular structures of estrone (E1), 17β-estradiol (E2), 17α-ethinylestradiol (EE2) and bisphenol A (BPA).

female ovaries [13]. Estrone (E1) is the primary and relatively persistent biotransformation byproduct of 17β-estradiol (E2) during aerobic digestion in the domestic sewage treatment plant (STP) process [14]. The principal synthetic estrogen, 17α-ethinylestradiol (EE2) is a pharmaceutical and biologically active steroid hormone that is mass produced as the main constituent of the birth control medicine and hormone replacement therapy [15]. Bisphenol A (BPA) is an endocrine disrupter and an industrial chemical, and heavily used as a monomer in the manufacture of polycarbonate, epoxy resin, numerous plastic products and dental sealants [16–18].

The photocatalytic activities for individual EDCs and for multicomponent mixtures were investigated. It is expected that the outcome from this research will provide an effective photocatalyst based on ZnO 1D nanostructure for degrading EDCs in a water environment.

Experimental

Materials

All chemicals of analytical grade and de-ionized (DI) water were used throughout this study. Milli-Q water was used for the preparation of EDC aqueous solutions and as a component of the mobile phase in the high performance liquid chromatography (HPLC) analysis.

Sample Preparation

Glass substrates were pre-coated with ZnO seed layers by magnetron sputtering. The detailed processes are described elsewhere [19]. The ZnO NRAs were grown from the

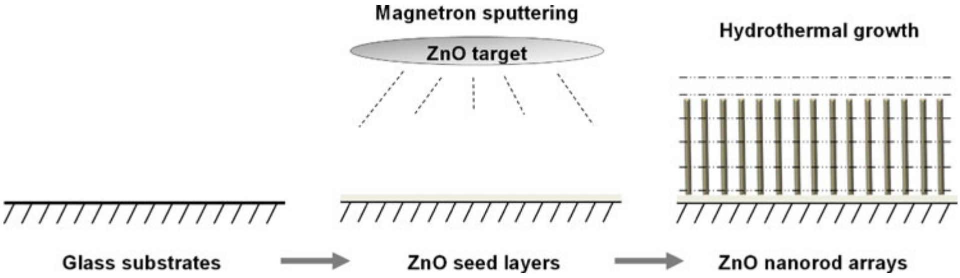

Figure 2. Schematic illustration of the formation procedure of the immobilized hierarchical ZnO nanostructures.

ZnO seeds layers via a hydrothermal growth method [4, 7]. An aqueous solution containing 25 mM zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$, 98%) and hexamethylenetetramine (HMT) ($C_6H_{12}N_4$, 99%) with an equal molar ratio was prepared. The aqueous solution was then transferred into a sealable glass jar in which the glass substrates with ZnO seed layers were held face-down. The whole set was put into an oven at 95°C for 4 h, after which the glass substrates were rinsed and dried [4]. The formation process of ZnO NRAs is schematically illustrated in Fig. 2.

Sample Characterization

Surface and cross-sectional morphologies of the ZnO NRAs were observed with a field-emission gun scanning electron microscope (FEG-SEM, Philips XL-30S). The crystal structure of the ZnO NRAs was identified by X-ray diffraction (XRD, Philips X'Pert MPD) using Cu Ka radiation ($\lambda = 0.15406$ nm).

Photocatalytic Degradation

The ZnO NRAs were immersed in 5.2 ml EDC aqueous solutions. The initial concentration was 1.85 μM. Prior to the degradation test, they were kept in the dark for 30 min to establish an adsorption/desorption equilibrium of the EDCs on the photocatalysts. This guarantees that the measured concentration changes during UV irradiation would be solely caused by photocatalysis. Lamps with different main wavelengths including UVA (365 nm) and blue (450 nm) lights were used as the light sources.

Determination of EDCs

The degradation of EDCs was monitored at an interval of 60 min by a high performance liquid chromatography (HPLC, SPD-20A, Shimadzu) equipped with a UV detector. Analyses were performed at 25°C in a C18 reversed phase column (5 μm, 4.6 × 150 mm, Agilent) with 50 μL injection volume. Acetonitrile 190 (far UV/gradient quality, 99.9%) and Milli-Q water were used as the mobile phase at a flow rate of 1.0 ml min^{-1}. Samples were measured at a detection wavelength of 205 nm. The degradation of EDCs was evaluated by the area of HPLC chromatographic peaks, since the concentration of EDCs was in linear proportion to the peak area [4].

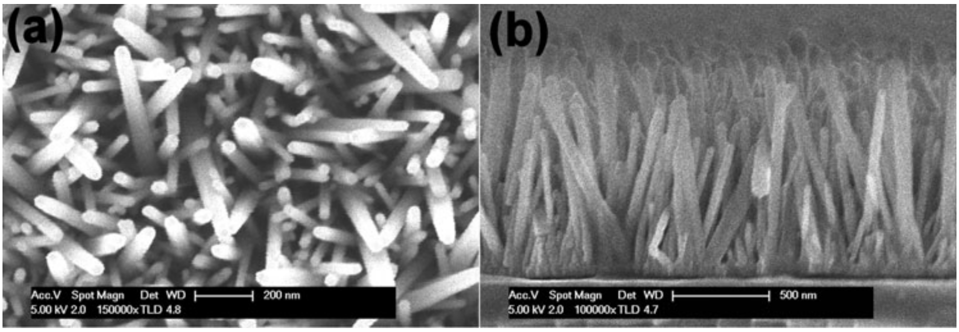

Figure 3. SEM images of the ZnO NRAs: (a) top view; (b) cross section view.

Results and Discussion

Morphology and Crystal Structure

Figure 3 reveals the SEM photographs of the ZnO NRAs grown on glass substrates. The top section image clearly shows that all ZnO nanorods were distributed uniformly and arranged in very large arrays. The cross section view indicates that the ZnO nanorods grew almost vertically from the substrates. The diameter and length of ZnO nanorods are 60–80 nm and ~1 μm, respectively, as discovered in our previous report [4].

The crystal structure of the ZnO NRAs was analyzed by XRD as depicted in Fig. 4, showing a typical hexagonal wurtzite phase crystal pattern [4]. In comparison with the standard XRD pattern, the much higher relative intensity of the (002) diffraction peak at 34.3° evidences that the ZnO nanorods have a preferential orientation perpendicular to the substrate in the [0001] direction along the c-axis. It was suggested that the preferential growth orientation is directly related to the presence of the ZnO seed layers [20]. The

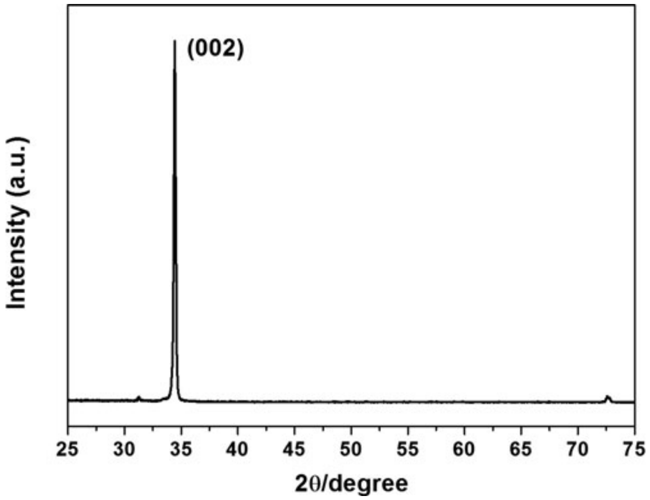

Figure 4. XRD patterns of the ZnO NRAs.

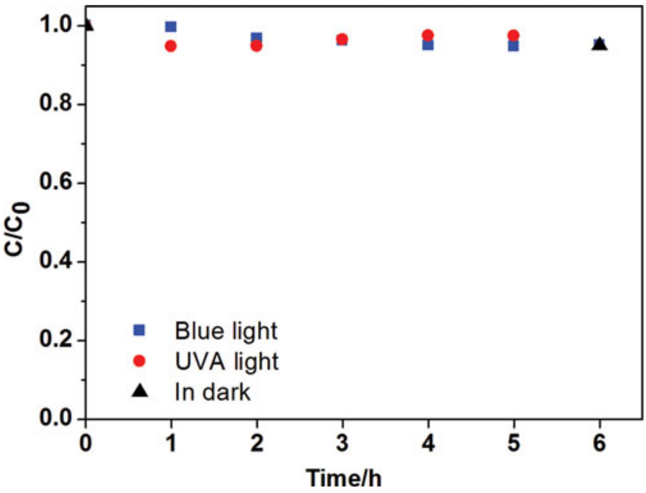

Figure 5. Degradation rate of E1 under blue light, under UVA light and kept in dark.

reason for the high alignment on ZnO seeded layers is because of the matching lattice and the polar nature of the ZnO surface [21].

Blank Experiments

E1 was selected as the model from the EDCs for blank experiments conducted before the photocatalytic degradation since as it is the most abundant estrogen found in aquatic systems [22]. The ZnO NRAs were first immersed in E1 solutions without UV light (in dark and under blue light). The degradation of E1 was negligible after 6 hours for both conditions as shown in Fig. 5, indicating that the absorption and the visible light degradation by photocatalysts are limited. A similar result was obtained by putting the solution under UVA light without the ZnO NRAs, which means the UVA light degradation of E1 is very weak.

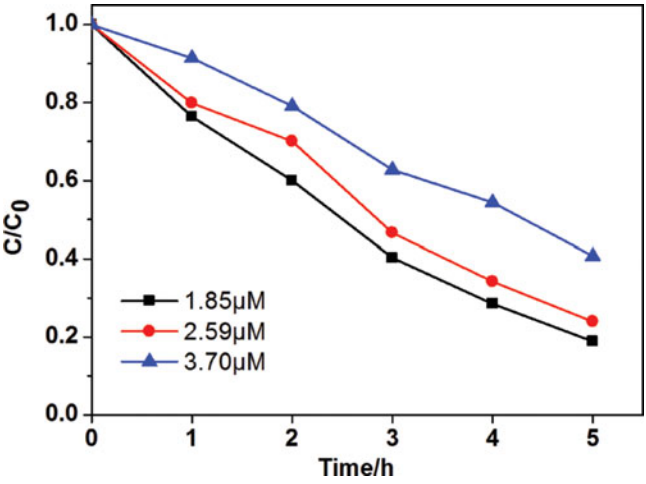

Figure 6. Photodegradation rate of E1 with different initial concentrations.

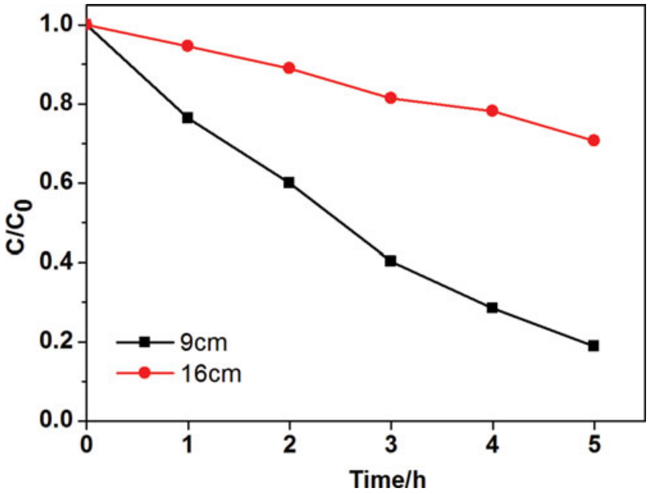

Figure 7. Photodegradation rate of E1 by different light source distance.

Therefore, UVA lamps were chosen as the light source for the photocatalytic degradation of EDCs.

Photodegradation

Figure 6 shows the degradation rates for E1 solution with different initial concentrations. As fewer E1 were included, they were more easily destroyed by the ZnO NRAs. The intensity of the light source was varied by adjusting the distance from the lamps to the solution surface. When the distance was enlarged from 9 cm to 16 cm, the irradiance intensity was decreased from 0.57 mW/cm^2 to 0.31 mW/cm^2 and the degradation efficiency was

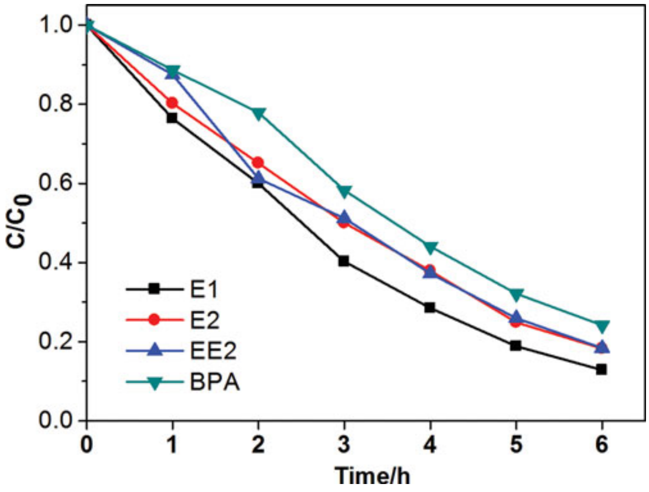

Figure 8. Photodegradation rate of E1, E2, EE2 and BPA.

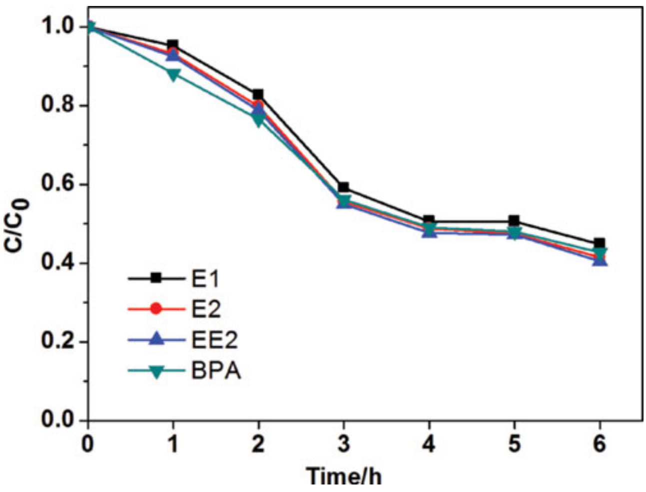

Figure 9. Photodegradation rate of multicomponent mixtures.

reduced significantly as shown in Fig. 7, indicating that the light intensity also affects the photodegradation of the EDCs.

The ZnO NRAs exhibited different photocatalytic activities when dealing with different EDCs solutions with near equal initial concentrations. As can be seem in Fig. 8, E1 is the easiest to be removed within a certain time, followed by EE2 and E2 with a similar trend. The degradation of BPA was the slowest among the EDCs.

When ZnO nanorods are irradiated by UV light with a photon energy hν higher or equal to their band gap energy, electrons will promote from the valance band to the conduction band, leaving holes behind, so the electron-hole pairs will appear. The electrons and holes will further react with H_2O and transform into hydroxyl radicals (OH•). These OH• radicals are reactive oxidative species, which will attack the EDC molecules and subsequently decompose them into CO_2 and H_2O. The holes can also directly oxidize the EDCs [4, 7].

This various photodegradation efficiency of ZnO NRAs towards different EDCs may be related to their molecular structures since it has been found that the phenol moieties of EDC molecules should be the starting point of the photocatalytic degradation [23, 24]. The BPA molecular has two phenol groups, while the others are all 18-C steroids with one phenol moiety (Fig. 1). The variation among E1, E2 and EE2 may due to the different bond numbers in the functional group at the C 17 position.

However, when the ZnO NRAs were applied to the near equimolar solution of mixed E1, E2, EE2 and BPA, the degradation rates for individuals was almost the same, as displayed in Fig. 9. The ZnO NRAs had no selective degradation in a multicomponent mixture and the competition among the EDCs is insignificant.

Conclusion

ZnO nanorod arrays have been prepared by magnetron sputtering and a hydrothermal technique. The ZnO nanorods have a wurtzite structure grown along the *c*-axis. The nanorod arrays demonstrated different photocatalytic activities towards various EDCs, but lost selectivity in a multicomponent mixture of E1, E2, EE2 and BPA.

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