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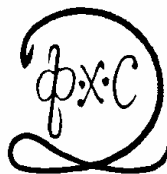
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*14th International Conference on
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Serbia*

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and

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ENHANCED PHOTO(ELECTRO)CATALYTIC PROPERTIES OF ZnO PARTICLES SYNTHESIZED BY CTAB-ASSISTED MICROWAVE PROCESSING

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ABSTRACT

ZnO/CTAB powder was prepared by microwave processing of a precipitate with the aid of cetyltrimethylammonium bromide (CTAB). The effects of CTAB on the crystal structure, morphology, optical and photo(electro)catalytic properties of ZnO particles were studied. The results showed that CTAB did not influence crystal structure or phase purity of ZnO. However, even low concentration of CTAB varies particles morphology; cone-like particles were prepared by processing without CTAB, while a mixture of spheroidal and plate-like ZnO particles were produced when 0.001 M CTAB was used. It was found that synthesized ZnO powders have ~0.10 eV lower band gap energy than bulk ZnO (3.37 eV). A high photocatalytic activity for decolorization of methylene blue water solution was established after 2 h of sunlight irradiation; efficiency was 100 and 67% for ZnO/CTAB and ZnO, respectively. Electrochemical test showed faster oxygen evolution kinetics when ZnO/CTAB was used as anode material. Enhanced photo(electro)catalytic activities of ZnO/CTAB particles are attributed to better absorption of visible light due to both, larger dimensions and surface sensitization by CTAB.

INTRODUCTION

Heterogeneous photocatalysis is recognized as an effective process for mineralization of a wide variety of organic and biological pollutants from drinking and wastewater [1]. Due to their high photoactivity and chemical inertness, semiconductors such as ZnO, TiO₂, SnO₂, etc. can be used to initiate photoreaction. Their application for the degradation of pollutants under direct sunlight irradiation is restricted by a wide band gap (> 3 eV),

allowing the absorption of UV light only. Such disadvantage can be overcome by particles' surface sensitization [1]. In this research, CTAB was used as surfactant to modify ZnO particles' surface; its influence on the optical and photo(electro)catalytic properties of ZnO powder was examined.

EXPERIMENTAL

ZnO powders were prepared by microwave (MW) processing of a precipitate. The starting materials were ZnCl_2 , NaOH, and CTAB as a surfactant. After the dissolution of zinc chloride and CTAB, an adequate amount of the aqueous solution of NaOH was added dropwise, resulting in a white precipitate. The as-prepared suspension was MW processed for 5 min in a domestic oven (2.45 GHz, 800 W). The powders synthesized without and with surfactant are designated as ZnO and ZnO/CTAB, respectively.

The phase purity and crystal structure were identified by XRD analysis (Philips PW-1050). The data were collected over a 2θ range $10\text{--}70^\circ$ with a step of 0.05° and a counting time of 5s. The particles morphology was observed by FE-SEM (ULTRA plus, Carl Zeiss). Optical properties were studied by UV-Vis diffuse reflectance (DR) (Thermo Scientific) and photoluminescence (PL) spectroscopy (Horiba Jobin Yvon).

The photocatalytic activity of ZnO particles was studied by the decolorization of methylene blue (MB) dye under direct sunlight irradiation. In each of the experiments 100 mg a powder was mixed with 100 ml of MB (10 ppm). Prior to sunlight irradiation, the suspension was magnetically stirred for 1 h in a dark to establish an adsorption-desorption equilibrium. Stirring was maintained during irradiation, too. At specific time intervals 3 ml of aliquots was withdrawn and centrifuged at 8000 rpm during 5 min. The concentration of MB after photocatalytic decomposition was determined by UV-Vis spectrophotometry (GBC Cintra) in the wavelength range of 450–750 nm. Electrochemical characterization was performed by the linear sweep voltammetry in the three-electrode quartz cell using Gamry PCI4/750. FTO glass coated by ZnO particles was used as the working electrode; Pt foil and saturated calomel electrode (SCE) were used as the counter and the reference electrode, respectively. An aqueous solution of 1 M KCl was used as the electrolyte. The scan rate was $20 \text{ mV}\cdot\text{s}^{-1}$.

RESULTS AND DISCUSSION

The XRD patterns of ZnO and ZnO/CTAB particles are shown in **Figure 1(a)**. The patterns indicate wurtzite hexagonal symmetry without other crystal phases or impurities. However, minor differences in the XRD patterns on their reflection ratios, especially on $I(100)/I(002)/I(101)$, implicating the differently oriented crystallites growth. This assumption is confirmed by the

FE–SEM analyses, **Figure 1(b-c)**. ZnO crystallites are organized in cone-shaped particles with the average length of 93 nm, while ZnO/CTAB powder is consisted of spheroidal particles with average diameter of 36 nm; the particles are scatterely organized in thin plate-like agglomerates with average width of 260 nm and thickness of 20 nm.

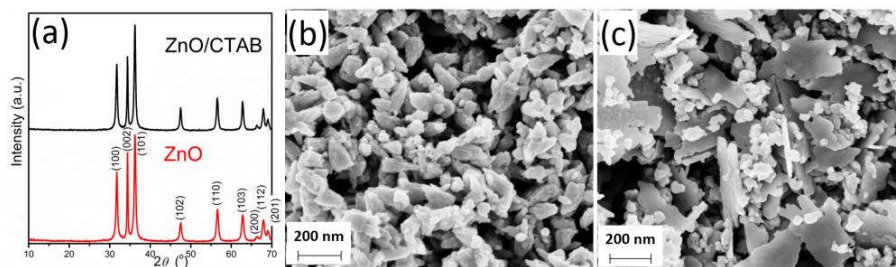


Figure 1. (a) XRD patterns, (b-c) FE–SEM images of ZnO and ZnO/CTAB particles, respectively.

The optical properties of processed powders were examined by UV–Vis DR and PL spectroscopy, **Figure 2**. In the visible light region ZnO/CTAB particles revealed ~5% higher absorbance capacity than ZnO particles, **Figure 2(a)**. The direct band gap energies, determined from Tauc plot, are about 3.25 eV with neglected difference. Two emission bands appeared in PL spectra of examined powders, **Figure 2(b)**, at 410 and 620 nm, and can be attributed to surface and deep-level defects, respectively. PL spectra implicate that ZnO/CTAB particles contained larger number of surface defects than ZnO particles, while number of structural defects is reduced.

Figure 2(c) shows the efficiency of the photocatalytic degradation of MB dye in the presence of examined powders. ZnO/CTAB shows 100% of efficiency after 2h of direct sunlight irradiation, while the efficiency of ZnO was 67%. The linear sweep voltammograms under dark was shown in **Figure 2(d)**. The oxygen evolution potential values were 1.315 and 1.324 V vs. SCE for ZnO/CTAB and ZnO, respectively. Thus, applying ZnO/CTAB as anode reduces the potential value for oxygen evolution. Besides, the anodic current at 1.35 V vs. SCE was increased when ZnO/CTAB was used as anode, indicating faster oxygen evolution kinetics comparing with ZnO.

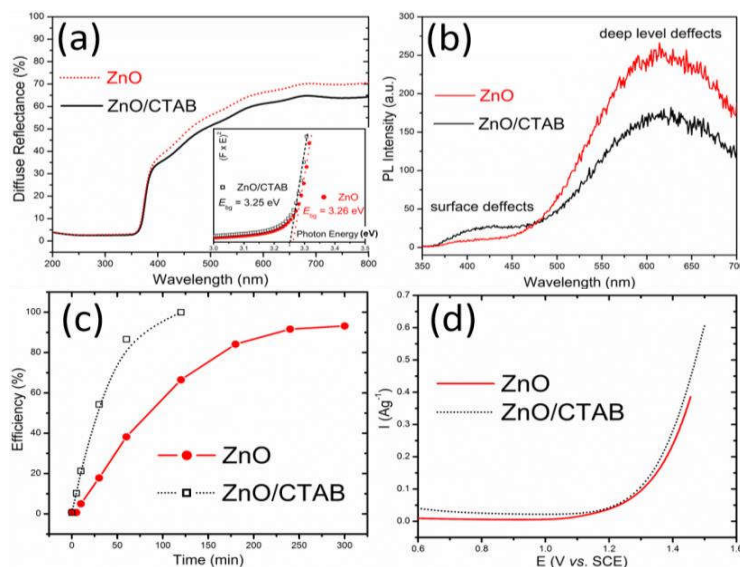


Figure 2. (a) UV–Vis DR spectra with inserted Tauc plots, (b) PL spectra of examined powders, (c) photocatalytic efficiency for the degradation of MB in the presence of examined powders, and (d) linear sweep voltammograms.

CONCLUSION

ZnO/CTAB powder prepared by a microwave processing consists mixture of spheroidal and plate-like particles with distinguished amount of surface defects. The band gap energy of ZnO/CTAB powder is 3.25 eV; in the Vis range it absorbs up to 70% of the incident light intensity. The plate-like particles' morphology combined with surface defects enhanced visible-light absorption and promoted photocatalytic activity under direct sunlight irradiation. Applying of ZnO/CTAB as anode material reduces the potential for oxygen evolution and the oxygen evolution kinetics become faster.

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