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Nanostructured ZnO photocatalysts prepared via surfactant assisted Co-Precipitation method achieving enhanced photocatalytic activity for the degradation of methylene blue dyes

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ABSTRACT

Zinc oxide nanopowders with different particle sizes have been successfully synthesized via co-precipitation method. Typically, X-ray diffraction (XRD) studies revealed that well crystalline single phase of ZnO nanopowders were formed with addition of surfactants (CTAB, AOT or PEG). SEM and TEM images of the formed ZnO nanopowders exhibited spherical structure either without or with addition of CTAB or PEG. Otherwise, the addition of AOT exhibited flower-like structure. UV–vis and PL spectrums privileged that the smaller the particle size led to the large band gap energy as well as the large the surface oxygen vacancies content. Consequently, the strongest the PL signal and the highest the photocatalytic activity were distinguished. Accordingly, The obtained ZnO nanopowders in the presence of CTAB as the cationic surfactant were the most effective in degrading the MB dye under ultraviolet (UV) light.

1. Introduction

Zinc oxide is a substantial group II–VI semiconductor with band gap energy (3.37 eV) as well as a large exciton binding energy of 60 meV at room temperature [1]. Accordingly, ZnO has been suggested as an alternative TiO_2 photocatalyst due to its commensurate electronic properties and higher photo efficiency [2]. Meanwhile, the main feature of ZnO is that it absorbs a larger fraction of the solar spectrum and larger quantum efficiency than TiO_2 [3]. In fact, the importance and advantage of addition ZnO to the structure can be noticed through the various applications occurred using the composite materials [4,5]. So, it has been considered as a promising material for water and waste treatment according to its high activity, environment-friendly merit and low cost. Subsequently, past essays have reported that ZnO can decay organic dyes such as methylene blue, Rhodamine B, methyl red and methyl orange under UV irradiation [6–10]. For instance, special attention is focused to promote the photocatalytic activity of ZnO by commanding the size of the particles, concentration of oxygen defects, and surface area. The surface defects on ZnO are a very remarkable factor affecting its photocatalytic activity [11,12]. Thereby, the defects on ZnO have been comprehensive distinguished by several modes, and their functions in the adsorption and the surface reactivity have been recognized [13–17]. In the past years, numerous access, including chemical vapor deposition [18,19], precipitation [20,21], hydrothermal [22–24], sol–gel process [25,26] and electrodeposition [27] strategies have been explored to prepare nanocrystalline zinc oxide powders with diverse microstructures and dimensions. However, all these processes demand intensive reaction considerations such as high temperature, sophisticated techniques, high purity of gas, adjustable gas flow rate, expensive raw materials and so on. Hence, it is necessary to discover a simple and cost-impact avenue for synthesis of ZnO nanoparticles. Compared with the above synthesis methods, co-precipitation method is relatively popular since it is easier, low-cost, environmentally friendly, enormous-scale production, low-temperature process and no catalyst is required [28–30]. The only disadvantage is that the materials prepared in aqueous solution are usually poor in terms of shape and size control. Fortunately, surfactants (organic additives) coupled with co-precipitation method are able to modify the surface chemistry of nanoparticles by changing their hydrophobic

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or hydrophilic properties. Therefore, the desired size and shape can be controlled [31]. Herein, in this study, a facile wet surfactant assisted chemical precipitation strategy to synthesize ZnO nanopowders in aqueous solutions as a base. Meanwhile, the effect of surfactants [cetyl trimethyl ammonium bromide (CTAB), (Bis (2-ethylhexyl) Dioctyl sodium sulfosuccinate (AOT) or poly ethylene glycol (PEG)] on the morphology, the size control and the optical properties of the ZnO nanopowders was investigated. Besides, the photocatalytic activities of ZnO nanopowders were assessed for decolorization of MB dye under UV irradiation in a batch reactor.

2. Experimental

2.1. Chemicals and materials

Zinc sulfate heptahydrate $ZnSO_4{\cdot}7H_2O$ (pure 99%, Dop Organic Chemical, Turkey), ammonium hydrogen carbonate NH_4HCO_3 (pure 99.8%, Riedel-de Haën, Germany), AOT as an anionic surfactant (pure 96.5%, Fluka), CTAB as a cationic surfactant (Fluka, 99%) and PEG polymer (Fluka, 99%)

2.2. Synthesis of ZnO nanopowders

ZnO nanopowders were synthesized by a simple co-precipitation method in the presence of different surfactants (CTAB, AOT or PEG). Four solutions are made separately, the first one containing (1 M) $ZnSO_4$ was mixed with (2 M) NH_4HCO_3 in deionized water and the other three solutions having (1 M) $ZnSO_4$ were mixed with (2 M) NH_4HCO_3 in 1000 ppm CTAB, AOT or PEG, respectively. Then, all solutions were gently stirred for 1 h separately for complete mixing and the temperature is kept at 50 °C. A white precipitate from zinc carbonate was obtained. After that, the precipitate is centrifuged and washed several times with deionized water and ethanol. Thereafter, it was dried at 60 °C for 24 h to get powder form of zinc carbonate precursor. Finally, the powder samples were calcined at 500 °C at rate of 10 °C/min in static air atmosphere and maintained at the temperature for annealed time 2 h.

The reactions can be expressed as the following:

$$ZnSO_4 + 2\ NH_4HCO_3 \rightarrow ZnCO_3 + (NH_4)_2SO_4 + CO_2 + H_2O \quad (1)$$

$$ZnCO_3 \rightarrow ZnO + CO_2 \quad (2)$$

2.3. Materials characterization

The crystal structure of ZnO samples was identified by X-ray diffraction (XRD) technique using a Brucker axis D8 diffractometer with crystallographic data software Topas 2 using Cu-Ka radiation. The crystallite size of zinc oxide powders were quantitatively estimated from XRD patterns for the most intense peak (101) based on Scherrer's formula. The particles morphology was performed using scanning electron microscopy (SEM) identified by JEOL-5410 and high resolution transmission electron microscopy (HR-TEM) recorded with a JEOL-2100 microscope. The UV–vis absorption spectrum was achieved by a UV–vis–NIR scanning spectrophotometer (Jasco-V-570 Spectrophotometer, Japan) using a 1 cm path length quartz cell. The ZnO nanostructures were ultrasonicated in deionized water to yield homogeneous dispersions and the spectrum which obtained was manipulated in determining the band gap of these samples. Pure distilled water solution was used as a blank. The photoluminescence of the colloidal solution was observed under the excitation of ZnO by UV light at 340 nm in air using an SHIMADZU RF-5301PC Fluorescence spectrophotometer, Japan (150 W xenon lamp) at room temperature.

2.4. Photocatalytic activity tests

The photocatalytic activity tests were evaluated by measuring the photocatalytic degradation of methylene blue (MB, $C_{16}H_{18}ClN_3S$) in water under the illumination of UV light using UV/Vis/NIR spectrophotometer (V-570, JASCO, Japan). The measurement of photocatalytic activity of the ZnO nanpowders were performed in homemade air-cooled photoreactor "Phocat 120.0, manufactured by SabryCorp", equipped with fifteen 8 W UVA lambs as shown in Fig. S1 (in the Supporting information). A quartz photoreactor was filled with 250 cm^3 max aqueous solution of MB at a concentration of 10^{-5} M (3.198 ppm) and mixed with 0.1 g of freshly prepared photocatalysts. UV irradiation was performed using a 150 W medium pressure Xenon lamp (Osram) immersed in a quartz jacket and equipped with a cooling tube. This lamp provides a relatively continuous light output from 250 to 700 nm, with a number of sharp lines occurring near 450 nm and above 800 nm. During the reaction, the reactor was cooled by circulation of water using cooler that attain reaction temperature at 25°C. The major absorption band of methylene blue was around 664 nm. Subsequently, in order to investigate the photocatalytic activities of ZnO, the mineralization of methylene blue was determined

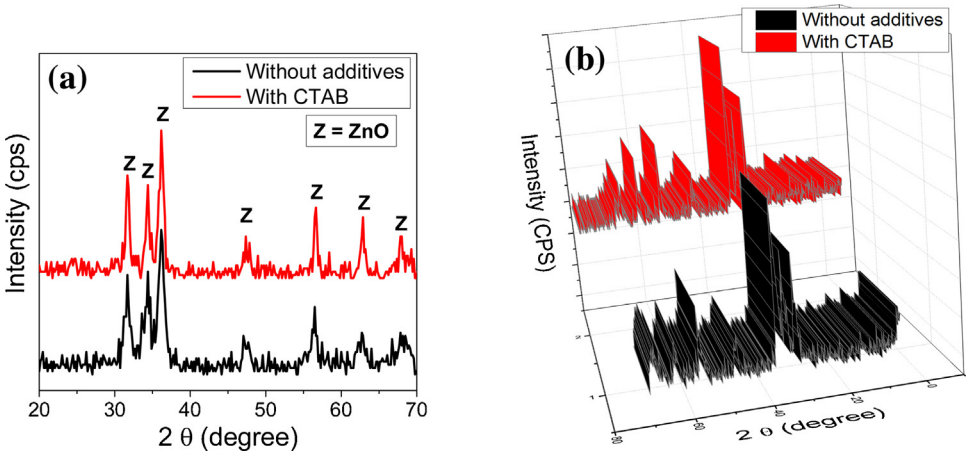

Fig. 1. (a) XRD patterns of prepared ZnO nanopowders without and with CTAB additives. (b) 3D Ribbons of the same samples show the planes and peaks of the prepared powders clearly.