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Effects of morphology on photocatalytic performance of Zinc oxide nanostructures synthesized by rapid microwave irradiation methods

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ABSTRACT

In this study, two different chemical solution methods were used to synthesize Zinc oxide nanostructures via a simple and fast microwave assisted method. Afterwards, the photocatalytic performances of the produced ZnO powders were investigated using methylene blue (MB) photodegradation with UV lamp irradiation. The obtained ZnO nanostructures showed spherical and flower-like morphologies. The average crystallite size of the flower-like and spherical nanostructures were determined to be about 55 nm and 28 nm, respectively. X-ray diffraction (XRD), scanning electronic microscopy (SEM), Brunauer-Emmett-Teller (BET), room temperature photoluminescence (RT-PL) and UV-vis analysis were used for characterization of the synthesized ZnO powders. Using BET N₂adsorption technique, the specific surface area of the flower-like and spherical ZnO nanostructures were found to be 22.9 m²/gr and 98 m²/gr, respectively. Both morphologies show similar band gap values. Finally, our results depict that the efficiency of photocatalytic performance in the Zinc oxide nanostructures with spherical morphology is greater than that found in the flower-like Zinc oxide nanostructures as well as bulk ZnO.

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1. Introduction

At present, environmental pollution has become a major threat to the lives of humans. Controlling environmental pollution will be imperative due to urban development, population growth and expanding industries. Pollutants, especially from polluted air and industrial effluents, pose a severe ecological problem as the bio-degradation of these pollutants is generally very slow and conventional treatments are mostly ineffective and not environmentally benign.

Generally, there are various processes for the purification of pollutants in both water and air. One such process for treatment of these pollutants is advanced oxidation. Producing highly active species such as hydroxyl radicals are the basis of this process. Among the advanced oxidation processes, heterogeneous photocatalysis is used as a successful method for analysis of organic pollutants. Heterogeneous photocatalysis refers to cases where the photosensitizer is a semiconductor [1–4]. Photocatalytic purification by semiconducting oxides of organic pollutants from industrial wastewater shows great potential for environmental remediation due to their peculiar and fascinating physicochemical properties [5–7], allowing the "green" mineralization of organic pollutants. By considering that under light irradiation, photocatalytic reactions mainly occur on the surface of the catalyst, for instance, a nanosize ZnO material is believed to perform much better than its bulk counterpart in photolysis processes due to a higher surface-to-volume (*S/V*) ratio. Moreover, when the size of the catalyst reaches the nanoscale, the probability of recombination of photo-generated electron-hole pairs diminishes owing to their fast arrival at reaction sites on the surface [8]. Therefore, much effort has been devoted in order to find suitable ways for controlled synthesis of various ZnO nanostructures with high *S/V* ratio [9–16].

Among various oxide semiconductor photocatalytic materials, ZnO occupies a special place due to various properties which include its photosensitive nature, non-toxicity and wide band gap. In addition to having a wide band gap (3.37 eV), ZnO also has a high activation energy [17–19]. This material has several applications in various fields such as electronics [20], catalysts [21] and optical devices [22,23]. Photocatalytic properties, oxidation and the removal of pollutants are some of the properties, which make ZnO desirable. When a photon with energy higher or equal to the band gap of ZnO is irradiated on the particle, valance band electrons are excited into the conduction band, creating electronhole pairs (EHP). When these EHPs combine, energy is released as heat or can react with an absorbed electron donor on the surface of the Zinc oxide. ZnO has a hexagonal closed pack structure where zinc atoms occupy half of the tetrahedral sites and all of the octahedral sites are empty. This yields a lot of interstitial spaces where other atoms or defects (such as $V_{\rm O}$, $V_{\rm Zn}$, $Z_{\rm NO}$ and $O_{\rm Zn}$) may exist. Therefore, ZnO typically has a significant amount of chemical defects [24–29]. These defects cause the formation of sub-bands and assist the photocatalytic property of ZnO. There are several oxidation and reduction reactions that cause the degradation of pollutants and convert them to non-toxic compounds [1,2,30,31].

Different methods have been used to synthesize variety of ZnO nanostructures in the literature [4– 37]. Here, we report the synthesis of two ZnO nanostructures (with flower-like and spherical morphologies) by a simple, fast and low cost microwave irradiation method. Microwaves are electromagnetic waves containing electric and magnetic fields propagating in the same direction perpendicular to one another. Microwave synthesis has many advantages such as fast crystallization, cost efficiency and low waste production. After interacting with matter microwaves can be reflected, passed or absorbed by the material. Polar molecules have molecular dipole moments which interact with the high frequency electromagnetic radiation. This interaction causes the molecules to vibrate and rotate which, in turn, causes the polar solution to heat [32–37]. In this study, polar molecules like water and NH₄OH were used in the synthesis of a flower-like zinc oxide, while methanol was used in synthesis of a spherical. During microwave irradiation, interaction of molecular dipole moments with the high frequency electromagnetic radiation will create heating. As-synthesized ZnO nanostructures were characterized in details in terms of their morphological, structural and photocatalytic properties by X-ray diffraction, SEM, BET, UV-visible and photoluminescence measurements. Finally, the efficiency of the morphological effect on the photocatalytic performance of synthesized ZnO nanostructures was compared.

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