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# Synthesis, characterization, and photocatalytic properties of ZnO nano-flower containing $TiO_2$ NPs

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## Abstract

In this study, $TiO_2$-impregnated ZnO nano-flowers were synthesized by one-pot hydrothermal process. Aqueous suspension containing ZnO precursor and commercial $TiO_2$ NPs (P25) is heated at 140 °C for 2 h. The morphology and structure of as-synthesized particles were characterized by field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), and X-ray diffraction (XRD), which revealed that $TiO_2$ NPs were attached on the surface of ZnO flower. It was observed that the presence of $TiO_2$ NPs in the hydrothermal solution could sufficiently decrease the size of ZnO flower. The hybrid nanostructure, with unique morphology, obtained from this convenient method (low temperature, less time, and less number of reagents) was found to be effective photocatalyst under UV-irradiation.


*Keywords:* B. Nanocomposite; Hydrothermal; Ceramic oxide; Photocatalyst

## 1. Introduction

Recent development in the area of water treatment gave birth to an improvement of the oxidative and catalytic degradation of organic compounds dissolved in aqueous media. Photocatalysis, known as green technique, offers great potential for complete elimination of toxic chemicals in the environment through its efficiency and broad applicability. Semiconductor metal oxides, such as $TiO_2$, ZnO, ZnS, CdS, $Fe_2O_3$ nanoparticles (NPs), have so far been shown to be the most promising materials in this field [1–5]. Among these semiconductor metal oxide, ZnO and $TiO_2$ (with wide band gaps of about 3.2 eV and 3.37 eV, respectively) have been recognized as the excellent materials because of their excellent electronic, chemical and optical properties with high photosensitivity and nontoxicity [6–8]. However, the rate of electron–hole (e–h) recombination during photocatalytic process limits the application of these materials under UV irradiation [5]. Furthermore, nano-sized particles (having high surface area) are found to be more effective photocatalyst but their recovery from the reaction system is very difficult, which limits their application environmentally (secondary pollution) and economically (loss of catalyst) [9]. Various attempts have been made to address the above mentioned drawback. Doping novel metal into the photocatalyst lattice [10,11] and coupling semiconductors [3,12,13] are effective ways to decrease the e–h recombination process whereas providing a fixed surface with sufficient surface area (such as polymeric nanofibers) is the way to increase its durability for repeated use. Our previous work showed that the Ag-loaded $TiO_2$/nylon-6 electrospun mat can prevent the loss of catalyst and can be repeatedly used [9].

Crystalline $TiO_2$ and ZnO, both in the pure form or as a composite, are semiconductor oxides widely used in photocatalytic reactions [14–16]. In principle the coupling of $TiO_2$

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with ZnO seems useful in order to achieve a more effective e–h pair separation under radiation and, consequently, a higher photodegradation rate. The increase of the lifetime of the photoproduced pairs, due to electron and hole transfer between the $TiO_2$ and ZnO, is invoked in many cases as the key factor for the improvement of the photocatalytic activity. Therefore, incorporating the two materials into an integrated structure is of great significance because the resulting products may possess improved physicochemical properties, which should find applications in variety of fields. But getting such structure in nano scale is still a giant challenge because of the structural complexity and difficulty in controlling the crystal growth of materials. Therefore, the suitable technique and reagents play an important role in the preparation of the photocatalyst. Several methods have been made to fabricate ZnO with $TiO_2$, which needed high temperature, long time, and more reagents [17–20].

Here, to exploit the effect of the unique shape of ZnO and incorporation of $TiO_2$ NPs to ZnO flower as well as the photocatalytic activity of hierarchical composite nanostructure, we synthesized ZnO nano flower decorated with $TiO_2$ NPs on their surface. The objective of the present study was to prepare $TiO_2$-doped ZnO flower as a photocatalyst with one-pot hydrothermal method under a short period of time and at low temperature. In this work polycrystalline powders were prepared by supporting $TiO_2$ NPs (Aeroxide P25) (P25 NPs) on the surface of ZnO nano-flower obtained from zinc nitrate hexahydrate during hydrothermal synthesis. Zinc oxide flower not only increase the photocatalytic efficiency by preventing e–h recombination process but also provide a fixed position for $TiO_2$ NPs which can prevent the loss of $TiO_2$ NPs during recovery from the reaction system. The photocatalytic activity as well as recovery of these samples for repeated use was evaluated by degradation of methylene blue (MB) solution under UV-irradiation.

## 2. Experimental procedure

### 2.1. Preparation of photocatalyst

$TiO_2$ NPs (Aeroxide P25, 80% anatase 20% rutile, average particle size of 21 nm and specific surface area of $50 \pm 15\ m^2g^{-1}$), bis-hexamethylene triamine, and zinc nitrate hexahydrate are used in this study. Pure ZnO particles were synthesized by hydrothermal treatment of aqueous suspension of the mixture of bis-hexamethylene triamine and zinc nitrate hexahydrate. Here, 0.5 g of bis-hexamethylene triamine in 50 g water and 0.75 g zinc nitrate hexahydrate in 50 g water were mixed and slurry was made by vigorously stirring which was then taken into a Teflon crucible and kept inside the autoclave. Similarly, the hybrid nanocomposite was prepared by adding 20 mg of $TiO_2$ NPs in the aforementioned solution. In each case, the autoclave with Teflon crucible (containing solution) was kept at 140 °C for 2 h. The obtained product after cooling was filtered off, washed several times by distilled water and alcohol, and dried at 60 °C for 12 h before analysis.

### 2.2. Characterization

The morphology of the as-prepared pristine ZnO and $TiO_2$/ZnO nanocomposite was observed by using FE-SEM (S-7400, Hitachi, Japan). High resolution images of different NPs were obtained via transmission electron microscopy (TEM, JEM-2010, JEOL, Japan). In addition, TEM (JEM-2200, JEOL, Japan) was used for selected area electron diffraction (SEAD) and line EDX of composite particles. Information about the phase and crystallinity was obtained with a Rigaku X-ray diffractometer (XRD, Rigaku, Japan) with Cu Kα ($\lambda$ = 1.540 Å) radiation over Bragg angles ranging from 10 to 80°. The photocatalytic activity of pristine ZnO flower, $TiO_2$ NPs (P25) and $TiO_2$-doped ZnO nano-flowers was evaluated by observing the degradation of MB dye solution. The process was carried out in a Petri dish which was equipped with an ultraviolet lamp ($\lambda$ = 365 nm). The distance between Petri dish and UV lamp was 5 cm. In each case, 25 ml of dye solution (10 ppm concentration) and 20 mg catalyst were mixed to make suspension by stirring. After 15 min stirring, the dye degradation test was carried out without stirring. At specific time intervals, 1 ml of the sample was withdrawn from the system and centrifuged to separate the residual catalyst, and then the absorbance intensity was measured at the corresponding wavelength. For cycling use experiments, $TiO_2$/ZnO NPs were separated from suspended solution by repeated centrifuging and washing.

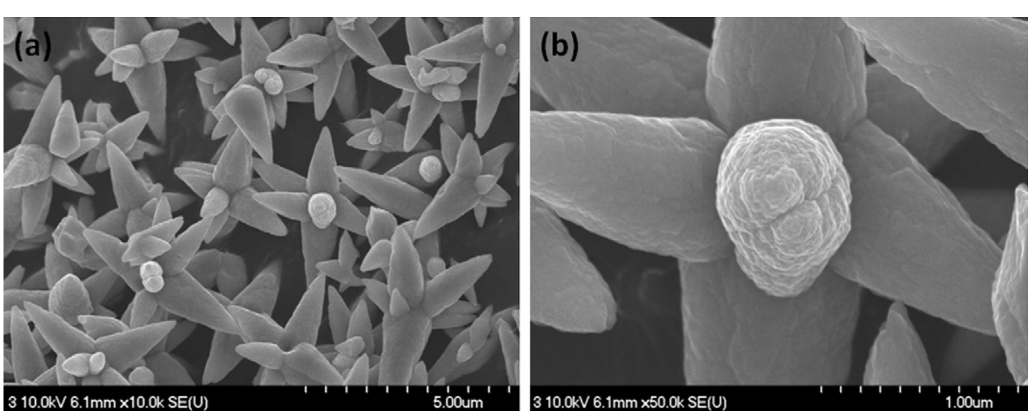


Fig. 1. (a) Low and (b) high magnification FE-SEM image of pristine ZnO micro-flowers.