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

Hem Raj Pant [a,b,1,**], Chan Hee Park [a,1], Bishweshwar Pant [a], Leonard D. Tijing [c], Hak Yong Kim [a], Cheol Sang Kim [a,c,*]

[a] Department of Bionanosystem Engineering, Chonbuk National University, Jeonju 561-756, Republic of Korea
[b] Department of Engineering Science and Humanities, Institute of Engineering, Pulchowk Campus, Tribhuvan University, Kathmandu, Nepal
[c] Division of Mechanical Design Engineering, Chonbuk National University, Jeonju 561-756, Republic of Korea

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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

* Corresponding author at: Department of Bionanosystem Engineering, Chonbuk National University, Jeonju 561-756, Republic of Korea. Tel.: +82 632704284; fax: +82 632702460.
** Corresponding author at: Department of Bionanosystem Engineering, Chonbuk National University, Jeonju 561-756, Republic of Korea. Tel.: +82 632704284; fax: +82 632702460.
E-mail addresses: hempant2002@yahoo.com (H.R. Pant), chskim@jbnu.ac.kr (C.S. Kim).
[1] These authors contributed equally to this work.

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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 ultra-violet 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.

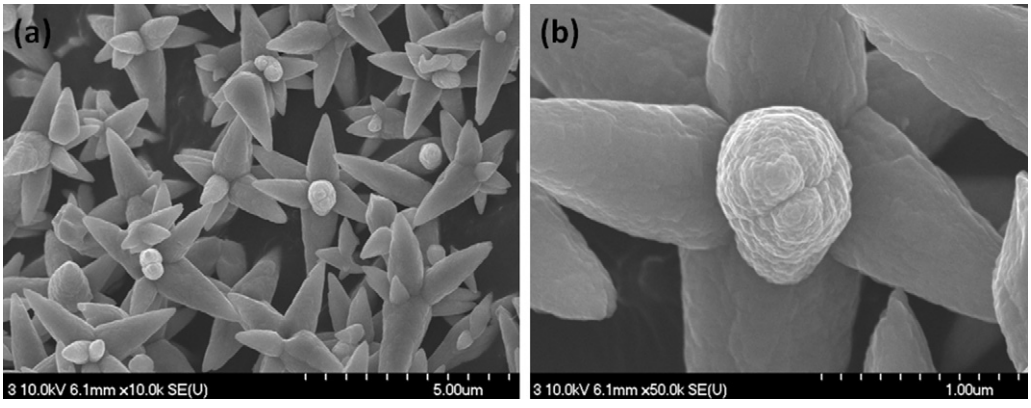

Fig. 1. (a) Low and (b) high magnification FE-SEM image of pristine ZnO micro-flowers.

3. Results and discussion

Figs. 1 and 2 show the morphology of obtained pristine ZnO micro-flower and TiO_2 doped ZnO nano-flower, respectively. It is clear from the FE-SEM images (Figs. 1 and 2) that the pristine ZnO particles are flower-like micro size particles whereas the TiO_2 impregnated ZnO particles are in nano size, even though they were obtained from the same hydrothermal

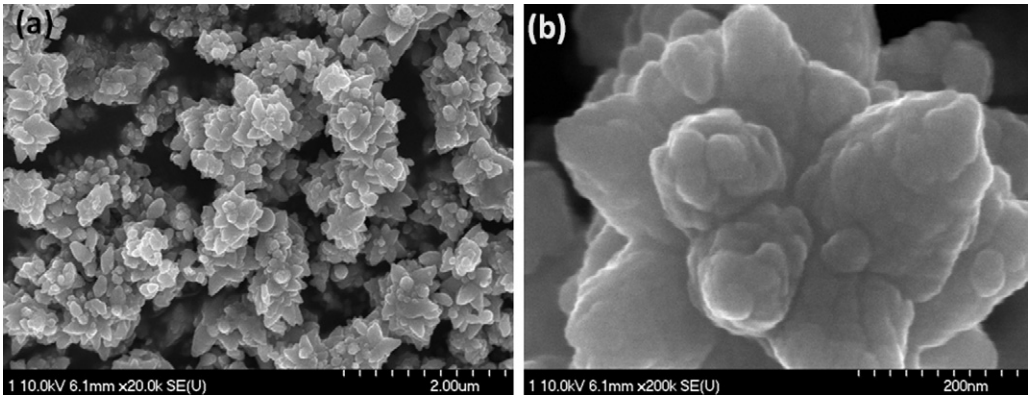

Fig. 2. (a) Low and (b) high magnification FE-SEM image of composite TiO_2/ZnO nano-flowers.

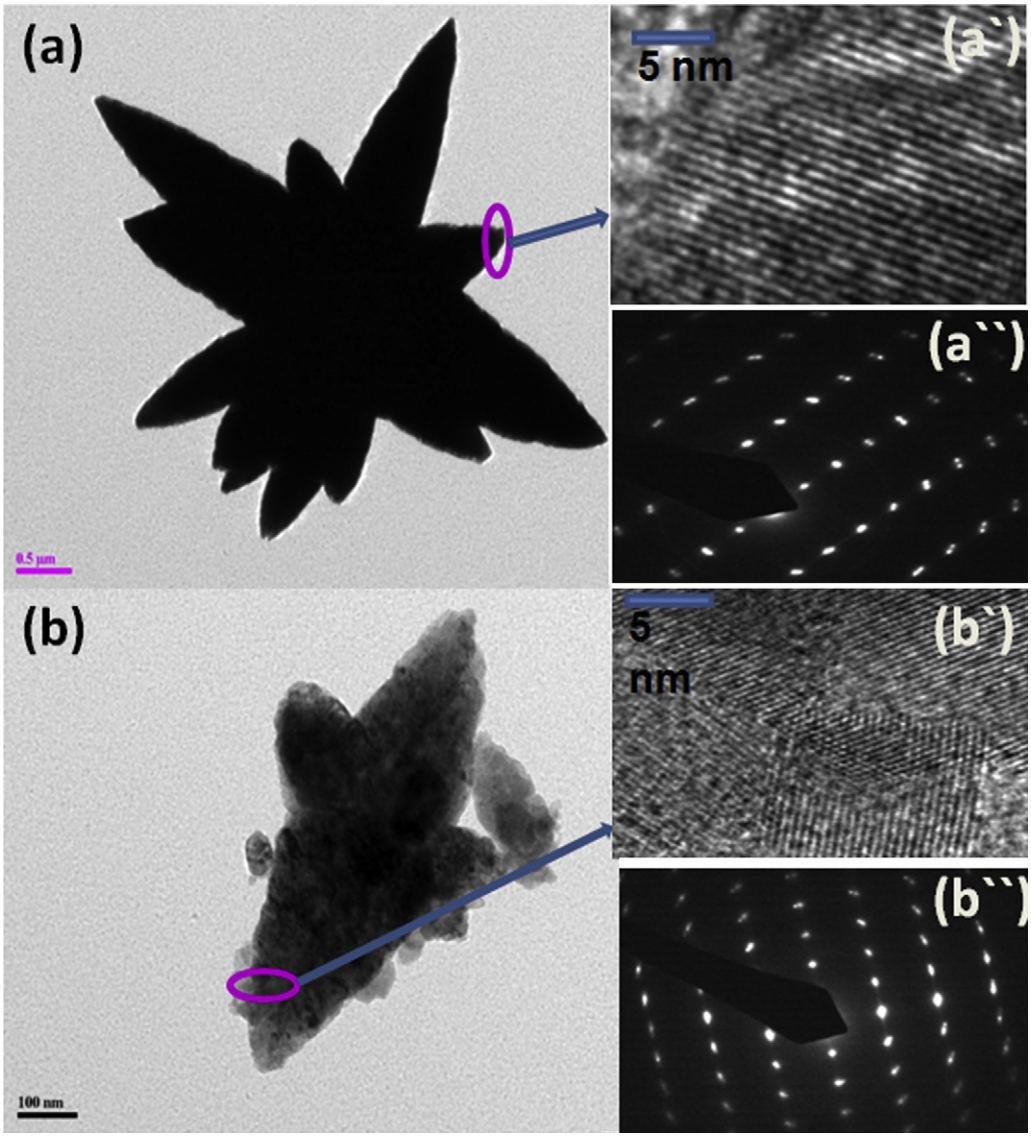

Fig. 3. TEM images of (a) pristine ZnO micro-flower and (b) composite TiO_2/ZnO nano-flower. Their upper and lower insets are respective HRTEM and SAED pattern.

condition. The addition of TiO_2 NPs in the system not only sufficiently decreased the size of zinc flower but also attached themselves on the surface of ZnO flowers without aggregation (Fig. 2). The formation of ZnO particles and their growth might be hindered when TiO_2 NPs were present in hydrothermal system. The good dispersion of TiO_2 NPs with ZnO precursor in hydrothermal solution can allow simultaneous deposition of TiO_2 NPs on the surface of in situ formed ZnO flower.

Transmission electron microscope analysis (TEM) can be used to examine the morphology as well as crystalline and amorphous state identification of the materials. Structural characterization of the as-prepared pristine ZnO flowers is shown in Fig. 3a, a′ and a″. The low-magnification TEM image (Fig. 3a) reveals a unique flower-shaped morphology, which is consistent with FE-SEM images (Fig. 1). Fig. 3a′ shows the high-resolution TEM image of the marked area and indicates the uniform distance between the two consecutive planes. Fig. 3a″ shows the SAED pattern of the marked area of Fig. 3a, which indicates that the flower-shaped ZnO grown are free from structural defects such as dislocation and stacking faults. Similarly, Fig. 3b shows the TEM results for the TiO_2 decorated ZnO nano-flower obtained from the hydrothermal process. As shown in Fig. 3a, some particulate outgrowths are seen everywhere on the surface of the flower, which is consistent with FE-SEM images in density, morphology, and dimension. Fig. 3b″ shows the HRTEM image for the marked area of Fig. 3b; the existence of two different type of parallel atomic planes not only reveals excellent crystallinity but also proved the coupling of two different ceramic oxides. Furthermore, the SAED results in Fig. 3b″confirm the excellent crystallinity of the nanocomposite; as shown in this pattern, no dislocation or imperfections could be detected. To investigate the homogeneous distribution of TiO_2 and ZnO along the produced nanocomposite, linear analysis TEM-EDX was utilized. Fig. 4 shows that both TiO_2 and ZnO are found along the selected line which confirmed that both oxides are mixed at the crystalline level.

The crystalline structure of the as-prepared pristine ZnO and TiO_2/ZnO nanocomposite with the corresponding 2θ values and crystal planes are presented in Fig. 5a. The apparent peaks at 2θ values of 31.8, 34.5, 36.4, 47.6, 56.6, 62.8, 66.3, 68.1, 69, and 76.8° correspond to the crystal planes of (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (2 0 0), (1 1 2), (2 0 1), and (2 0 2), conforming the formation of pure ZnO, which were found to be similar to that reported in literature [21]. The presence of sharp peak at $2\theta = 24.6°$ (crystal plane 101, for rutile phase of TiO_2) [22] in nanocomposite revealed that TiO_2 is well-doped on the surface of ZnO nano-flower. Furthermore, the shifting of 2θ peaks of ZnO towards lower values in nonocomposite flower is an indication of the mixing of two oxides in crystalline level. The amount of TiO_2 doped on the surface of TiO_2/ZnO nanocomposite was evaluated by general TEM-EDX as shown in Fig. 5b, The atomic wt% of Ti (4.09) indicated that sufficient numbers of TiO_2 NPs were attached with the ZnO particles during the hydrothermal process. This result confirms the incorporation of TiO_2 NPs in ZnO flower and simultaneously supports the XRD analysis.

In order to elucidate the effect of coupling of TiO_2 with ZnO particles, photocatalytic activity of pristine ZnO and TiO_2/ZnO nanocomposite was measured by using MB dye. Fig. 6 shows the effect of TiO_2 doping on the surface of ZnO nano-flower for the photodecomposition of MB. It clearly shows that the efficiency of pristine ZnO particles is greatly increased by the deposition of TiO_2 NPs. Result showed that TiO_2/ZnO composite nano-flower had greater photocatalytic efficiency than that of P25, eventhough the size of composite nano-flowers is far greater than that of P25. The higher photocatalytic activity of TiO_2/ZnO composite nano-flower is related to the role of

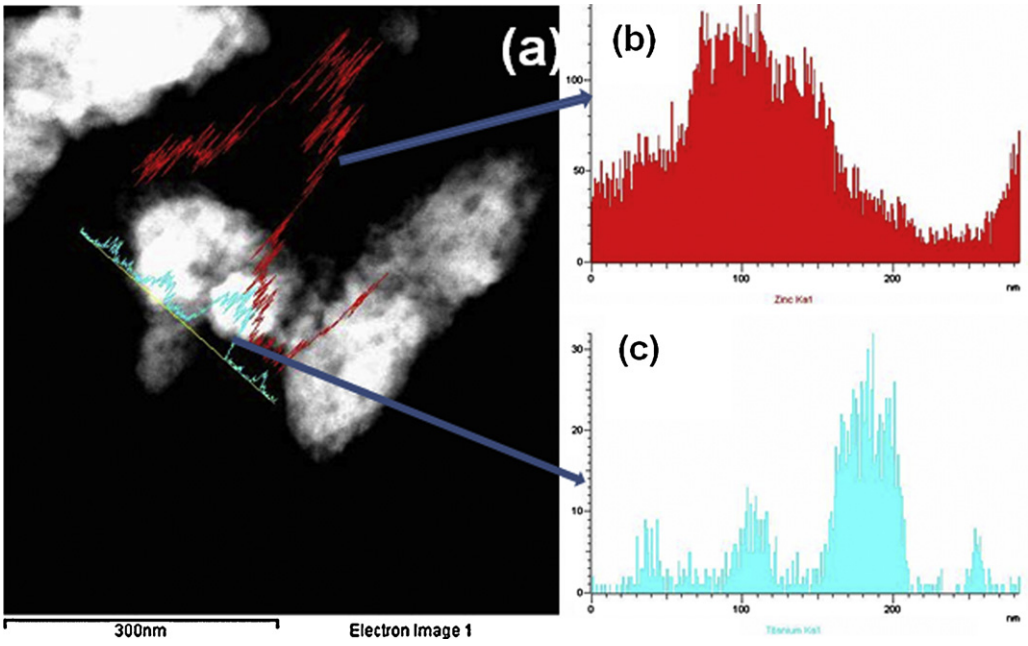

Fig. 4. (a) TEM image of nanocomposite along with the line TEM-EDX, (b) for ZnO and (c) for TiO_2.

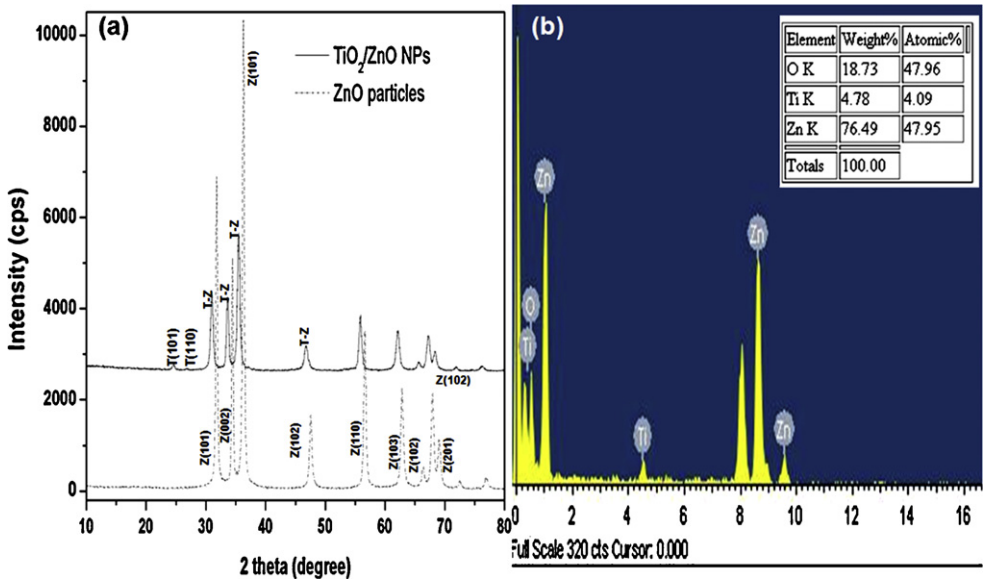

Fig. 5. (a) XRD patterns of prepared samples, and (b) TEM EDX showing atomic wt% of different atoms in TiO_2/ZnO nanocomposite.

TiO_2 on the surface of ZnO flower. Here, the electron transfer occurs from the conduction band of light activated TiO_2 to the conduction band of light-activated ZnO and, conversely, hole transfer can take place from the valence band of ZnO to the valence band of TiO_2 [3,23]. This efficient charge separation increases the photocatalytic activity of TiO_2/ZnO nano-flower. To further support the superiority of composite nano-flower, photoluminescence (PL) spectra were recorded for different particles (Fig. 7). It is clear that ZnO exhibited higher emission intensity than P25 and composite particles. Furthermore, with compared the intensity of P25, composite nano-flowers exhibited lesser emission intensity. The PL emission intensity is related to the recombination of excited electrons and holes, and thus, the lower emission intensity is inductive of a decrease in recombination rate [24]. The proper attachment of P25 NPs on the surface of ZnO nano-flower, during hydrothermal growth of ZnO particles, can play an important role in efficient charge separation [23]. In composite TiO_2/ZnO nano-flower, the presence of a TiO_2/ZnO heterojunction may decrease the recombination of e–h pairs. This increases the availability of the electrons (holes) to migrate to the TiO_2 (ZnO) surface of the composite photocatalysts and consequently improves the occurrence of redox process (electrons reduce dissolved molecular oxygen to superoxide radical anions while holes forms hydroxyl radicals). Organic molecules present in aqueous solution will then react with these oxidizing agents to induce degradation to CO_2 and H_2O [25]. The higher photocatalytic activity of composite nano-flowers may also be related to the decreased particle size (higher surface area) of ZnO in composite as compared to the pristine ZnO (Figs. 1 and 2) [26]. Initially, the photocatalytic activity of TiO_2/ZnO was found significantly better than P25 NPs. However, after certain time interval the difference in the efficiency of these two NPs was decreased (Fig. 6), which reveals that the composite NPs

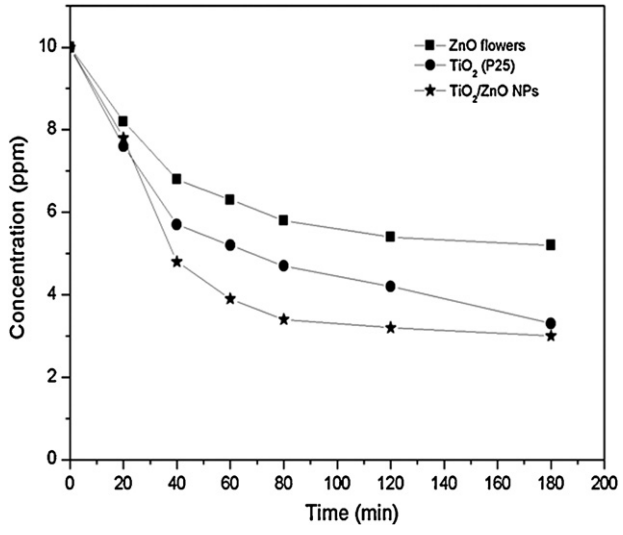

Fig. 6. Comparison of the MB photodegradation in different specimen under UV radiation.

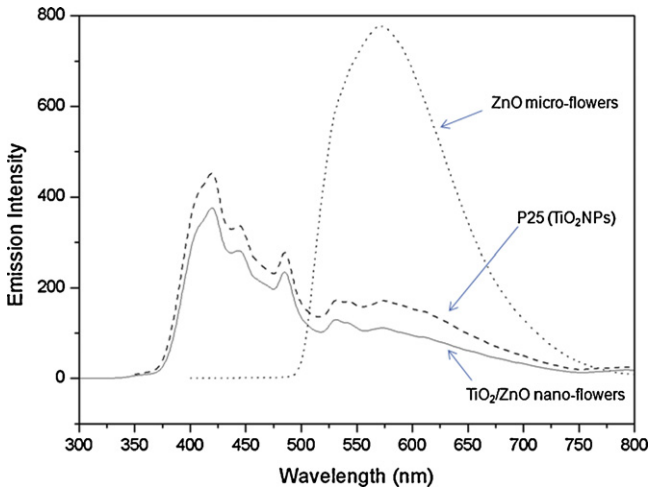

Fig. 7. Photoluminescence (PL) emission spectra of different photocatalysts.

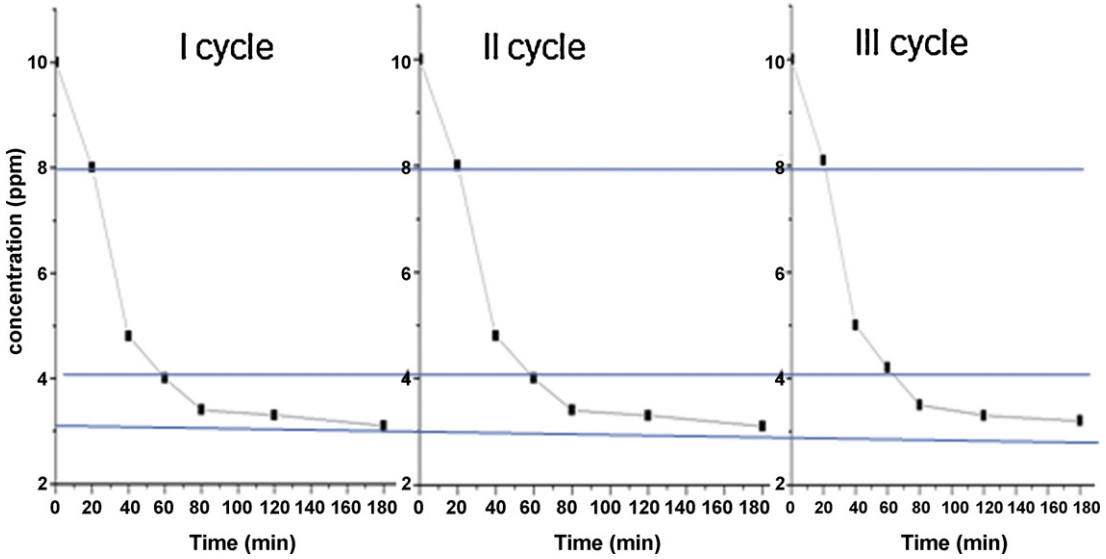

Fig. 8. Catalytic reusability efficiency of TiO_2/ZnO nanocomposite up to three-cycles.

were sedimented where as P25 NPs were still well distributed throughout the suspension. Because our aim is to make a cost effective photocatalyst which can be easily recovered from the reaction system, we performed the separation ability of nanocomposite and their efficiency in recycle use. As shown in Fig. 8, after a three-time recycling of nanocomposite, there is no significant decreased in photodegradation of MB in the aqueous solution upon UV-irradiation. We observed a slight decrease in the photocatalytic efficiency of the reused composite, which may be due to the deposition of the by-product particles on the surfaces of the NPs. TiO_2 forms a milky white turbid suspension in aqueous media, when it is used as photocatalyst. It does not settle quickly, which hinders its separation from the reaction mixture. The TiO_2 NPs that remain in natural water after the reaction are toxic to humans [27]. We performed a recovery of different photocatalysts from their

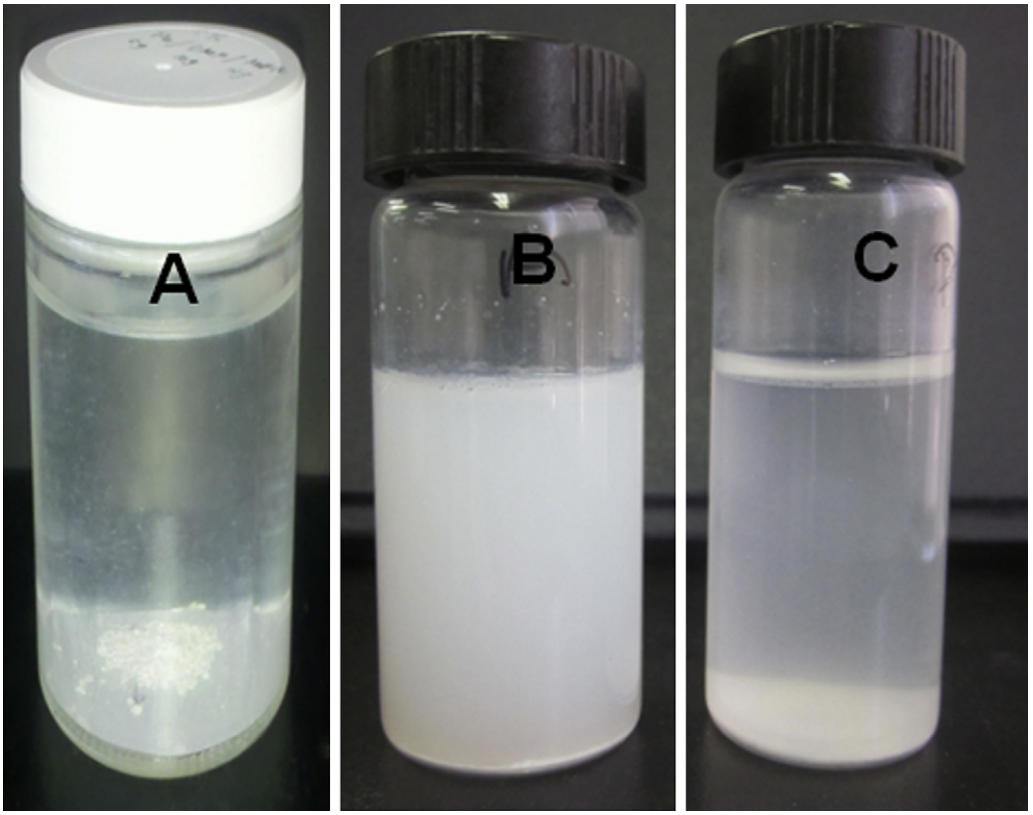

Fig. 9. Sedimentation for 2 h in aqueous suspension of (A) ZnO micro-flowers, (B) TiO_2 (P25) NPs, and (C) TiO_2/ZnO nano-flowers (ultrasonic treatment of suspension was carried out for 15 min).

aqueous suspension at same concentration. For this, equal amount of prepared ZnO micro-flowers, commercial TiO_2 (P25) NPs, and as-prepared TiO_2/ZnO nano-flowers were taken in to the same volume of distilled water and suspension was made by ultrasonic treatment for 10 min. The solutions were kept for sedimentation and photograph was taken at 2 h of sedimentation (Fig. 9). It clearly shows that almost all ZnO micro-flowers and TiO_2/ZnO nano-flowers sediment in the aqueous solution within 2 h, while the aqueous solution of TiO_2 (P25) is still relatively turbid. This result indicates that the larger sized ZnO nano-flower can provide the surface to TiO_2 NPs and allow recovering easily from the reaction system after completion of photocatalytic reaction. Therefore, the doping of TiO_2 with ZnO can prevent the loss of photocatalyst. The nanocomposite material obtained by this simple method may have great commercial potential as an environmentally friendly photocatalyst.

4. Conclusion

In this study, a very simple technique (performed at low temperature, less time, and from few reagents) is presented to prepare a flower-like TiO_2/ZnO composite photocatalyst by hydrothermal process. Uniquely shaped ZnO nano-flowers not only provide the fixed surface to the TiO_2 NPs but also prevent the e-h recombination process. The well-attached TiO_2 NPs on the surface of ZnO prevent the agglomeration of TiO_2 NPs in aqueous solution as well as the lost of the photocatalyst during reaction. The prepared material has high photocatalytic efficiency, good ability to be recovered from the reaction system after reaction, and is an economically and environmentally friendly photocatalyst.

Acknowledgments

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