



Preparation of TiO₂ Coated ZnO Nanocomposite by a Two-Step Chemical Method

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Nanocrystalline TiO₂ coated ZnO particles were synthesized by a two-step chemical method, which were prepared by the polymerization of ZnO nanoparticles and followed by a sol-gel coating with a TiO₂ nanolayer. The variation in zeta potential of ZnO and TiO₂ with pH exhibited isoelectric points (IEP) at 9.3 and 3.5, respectively. The ZnO particles coated with TiO₂ nanoparticles show a uniformly dispersed morphology without any agglomeration. The average particle size of ZnO particles coated with TiO₂ particles was *ca.* 120-140 nm. The size of the ZnO particles was 100 nm and the size of the TiO₂ coating was below 10-20 nm. The size, morphology, composition and structure of the nanocrystalline TiO₂ coated ZnO particles were characterized by TG/DTA, XRD, SEM, EDS and TEM in detail.

Key Words: Nanocrystalline, TiO₂ coated ZnO, Two-step chemical method, Interdependent attraction.

INTRODUCTION

In recent years, semiconductor photocatalysis has attracted a great deal of research attention due to its potential application to solve environmental problems^{1,2}. Among the various semiconductors employed, TiO₂ is a versatile material and good photocatalyst for the degradation of environmental contaminants due to its high photocatalytic activity, absence of toxicity, relatively low cost and excellent chemical stability under various conditions^{3,4}. The excellent photocatalytic property of TiO₂ is due to its wide band gap and the long lifetime of photogenerated holes and electrons. With an appropriate light source, the TiO₂ photocatalyst generates electron/hole pairs to initiate the chemical reactions that eventually mineralize the pollutants^{5,6}. As another photocatalyst, ZnO has unique electrical and optical properties that have many important applications, such as for transparent conducting films, waveguides, ultraviolet lasers, solar cells, photocatalysts and varistors⁷. In particular, it has played an important role as a semiconductor for photocatalytic degradation of environmental pollutants, because its photodegradation mechanism has been shown to be similar to that of TiO₂^{8,9}. The band gap energy of ZnO is similar to that TiO₂ (*ca.* 3.2 eV)¹⁰.

Since a photocatalytic process is based on the generation of electron/hole pairs by means of band-gap radiation, the coupling of different semiconductor oxides seems useful to achieve a more efficient electron/hole pair separation under irradiation and a higher photocatalytic activity¹¹. Thus, it is possible to enhance the activity of a TiO₂ photocatalyst by

means of ZnO coupling. Moreover, the electronic excitation of TiO₂ nanoparticles needs a higher input energy when the particle size decreases because of the quantum size effect¹². Therefore, it is highly desirable to synthesize TiO₂ nanoparticles with a high photocatalytic activity. TiO₂/ZnO nanocomposites have strong physical and chemical interactions with adsorbed species and have a variety of applications as gas sensing materials, thermoelectric materials, dye-sensitized solar cells, piezoelectric devices and semiconductor photocatalyst¹³⁻¹⁷.

The physical, chemical and photochemical properties of the TiO₂/ZnO composites formed are dependent on the manufacturing method. To enhance the photodegradation efficiency of TiO₂ catalyst, coupled semiconductor photocatalysts TiO₂/ZnO have been prepared by several different processes, such as a solid-state reaction method^{11,14}, thermal evaporation^{12,13}, a hydrothermal reaction^{18,19}, magnetron sputtering^{19,20}, templating^{21,22}, electro spinning²³ and a sol-gel process^{17,24-27}. For a large variety of coupled nanocrystalline TiO₂/ZnO systems, the particles adhere to each other in so-called sandwich structures or present a core/shell geometry. There are some investigations on core/shell structured TiO₂/ZnO. Zhang *et al.*¹², suggested that anatase TiO₂/ZnO nanoparticles at a size of 6 nm were immobilized on single-crystalline tetrapod-like ZnO with dimensions up to 20-50 μm produced by a vapour hydrolysis method. The sol-gel process has notable advantages such as high purity, good uniformity of the microstructure, low temperature synthesis, easily controlled reaction condition and hence has been widely adopted for preparing nanostructured TiO₂/ZnO composite.

However a few studies have been focused on the sol-gel system combined with polymerization complex method. In this study, ZnO nanoparticles were coated with TiO₂ nanolayers by a simple wet chemical route. Generally, in order to maintain high photocatalytic properties, the inorganic particles should be small and highly distributed uniformly with a spherical particle morphology. In this study, nanocrystalline TiO₂ coated ZnO particles were synthesized by two-step chemical method. ZnO nanoparticles were synthesized *via* polymerization complex method and TiO₂ nanolayers were coated on the surface of ZnO nanoparticles by a sol-gel route. The nanocomposite TiO₂/ZnO prepared was characterized in detail by means of TG/DTA, XRD, SEM, EDS and TEM.

EXPERIMENTAL

Nanocrystalline TiO₂ coated ZnO particles were synthesized by a two-step chemical method. ZnO nanoparticles were prepared by a polymerization complex method and TiO₂ nanopowders by a sol-gel method. For the ZnO nanoparticles by the polymerization complex method, zinc nitrate hexahydrate [Zn(NO₃)₂·6H₂O, Junsei Chemical, Japan] was used as a metal cation source, citric acid (CA, HOC(CO₂H)(CH₂CO₂H)₂, Yakuri Oure Chemical, Japan) for a chelating agent and ethylene glycol (EG, HOCH₂CH₂OH, Tedia, USA) for a solvent. Ethylene glycol and citric acid with a molar ratio of 20:5 were heated in a microwave oven for 3 min in order to increase the solubility and mixed thoroughly until the mixture became a transparent solution without any observed precipitation. One mole of zinc nitrate hexahydrate was then added to this transparent solution and was mixed in the microwave oven until a transparent solution was once again obtained. The transparent reactants were stirred at 200 °C for 3 h inducing a polyester reaction. During this time the solution transformed gradually from a transparent liquid to a highly viscous black gel. The polymeric precursor was obtained by heating this polymerized complex in a drying oven at 250 °C for 24 h. ZnO nanoparticles were obtained after a calcination process at a temperature of 700 °C for 24 h.

For the TiO₂ nanopowders produced by a sol-gel method, titanium tetra-isopropoxide (TTIP) was used as a metal precursor and isopropyl alcohol (IPA) as a solvent. Both were mixed in a molar ratio of 1:10 and stirred for 1 h. Another solution was prepared from a mixture of H₂O and isopropyl alcohol with a molar ratio of 10:1. This solution was then titrated into the TTIP-IPA solution and stirred for 2 h until a uniform colloidal TiO₂ sol was produced. The TiO₂ sol obtained was analyzed in the neutral pH range by thermogravimetry/differential thermal analysis (TG/DTA, SDT-2960 TA instrument, USA).

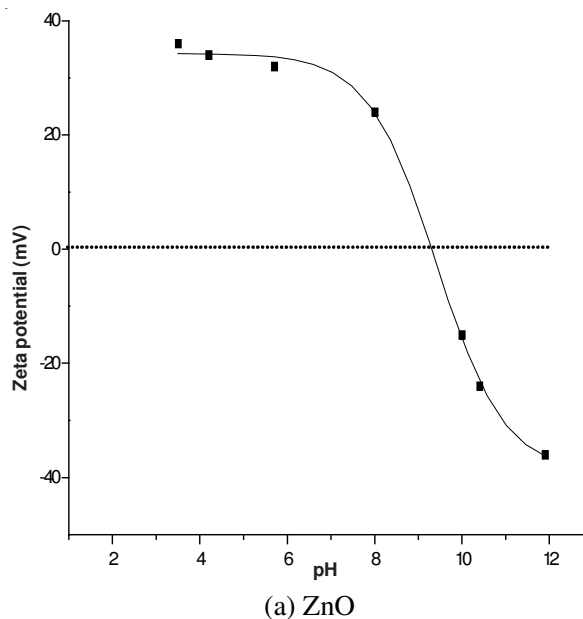
For the production of TiO₂ coated ZnO nanopowders, the difference in surface charges is associated with variations in pH to produce a uniform coating of colloidal TiO₂ on the surface of ZnO particles. TiO₂ sol is chemically very unstable in the neutral pH range and therefore it easily agglomerates when it transforms into the gel state. However, this instability can be controlled by adding an acid. The TiO₂ sol was maintained at pH 3 by adding HCl. The ZnO nanoparticles were mixed with IPA and HCl. The TiO₂ sol yielded 5.5 % of crystallized particles after volatilization of the organic species, H₂O

and alcohol radicals during the heat treatment. Taking this percent yield into account, TiO₂ sol and IPA were mixed together in order to produce TiO₂ and ZnO particles with a weight ratio of 1:10. Mixing these components resulted in a colloidal suspension of ZnO and TiO₂.

The absorption process between the two heterogeneous particles was then initiated. After heat treatment in a drying oven at 250 °C for 24 h, TiO₂ coated ZnO nanoparticles were obtained by calcination at 500 °C for 3 h. The crystallization temperature, particle size and morphology were investigated using an X-ray diffractometer (XRD, Rigaku Denki, Japan, 40 kV, 30 mA, 5 min⁻¹), scanning electron microscopy (SEM, JSM-5900LV, Jeol, Japan) and energy dispersive X-ray spectroscopy (SEM-EDS). Furthermore, transmission electron microscopy (TEM, 2000FX2, Jeol, Japan) and selected area electron diffraction (TEM-SAED) were employed to investigate the coating state and composite particle morphology.

RESULTS AND DISCUSSION

Fig. 1 shows the difference in surface charges associated with variations in the pH. Heterogeneous particles, which are electrically charged with '+' and '-', bond interdependently by strong Coulomb attraction and the degree of agglomeration is related to the neutralization of these charges. The variation in zeta potential of ZnO in Fig. 1(a) and TiO₂ (b) with pH exhibited their isoelectric points (IEP) at 9.3 and 3.5, respectively. In order to obtain a maximum surface charge difference between the ZnO and TiO₂ particles, NH₄OH was added until a neutral pH was obtained (this was the average between the pH state of the two solutions). Fig. 2 shows the TG-DTA curves for the TiO₂ sol heated from room temperature to 900 °C in air. The weight loss begins above 300 °C and continues up to 450 °C, resulting from the evaporation and the combustion of organic species. This region corresponds to the DTA result of an exothermic peak for the crystallization of TiO₂. It is assumed that the nuclei of TiO₂ produced near 450 °C and the growth of particles was propagated with increasing temperature.



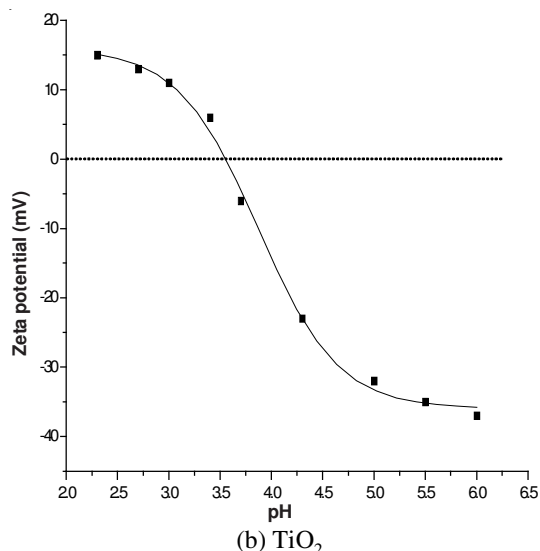


Fig. 1. Variation of the zeta potential with pH value showing the isoelectric points (IEP) at (a) pH 9.3 of ZnO and (b) pH 3.5 of TiO₂, respectively

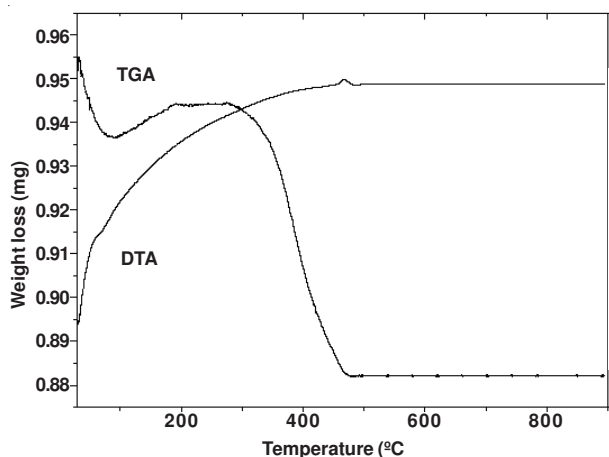


Fig. 2. TG-DTA curves for the TiO₂ sol heated from room temperature to 900 °C in air

Fig. 3 shows XRD result of the prepared ZnO particles heat-treated at 700 °C. The crystalline peaks marked by their Miller indices (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) and (202) were identified as a pure hexagonal ZnO with a wurtzite structure (JCPDS No. 36-1451). Fig. 4 shows TEM images of (a) ZnO particles prepared by the polymerization complex method heat treated at 700 °C and (b) TiO₂ particles by the sol-gel method heat-treated at 500 °C. The ZnO particles in Fig. 4(a) show a uniformly spherical shape with a size of 120-140 nm, while the TiO₂ particles in Fig. 4(b) show a homogeneous morphology with a size of 10-20 nm, approximately.

Fig. 5 shows XRD patterns of the TiO₂ coated ZnO nanoparticles prepared at 500 °C indicating the A (anatase TiO₂), R (rutile TiO₂) and Z (ZnO). After TiO₂ coating, the XRD pattern had some significant changes and characteristic peaks for anatase and rutile TiO₂ crystalline were observed. The 2θ peaks at about 31°(100), 34°(002) and 36°(101) represent the major peaks of ZnO and a major peak of the metastable anatase TiO₂ phase at 25°. On the other hand, the peaks of the stable rutile TiO₂ phase, which is more stable at higher temperatures, are weaker than the peaks from the anatase phase.

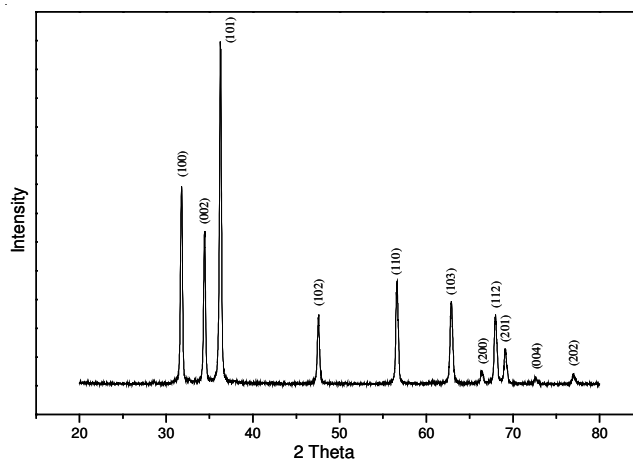
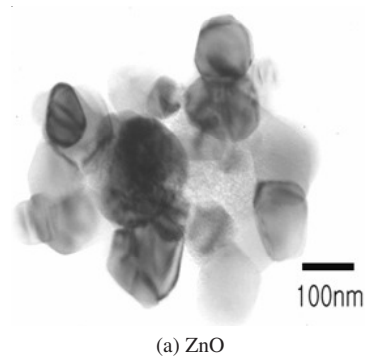
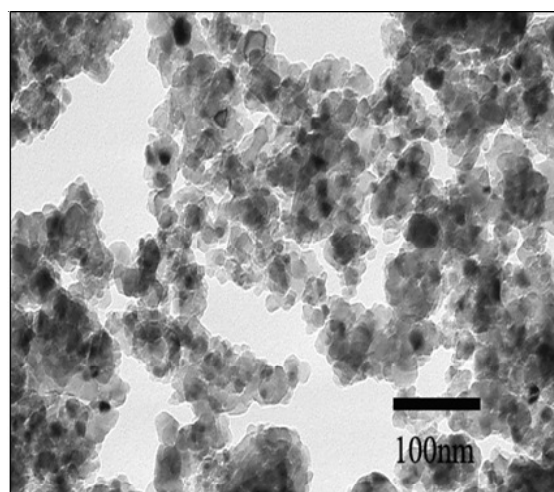


Fig. 3. XRD result of the prepared ZnO particles heat-treated at 700 °C



(a) ZnO



(b) TiO₂

Fig. 4. TEM images of (a) ZnO particles prepared by the polymerization complex method heat treated at 700 °C and (b) TiO₂ particles by the sol-gel method heat-treated at 500 °C

Fig. 6 shows a SEM image of TiO₂ coated ZnO nanoparticles (a) and compositional data using EDS (b). The insert in Fig. 6(a) shows at high magnification the morphology of a TiO₂ coated ZnO nanoparticle. The SEM image of the ZnO particles coated with TiO₂ nanoparticles in Fig. 6(a) shows a uniformly dispersed morphology with a size of 120-140 nm, without any agglomeration. It is emphasized, that the driving force controlling this coating process as described in Fig. 1, is electrical, as a consequence of Coulomb attraction resulting from induced charges on each component in the neutral

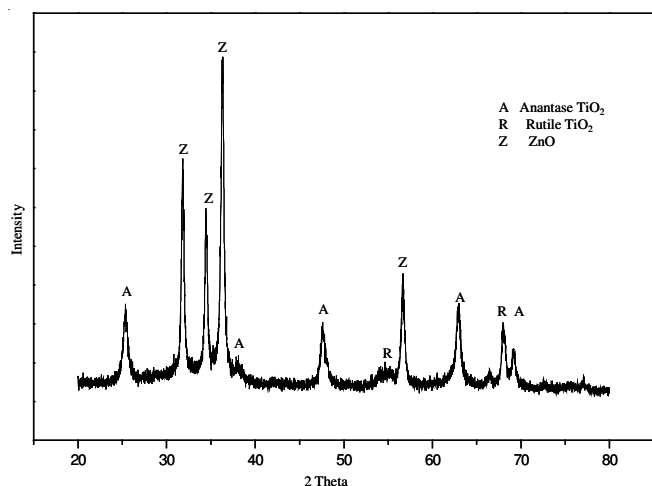


Fig. 5. XRD patterns of the TiO₂ coated ZnO nanoparticles prepared at 500 °C indicating peaks from the A (anatase TiO₂), R (rutile TiO₂) and Z (ZnO)

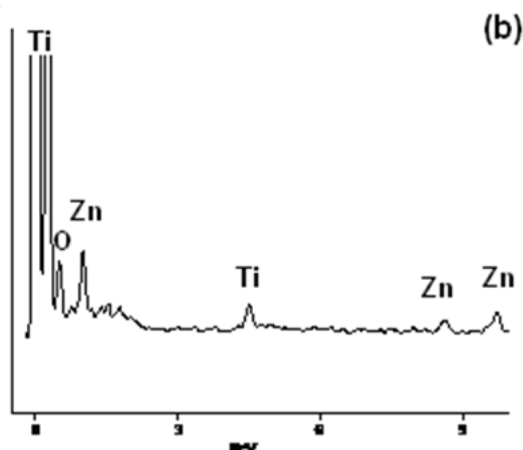
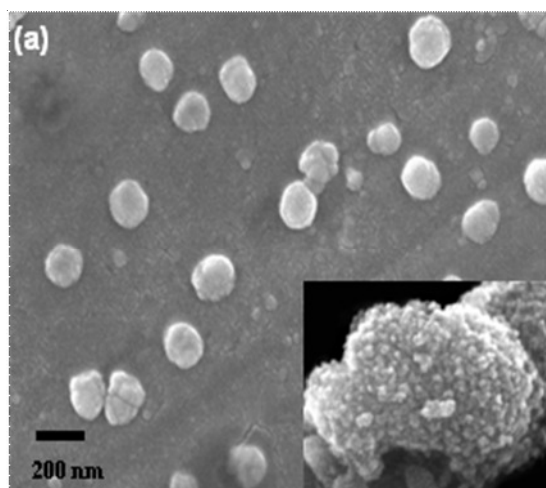


Fig. 6. SEM image of TiO₂ coated ZnO nanoparticles (a) and compositional data using EDS (b). The insert shows at high magnification the morphology of a TiO₂ coated ZnO nanoparticles

pH region. The driving force for the heterogeneous bonding between the ZnO and TiO₂ particles was Coulombic attraction which is interdependent of the respective surface charge of each component. Also, as confirmed from the EDS results in Fig. 6(b), the particle is composed of TiO₂ and ZnO without any impurity.

Fig. 7 shows a TEM image and SAED patterns in the insert of a TiO₂ coated ZnO particle. The TEM image in Fig. 7 reveals that the resultant TiO₂ coated ZnO particle is discrete essentially with a mean diameter of about 120-140 nm. The thickness of the ZnO shell was 10 nm. It is observed that the darker ZnO core is surrounded by the lighter TiO₂ shell. Individual particles exhibit a TiO₂ nanolayer on the ZnO surface and the shell thickness is about 10-20 nm. The SAED pattern in the insert is identified with the phases of TiO₂ (anatase), TiO₂ (rutile) ZnO, ZnO/TiO₂. This is in agreement with results of the XRD and EDS confirming this coexistence of crystalline TiO₂ and ZnO in each particle.

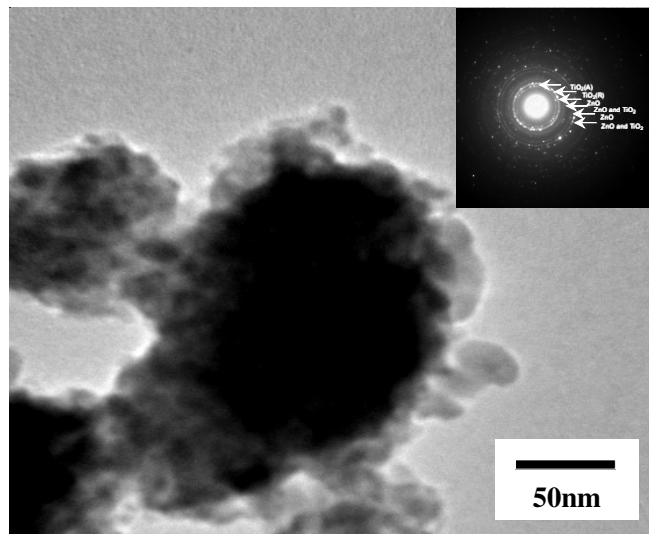


Fig. 7. TEM image and SAED pattern in the insert of a TiO₂ coated ZnO particle showing the darker ZnO core and the lighter TiO₂ shell surrounding it. The SAED pattern in the insert is identified with the phases of TiO₂ (anatase), TiO₂ (rutile), ZnO, ZnO/TiO₂

The coupling of TiO₂ coated ZnO nanoparticles like a layer-by-layer assembly is useful to achieve a more efficient electron/hole pair separation under irradiation and a higher photocatalytic activity¹¹. It is possible to enhance the activity of a TiO₂ photocatalyst by means of ZnO coupling like the layer-by-layer assembly. The electronic excitation of TiO₂ nanoparticles needs a higher input energy when the particle size decreases because of the quantum size effect¹². Therefore, it is highly desirable to synthesize TiO₂ nanoparticles with a high photocatalytic activity. The TiO₂/ZnO nanocomposites have strong physical and chemical interactions with adsorbed species and can support a variety of applications¹³⁻¹⁷. The coupled nanocrystalline TiO₂/ZnO particles adhere to each other in so-called sandwich structures or present a core/shell geometry. There are some investigations on core/shell structured TiO₂/ZnO. Zhang *et al.*¹², suggested that anatase TiO₂/ZnO nanoparticles at a size of 6 nm were immobilized on a single-crystalline tetrapod-like ZnO with dimensions up to 20-50 μm by a vapor hydrolysis method. The mechanism of this uniform deposition of TiO₂ nanoparticles on the surface of ZnO particles can be described as follows. Upon heating during the synthetic processing, the ethanol evaporates first since it has a low boiling point compared to water and the vapour of water promoted the hydrolysis. The surface of ZnO acts as the nucleation sites

during the initial stage of TiO₂ formation and the as-formed TiO₂ nuclei subsequently act as the nucleation sites for further deposition of TiO₂ nanoparticles like the layer-by-layer assembling.

Conclusion

Nanocrystalline TiO₂ coated ZnO particles were successfully synthesized by a two-step chemical method, which were prepared by the polymerization synthesis of ZnO nanoparticles and followed by sol-gel coating of a TiO₂ nanolayer. The variation in zeta potential of ZnO and TiO₂ with pH exhibited their isoelectric points (IEP) at 9.3 and 3.5, respectively. ZnO nanoparticles are surrounded by the lighter crystalline TiO₂ layers. ZnO particles coated with TiO₂ nanoparticles show a uniformly dispersed morphology without any agglomeration. The average particle size of ZnO particles coated with TiO₂ particles was ca. 120-140 nm. The size of a ZnO nanoparticle was 100 nm and the thickness of the TiO₂ coating was below 10-20 nm. The driving force for the heterogeneous bonding between the ZnO and TiO₂ particles was Coulombic attraction which is interdependent on the respective surface charge of each component.

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