



Synthesis of nanoparticulate Ti-doped ZnO by solution combustion technique

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Abstract

ZnO and TiO₂ have been widely accepted as prominent photocatalysts. Enhancement of their photocatalytic activities can be achieved through particle refinement and doping. Solution combustion technique is a simple and cost-effective method capable of producing fine ceramic powders with homogeneous chemical compositions. It is, therefore, employed in this research project as the technique to synthesize nanometer-sized Ti-doped ZnO powders.

The research also aimed at examining a relationship among doping contents, chemical composition, particle sizes, and photocatalytic performance of the synthesized powder. Compositional analysis revealed that the solubility limit of Ti in zinc oxide was within the range of 3 at% Ti. Within the solubility limit, photocatalytic activity was enhanced with the titanium doping. Reduced photocatalytic performance, however, was observed in the powders with titanium contents beyond the solubility limit. The results also indicated that doping concentration did not have a significant effect on particle size and morphology. Equiaxial particles, with the average particle sizes ranging from 46.4 to 48.4 nm, were observed from the SEM micrographs.

1. Introduction

Zinc oxide is a well-known electronic material used in fabrication of gas sensor, photodetectors and light modulators. Zinc oxide also exhibits prominent photocatalytic activities. It is, therefore, exploited as air purification, water treatment, and anti-microbial agent. [1] Zinc oxide has band gap energy approximately 3.3 eV [2], which exceeds active range in visible light. UV is then employed in stimulation of photocatalytic activity in zinc oxide. It has been generally accepted that main factors contributing to alteration of photocatalytic performance included particle size, chemical composition, and electronic property, specifically recombination rate, of the photocatalysts [3].

Refinement of the particle size greatly enhance reactivity through enhanced specific surface area [4, 5]. Nanoparticulate photocatalysts are therefore desired for photocatalytic applications. Chemical composition is one of factors affecting photocatalytic performance of the materials. Multi-phase mixtures can be either beneficial or disadvantageous to the photocatalytic performance, depending on their surface characteristics. It was reported that

combination of titanium dioxide and zinc oxide could lead to synergic effects on photocatalytic performance [6], when heterostructure uniformed bonded surface. For the mixtures with non-uniformed surface bonding, deleterious effects could occur as a result of active surface obstruction [7].

It has been well established that doping can alter electronic structure of materials. Doping can create extra energy levels between the valence and conduction band. These energy levels acted as electron trapping centers, which resulted in diminution of electron-hole pair recombination and consequently led to enhanced photocatalytic performance. According to Ravishankar et al. (2014) [8], Ag-doped ZnO retained higher photocatalytic activity, when compared to pure ZnO. Enhancement of the photocatalytic performance in nano-particulate Ag-doped ZnO was attributed to low recombination rate and large surface area. Chen et al. (2016) [9] and Seery et al. (2008) [10], reported a similar trend. Doping ZnO by Ag resulted in improved electron trapping efficiency, which resulted in low recombination rate and enhancement of photocatalytic activity [10] Zn-doped titanium dioxide nanofibers with 1 wt% was also found to

have high Zn through low recombination rate photocatalytic performance.

Thus, synthesis techniques capable of producing photocatalyst powders with controllable doping content, chemical composition, and particles sizes are greatly desired. Solution combustion is a robust synthesis technique in synthesizing photocatalytic materials. This is attributed to its capability in producing nano-sized particle with desired chemical composition [11,12]. In addition, the technique required low energy supply and simple synthesis equipment, leading to cost-effectiveness.

This research, therefore, aimed at synthesizing nano-sized Ti-doped ZnO powders by solution combustion technique. Relationship among doping concentrations, chemical compositions, particle morphology, particle sizes, and photocatalytic performance of the synthesized powders were also examined.

2. Experimental

2.1 Preparation of ZnO and Ti-doped ZnO

Nanoparticulate zinc oxide powder with 1.0, 3.0, 5.0, and 7.5 at% titanium were prepared by solution combustion technique. The solution combustion method involved preparation of an aqueous solution containing metal nitrate and combustion fuel.

For the pure ZnO, zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, Daejung[®], 98%) was used as initial reagent, while zinc nitrate hexahydrate and titanium (IV) isopropoxide (TTIP) (Aldrich chemistrys[®], 97%) were employed in synthesis of zinc oxide doped with titanium. The initial reagents were mixed with deionized water to obtain homogeneous solution of 0.34 M. Combustion fuel, glycine (NH_2CH_2COOH , Daejung[®], 99%) at a ratio of 0.25:1 glycine: zinc, was added to the prepared zinc-titanium solution mixtures.

The mixtures were subsequently stirred by a magnetic stirrer and placed in an ultrasonic bath for 10 min. A low heating temperature of less than 300°C was applied to the solution to initiate combustion. Upon completion of the combustion reaction, the powder products were collected and calcined at 350°C for 2 h.

2.2 Characterization

The synthesized powders were tested for chemical compositions, particle morphology,

particle sizes, optical properties, and photocatalytic activities.

To examine chemical composition of the calcined powders were investigated using an x-ray diffractometer (Bruker, D8 Advance), over angles ranging from 20° to 80° in 2θ , at a step size of 0.021 and a scanning rate of 1.31/min. In addition to the phase identification, compositional mapping was conducted, using an energy dispersive spectrometer (EDS) (OXFORD INSTRUMENTS, X-Max 50 mm²).

A scanning electron microscope (SEM) (FEI, Quanta 450) was employed in the morphological examination as well as particle sizes of the powders. To prepare the powders for SEM investigation, the powders were coated by gold to ensure that the powders were conductive. Particle sizes were determined using Image J Software.

Photocatalytic activities of the powders were test by evaluating optical transmission of methylene blue upon decomposition. 0.0375 g of the synthesized powders were added into 10 ml of methylene blue ($C_{16}H_{18}ClN_3S \cdot 3H_2O$, Daejung[®]) solution with 0.01 M concentration. The suspensions were exposed to ultraviolet (UV) light radiation with the intensity of UVA was 0.77 W/m²/nm and wavelength ranging 340 nm for 30 minutes, controlled by a weather meter (QUV, Q-LAB). The suspensions subsequently tested for their optical absorption using a UV-VIS spectrophotometer (Shimadzu, UV-1700 PharmaSpec), over the wavelength ranging from 350 to 500 nm.

3. Results and discussion

3.1 Chemical composition

Results from x-ray diffraction indicated prominent peak at $2\theta = 31.8, 34.4, 36.3, 47.5$ and 56.6 , which corresponded to zinc oxide phase (JCPDS 00-005-0664), shown in Figure 1. No secondary phase was observed in all powders. It is noted that generally detection limit of x-ray diffraction ranges from 3-5 wt% [13]. Further investigation on chemical composition was conducted using an energy dispersive spectrometer (EDS) technique.

Compositional mapping mode in the EDS was employed in analyzing dispersion of titanium in the synthesized powders. Pure zinc oxide was also examined as the controlled powder. The mapping showed no evidence of titanium in pure zinc oxide. For the Ti-doped zinc oxide powders, the results

revealed that titanium dispersed homogeneously in zinc oxide powders with 1 at% Ti. For zinc oxide powders with 3, 5, and 7.5 at% Ti, agglomeration of titanium occurred, shown in Figure 2. The results suggested that secondary phase formation possibly occurred at higher concentration of titanium addition. The compositional analysis was in agreement with the results reported earlier, which observed that complete substitution of Zn^{2+} by Ti^{4+} occurred at the concentration of Ti not exceeding 2 at% [14].

3.2 Particle sizes and morphology

Scanning electron micrographs of the pure zinc oxide powder and zinc oxide powders with 1.0, 3.0, 5.0, and 7.5 at% Ti, revealed fine equiaxed particles, shown in Figure 3. Particle sizes measured by an image analysis technique indicated average particles sizes ranged from 46.67 to 48.42 nm, shown in Table 1. The results revealed that concentrations of titanium addition did not have a significant effect on particle morphology and particle size.

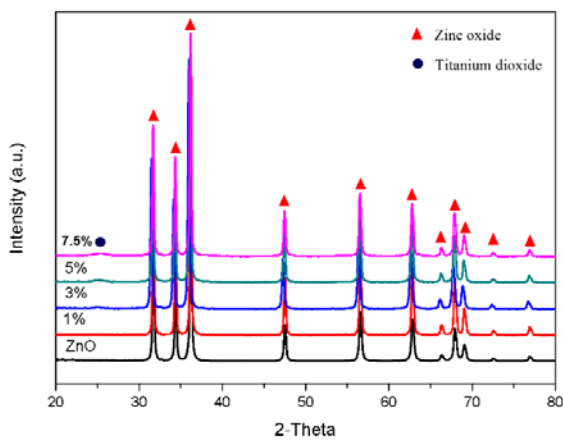


Figure 1. X-ray diffraction patterns of pure zinc oxide and titanium-doped zinc oxide powders with 1.0, 3.0, 5.0, and 7.5 at%.

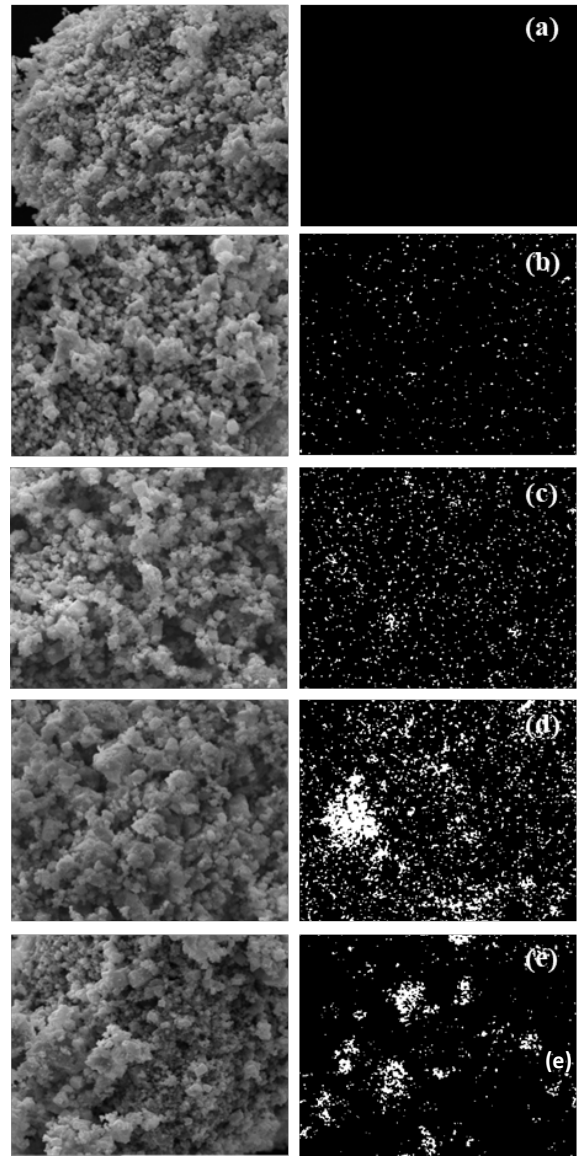


Figure 2. Elemental mapping showing dispersion of titanium in pure zinc oxide (a) and zinc oxide powders with 1.0 (b), 3.0 (c), 5.0 (d), and 7.5 (e) at% Ti.

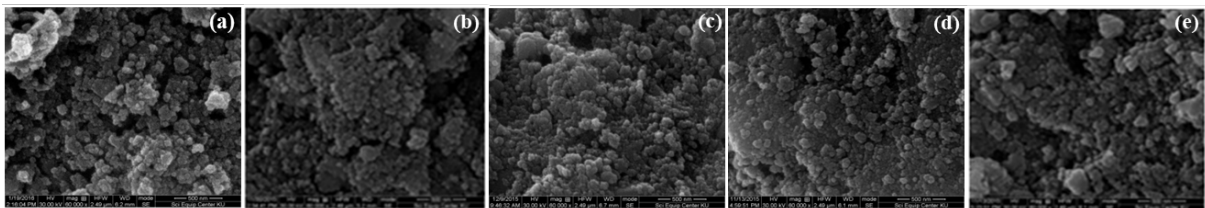


Figure 3. Scanning electron micrographs showing pure zinc oxide (a) and titanium-doped zinc oxide powders with 1.0 (b), 3.0 (c), 5.0 (d), and 7.5 (e) at%.

Table 1. Particle sizes of pure zinc oxide and titanium-doped zinc oxide powders with 1.0, 3.0, 5.0, and 7.5 at%.

Ti content (at%)	Particle Size (nm)	
	SEM	Scherrer
0	46.67 ± 4.6	42.56
1	46.80 ± 3.9	44.97
3	46.39 ± 4.3	42.72
5	47.96 ± 4.2	44.43
7.5	48.42 ± 3.7	45.83

3.3 Photocatalytic activity

Photocatalytic performance of the synthesized powders was evaluated through decomposition of methylene blue. It was observed that bluish methylene suspension containing the synthesized powders turned clearer upon UV exposure. The observation suggested that all powder exhibited photocatalytic activity, as shown in Figure 4.

To obtain quantitative interpretation, the methylene blue suspensions were tested by the UV-VIS spectroscopy, shown in Figure 5. Results from uv-absorption of suspensions indicated that absorption decreased as Ti addition increased from 0 to 1 at%. Reduced light absorption suggested greater decomposition of methylene blue and enhanced photocatalytic activity. On the contrary, absorption increased in suspensions containing the powders with Ti between 5 and 7.5 at%, implying lower decomposition and reduced photocatalytic activity.

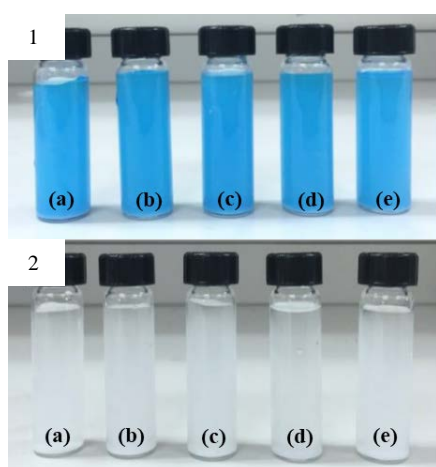


Figure 4. 1) Methylene blue before decomposition 2) Decomposition of methylene blue of suspension containing pure zinc oxide (a) and zinc oxide powders with 1.0 (b), 3.0 (c), 5.0 (d), and 7.5 (e) at% Ti.

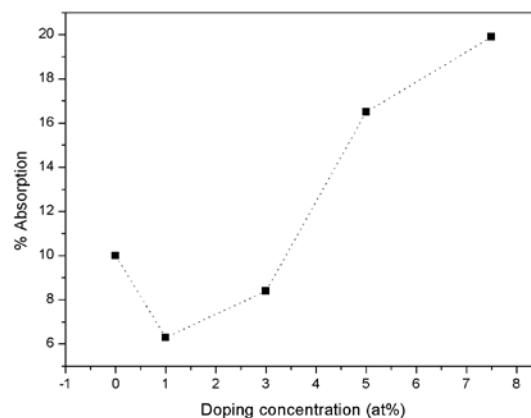


Figure 5. Relationship between Ti content and UV absorption methylene blue suspension.

Enhancement of photocatalytic performance in powders with titanium below the solubility limit was in agreement with the results reported by Seery et al. (2008) [10], Ravishankar et al. (2014) [8], and Cheng et al. (2014) [7]. As Ti is doped in zinc oxide, extra energy levels, also referred to as defect levels, were created. These energy levels acted as electron trapping centers, which resulted in diminution of electron-hole pair recombination and consequently led to enhance photocatalytic performance. Reduced photocatalytic activity in powders with high concentration of titanium could be explained as follows. As doping concentration of titanium reached beyond solubility limit, formation of titanium compound potentially occurred. Although it was reported that combination of titanium dioxide and zinc oxide could lead to synergic effects on photocatalytic performance [6], the effects could only occur when heterostructure uniformed bonded combination where the surface of the particles was randomly adhered, reduction of activity could be observed [7]. Diminished photocatalytic performance in the multi-phase mixture was also reported. According to Johar et al. (2015) [6], reduced photocatalytic performance in multi-phase mixture might be attributed to obstruction the reactive surface by the secondary phase.

4. Conclusions

Nanometer-sized Ti-doped ZnO powders were successfully synthesized by the solution combustion technique. Relationship among doping contents, chemical composition, particle sizes, and photocatalytic performance of the synthesized powders was also conducted. The results indicated that the solubility limit

of titanium in zinc oxide was within the range of 3 at% Ti. Within the solubility limit, photocatalytic activity increased with the titanium doping. This may be attributed to creation of extra energy levels, which reduced recombination process. For the powders with titanium concentrations exceeding the solubility limit, secondary phase formation occurred, leading to reduced photocatalytic performance. Nevertheless, titanium concentration did not have a significant effect on particle size and morphology. Equiaxial particles, with the average particle sizes ranging from 46.4 to 48.4 nm, were observed from the SEM micrographs.

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