Photocatalytic degradation of TOC from aqueous phenol solution using solution combusted ZnO nanopowders

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Abstract ZnO nanopowders were prepared by solution combustion method (SCM). The ZnO nanopowders synthesized using $Zn(OH)_2$ and glycine as an oxidant and a fuel (with fuel/oxidant ratio, F/O=0.8), showed excellent crystalline and photocatalytic characteristics. In order to evaluate the photocatalytic reactivity of the prepared ZnO nanopowder, it was tried to decompose total organic carbon (TOC) from aqueous phenol solution. Several kinds of TiO_2 nanopowders were also tried to compare the photocatalytic reactivity. Surprisingly, SCM ZnO nanopowder shows 1.6 fold higher destruction rates of the organic pollutant than P-25 TiO_2 nanopowder that is known as a kind of standard photocatalyst.

Keywords ZnO nanopowder ·
Solution combustion method · Photocatalytic degradation ·
Total organic carbon

1 Introduction

The study of photocatalytic reactions is recently an emerging area in the field of catalytic chemistry. In general, photocatalytic reaction is an interaction between molecules and

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surfaces including electron transfer between molecules and catalysts. Semiconductors are usually used for the photocatalysts because their carrier concentration can be controlled [1, 2].

Nano-sized particles have different physical and chemical properties compared to bulk materials. High catalyst activity may be expected because of their large surface area and different surface properties such as surface defects, if these nano-sized particles are used as catalysts. The fabrication of nano-sized particles with low surface defect levels is essential to obtain high photocatalytic activity [3, 4].

In this study, synthesis of ZnO powder was tried to obtain the nano-sized semiconductor particles for photocatalytic application. Two methods are generally used to obtain such ZnO powder. One is vapor method and the other one is sol-gel method. In the case of vapor method, the resulting powders are agglomerates rather than separated particles because it is very difficult to control the reaction condition during the process. This means that the vapor method is not a proper method to obtain nano-sized ZnO powders. On the other hand, the sol-gel method could provide uniform-sized ZnO powders. However, it is required to control the reaction condition strictly because of its violent hydrolysis reaction in the air during synthetic process. In addition, the material cost for this method is high. This is why the method is still not commercialized but is being tried only in a small laboratory scale [5, 6]. S. Park et al. developed a unique synthesis method, solution combustion method (SCM), which makes possible to synthesize highly pure and fine ceramic powders. Using this method, the heating and evaporation of metal nitrate solution with glycine results in self-firing and generates intense heat by exothermic reaction. This intense heat is used to synthesize the powders.
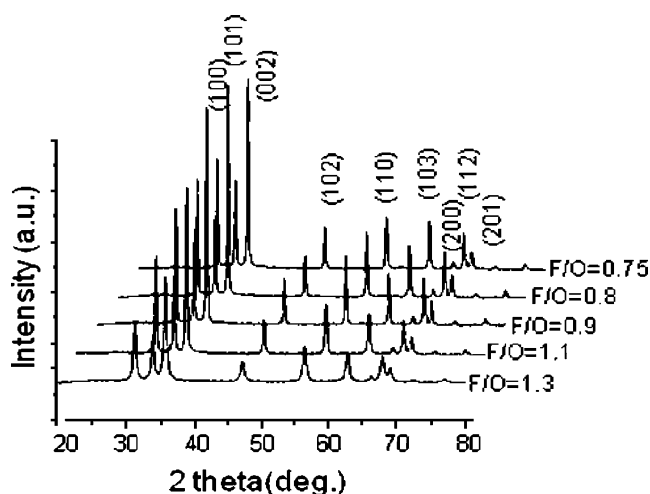
Fig. 1 XRD peaks of ZnO nanopowders synthesized by SCM with various fuel/oxidant ratios

Fig. 2 (a) SEM and (b)TEM photograph of ZnO nanopowder synthesized by SCM with fuel/oxidant ratio of 0.8

Using this solution combustion method, nano-sized ZnO powder was prepared. Its crystalline characteristics and photocatalytic efficiency to decompose TOC will be discussed.

2 Experimental

Required raw materials, zinc hydroxide ($Zn(OH)_2$) as a precursor, and glycine (H_2NCH_2COOH) as fuel, were purchased from Junsei Chemicals Ltd (Japan) and Yakuri Pure Chemicals Co. Ltd. (Japan), respectively. The zinc hydroxide powder was dissolved in nitric acid (Aldrich, USA) thus forming zinc nitrate solution, which acts as an oxidant. Glycine was added to the zinc nitrate solution in the proportion of 0.8 (fuel/oxidant). The solution mixture was then heated on a hot plate with stirring. As the water was evaporated, the solution became viscous generating large number of air bubbles. At this point, the oxidant reacted with the fuel generating intense heat. This intense heat resulted in instantaneous high pressure, which led to explosion. This high temperature and pressure environment were helpful to form ZnO nanopowder. The large number of local explosions occurred simultaneously but each explosion occurred in tiny space. Each explosion was like a very small bright spot. The spot size was in the range of mm. The explosion power was as large as corn-popping. The experiment was performed inside a stainless steel chamber seeing the explosive nature of the reaction. The formed ZnO nanopowder was collected and annealed at 400°C for 1 h to remove the adsorbed gases and other organic species.

Other photocatalyst powders were used to compare the photocatalytic reactivity. P25 TiO_2 (Degussa, Germany) was purchased, nanotube powder type TiO_2 was prepared in
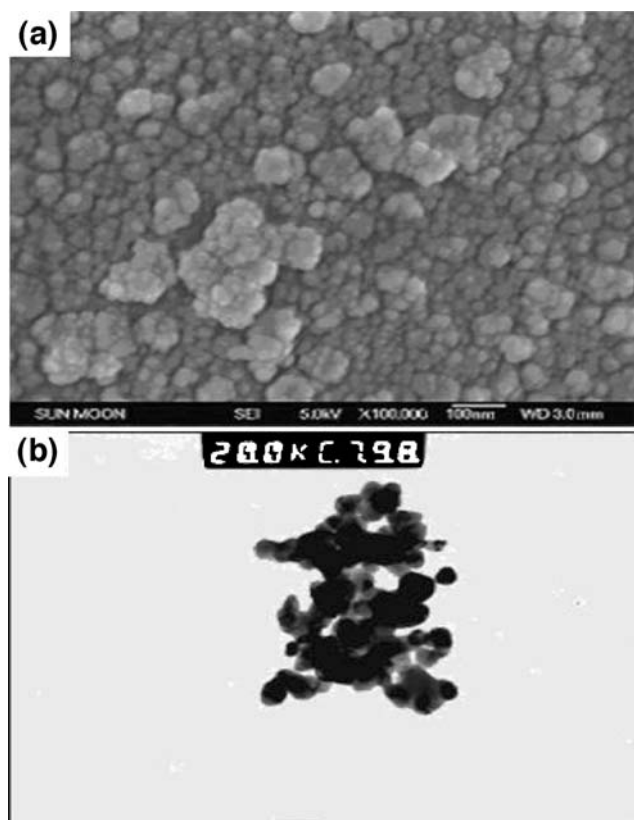
the present laboratory and rutile TiO_2 powder was prepared by the homogeneous precipitation process at low temperature (HPPLT) [7].

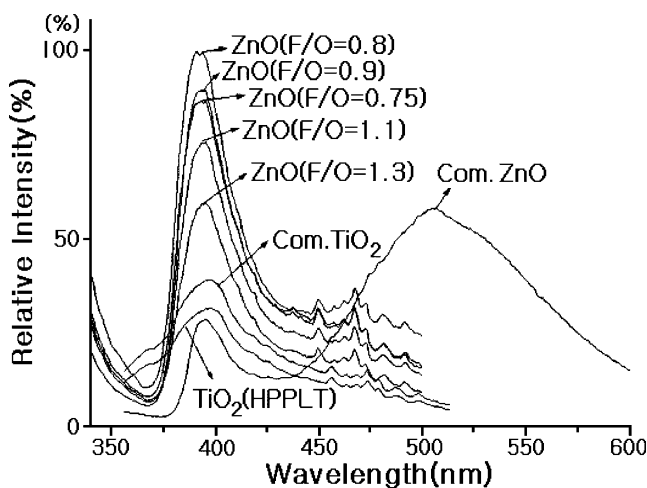X-ray diffractometer (XRD) was used to confirm the crystalline phase of the synthesized ZnO powder. Scanning

Fig. 3 PL spectra of commercial ZnO (Junsei, Japan), HPPLT (Homogeneous Precipitation Process at Low Temperature) TiO_2, commercial TiO_2 (P-25 Degussa, Germany) and ZnO nanopowders synthesized by SCM with various fuel/oxidant ratios

E_c
E_d (shallow) : O Vacancy
E_d (deep) : Zn interstial

$E_g=3.2$

E_a : Zn Vacancy

E_v
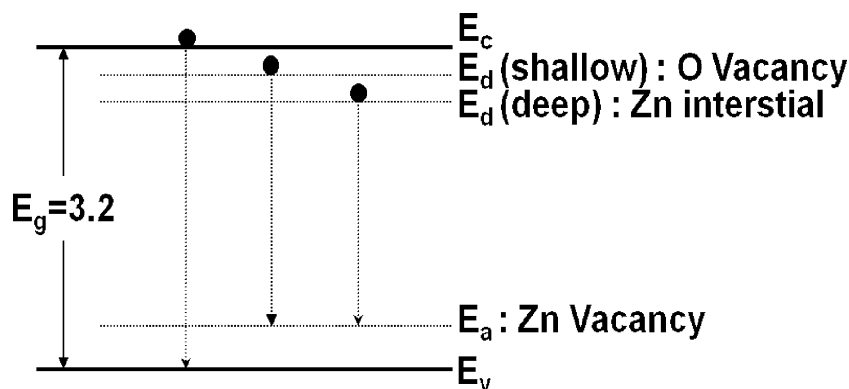
electron microscope (SEM) and transmission electron microscope (TEM) were also used to investigate the average particle size and shape. Fluorospectrometer (SIM-AMINCO) was used to measure photoluminescence (PL) emission values as a function of wavelength. SCM ZnO nanopowder was used as a photocatalyst to decompose the total organic carbon (TOC) from aqueous phenol solution. TOC remained in the solution as a function of UV exposure time was detected by TOC analyzer (Shimadzu). Before the detection of TOC, the solution was filtered through a syringe filter having pore size of 0.2 μm for the removal of photocatalyst particles. The same experiment was repeated for other photocatalyst powders (P25 TiO_2, nanotube type TiO_2 and HPPLT TiO_2). The removal rate of TOC using the SCM ZnO nanopowder was compared to those using other photocatalytic powders to confirm its relative photocatalytic efficiency.

3 Results and discussion

In general glycine-nitrate process, oxide powders are synthesized by adding the fuel on equilibrium condition (fuel/oxidant=1). However, in this study ZnO powder was prepared on fuel lean condition considering the vapor pressure of Zn or ZnO. Five different ZnO powders were prepared with the variation of the fuel/oxidant ratio.

Single phase ZnO was obtained by the above method (Fig. 1). Especially the ZnO powder with fuel/oxidant ratio of 0.8 showed highest XRD peaks indicating best crystalline quality. The average particle size of the above SCM ZnO powders was about 30 nm and they have spherical shape (Fig. 2).

As shown in Fig. 3, commercial ZnO powder showed two PL peaks: one is in the vicinity of 500 nm, and the other one is near 400 nm. The peak near 500 nm probably came from the energy transition between oxygen vacancy level and valence band edge as shown in Fig. 4. The UV

peak near 400 nm might be from band to band transition. However, ZnO powder synthesized by the SCM showed only one sharp peak near 390 nm that was little bit shifted to UV side. This peak is equivalent to the energy gap of ZnO (~3.2 eV). These results indicate that the ZnO powder synthesized by the SCM did not show defect energy levels inside the energy gap. The defects were probably annealed out due to the high temperature during the synthesis process. Again, the SCM ZnO powder showed higher PL intensity at UV region than other ZnO and TiO_2 powders. Especially SCM ZnO powder with fuel/oxidant ratio of 0.8 showed highest PL intensity at UV region. This means that the SCM ZnO powder absorbs 3 fold more UV light than the commercial TiO_2 powder.

As mentioned above, results from XRD and PL measurements led to select the SCM ZnO powder with fuel/oxidant ratio of 0.8 for photocatalytic reaction. To confirm the photocatalytic activity, TOC was tried to be removed from aqueous phenol solution. As shown in Fig. 5, When UV
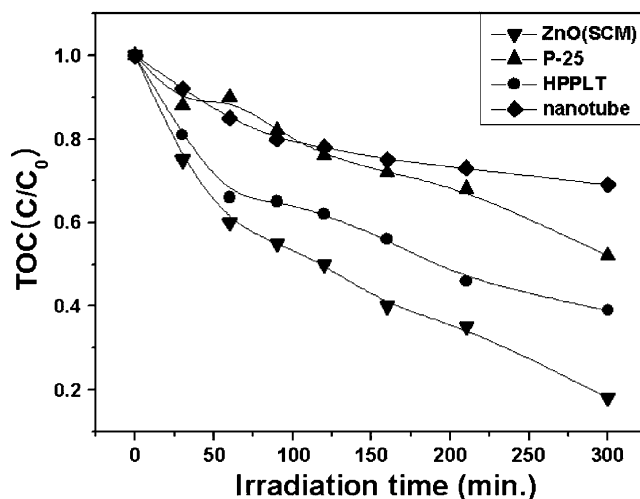

Fig. 5 Removal of TOC from aqueous phenol solution by photocatalytic reaction using nanotube TiO_2, HPPLT TiO_2, commercial TiO_2(P-25), SCM ZnO nanopowder with fuel/oxidant ratio of 0.8

light was irradiated for 300 min, the nanotube type TiO_2 destructed just 30% of phenol, P-25 TiO_2 nanopowder destructed 50%, HPPLT TiO_2 nanopowder destructed 60%, SCM ZnO nanopowder destructed 80%. The commercial ZnO powder (Junsei Chem.) did not show any photocatalytic reaction. Therefore, SCM ZnO nanopowder shows 1.6 fold higher destruction rates of the organic pollutant than P-25 TiO_2 nanopowder that is known as a kind of standard photocatalyst. This high photocatalytic efficiency of SCM ZnO nanopowder might be strongly dependent on the UV absorption sensitivity.

This high quality of the SCM ZnO nanopowder might be due to the defect removal by the high temperature generated during the SCM. The ZnO nanopowder synthesized by the SCM could be applied for high efficiency photocatalytic reaction, UV-blocking cosmetics and other UV-related areas.

4 Conclusions

Single-phase ZnO nanopowders were obtained by the SCM. Using $Zn(OH)_2$ and glycine (F/O=0.8), the synthe-sized ZnO nanopowders showed high photocatalytic activity. Surprisingly, SCM ZnO nanopowder shows 1.6 fold higher destruction rates of the organic pollutant than P-25 TiO_2 nanopowder that is known as a kind of standard photocatalyst, even though the commercial ZnO powder (Junsei Chem.) did not show any photocatalytic reaction. This might be due to the defect-free crystalline quality of the SCM ZnO nanopowder.

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