Effects of ZnO nanopowder dispersion on photocatalytic reactions for the removal of Ag$^+$ ions from aqueous solution

Sung Park · Ju-Hyeon Lee · Hong-Sick Kim · Hye-Jung Park · Jae Chun Lee

Abstract ZnO nanopowders were prepared by solution-combustion method (SCM). The SCM ZnO nanopowders were treated by five different dispersants. They were used as photocatalysts to remove Ag$^+$ ions from used photographic developing solutions. The Ag$^+$ ion removal rates by the dispersed SCM ZnO nanopowders were then compared with those by other photocatalyst powders such as commercial ZnO(Junsei, Japan), P25 TiO$_2$ (Degussa, Germany) and TiO$_2$ powder prepared by homogeneous precipitation process at low temperature (HPPLT). The dispersion of SCM ZnO nanopowders in the solution enhanced the Ag$^+$ ion removal rate up to about 13 folds compared with P25 TiO$_2$ nanopowders and 2 folds to SCM ZnO nanopowders without dispersion. Sodium hexametaphosphate was the most effective dispersant among them.

Keywords Synthesis of ZnO nanopowders · Dispersion · Photocatalytic reaction · Ag$^+$ ion removal

1 Introduction

Many researchers have studied photocatalysts because of their unique advantages such as clean and easy process and possibility of sunlight utilization. However, their photocatalytic efficiency is not high enough for practical applications. Dispersion could be one of choices to improve the photocatalytic efficiency.

The photocatalytic reaction occurs at the photocatalyst surface. This fact requires as much surface area as possible for high efficiency photocatalytic reactions. However, for powder type reactors, the photocatalyst powders could be easily flocculated in the aqueous solution. This could decrease the surface area on which the photocatalytic reactions occur. Dispersion of photocatalyst powders is, therefore, required to prevent the flocculation of the powders. The dispersion is achieved by separating photocatalyst powders from each other. This could be obtained by making the powder surface positively charged or negatively charged. Cation or anion could be easily adsorbed on powder surface. Then the charged powders repulse each other and eventually lead to larger surface area for photocatalytic reactions. This also could result in hydrophilic surface properties which improve wettability with wastewater because water is a polar molecule. In this paper, the effect of dispersion on the photocatalytic reactions will be discussed.

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2 Experimental

Four different SCM ZnO nanopowders were synthesized using different oxidant and fuel combinations such as Zn(NO$_3$)$_2$ · 6H$_2$O and carbohydrazide, Zn(OH)$_2$ and carbohydrazide, Zn(NO$_3$)$_2$ · 6H$_2$O and glycine, and Zn(OH)$_2$ and glycine. Zn(NO$_3$)$_2$ · 6H$_2$O (5N, High purity chemicals, Japan) or Zn(OH)$_2$ (5N, Junsei, Japan) powder dissolved in nitric acid was used for the starting material. Glycine (5N,

H_2NCH_2COOH, Yakuri pure chemicals co. Ltd, Japan) or carbohydrazide (5N, $H_2NNHCONHNH_2$, Aldrich, USA) was used for the fuel. Each starting material was then dissolved in distilled water in each beaker. Glycine or carbohydrazide was then added to the starting solution in each beaker. Fuel/oxidant ratio was fixed at 0.8. Each solution in the beaker was heated on hot plate with stirring. As the distilled water was evaporated, the solution became viscous and generated small bubbles. The nitrate ion (NO_3^-) reacted with the fuel and intense heat was generated (about 1500–1800°C). The temperature was measured by IR thermometer (Pyrometer Instrument Company, USA). This high temperature resulted in high pressure. This instantaneous high pressure led to explosion. The ZnO powder was formed in this high temperature and pressure environment. At this point the powder was gathered up by the collector (consists of a metal sieve screen and filter) which was placed above the beaker.

Other photocatalyst powders such as commercial ZnO (Junsei, Japan) and commercial TiO_2 (P25, Degussa, Germany), were purchased and rutile TiO_2 powder was prepared by the homogeneous precipitation process at low temperature (HPPLT) [1, 2].

Scanning electron microscope (SEM) (JEOL ABT DX-130S:3 kV) images of the four kinds of SCM ZnO powders were captured to observe their particle shape and size. The SCM ZnO nanopowders were treated by five different dispersants such as Sodium Hexametaphosphate, Nonidet Np40 (Octyl phenoxypolyethoxyethanol), HS-dispersant5066 (San Nopco, Japan), SN-sperse70 (San Nopco, Japan) and

Cerasperse-44cf (San Nopco, Japan). Dispersant of 0.3 wt% was added to the solution which contains ZnO nanopowders and wastewater. The dispersant dissolves in the solution and form charged particles (ions). These charged particles are easily adsorbed on the ZnO nanoparticle surface. Each ZnO nanoparticle has the same polarity of charges. A repulsive force between the ZnO nanoparticles is, thus, generated. This leads to the dispersion of ZnO nanoparticles. The treated dispersants were confirmed by FT-IR. Zeta Potential and mobility were also measured to see the effect of dispersant treatment.

The SCM ZnO nanopowders treated with above dispersants were then used as photocatalysts to remove Ag^+ ions from used photographic developing solutions. The ratio of photocatalyst-to-waste water was 3.0 g/L. The reaction was carried out in a 100 ml batch-type quartz reactor with the diameter of 37 mm and height of 120 mm. A high-pressure mercury arc lamp was used as an external UV source. Here, Ag^+ ion concentration in the solution was 120 ppm. The Ag^+ ions were reduced to Ag atoms receiving the electrons generated at the surface of photocatalyst nanopowders by UV light irradiation. The concentration of Ag^+ ions remaining in the solution in different time intervals was detected with an AA (atomic absorption) spectrophotometer (Perkin-Elmer 5100 PC). Fluorospectroscopy (SIM-AMINCO, Bowman, New York, NY) was used to measure photoluminescence (PL) emission values as a function of wavelength. The same experiment was also repeated for other photocatalyst powders (commercial ZnO, P25 TiO_2 and HPPLT TiO_2).

Fig. 1 SEM photographs of ZnO powders synthesized by SCM using (**a**) $Zn(NO_3)_2 \cdot 6H_2O$ and carbohydrazide, (**b**) $Zn(OH)_2$ and carbohydrazide, (**c**) $Zn(NO_3)_2 \cdot 6H_2O$ and glycine and (**d**) $Zn(OH)_2$ and glycine
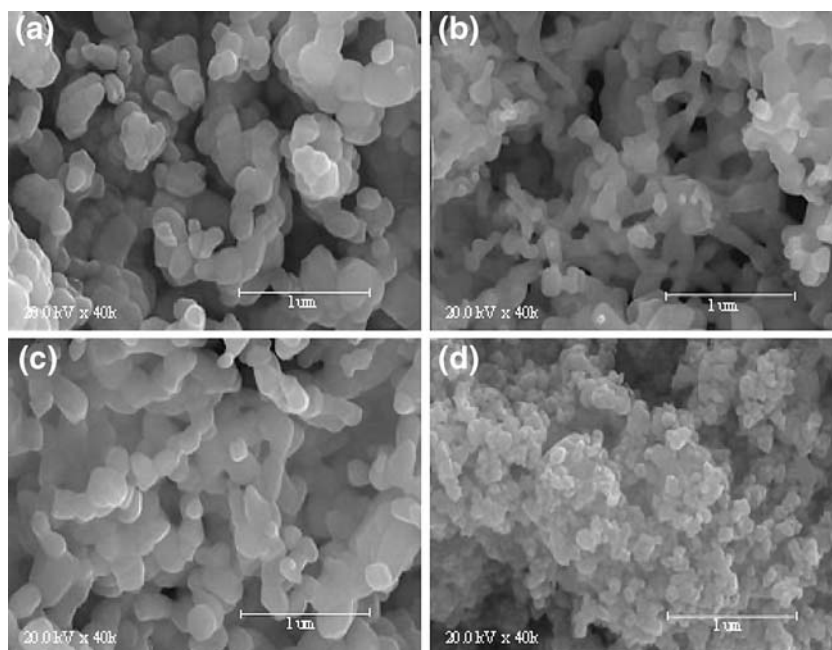
3 Results and discussion

The average particle size was calculated by linear intersection method using SEM images shown in Fig. 1. Here, the particle size was greatly dependent on the kinds of oxidants and fuels. The difference in the particle size was more than 10 folds depending on kinds of oxidants and fuels. The particle size of 320 nm was obtained when the ZnO powders were synthesized using $Zn(NO_3)_2 \cdot 6H_2O$ and carbohydrazide, even though that of 30 nm was obtained when $Zn(OH)_2$ and glycine were used (Fig. 2). The particle sizes of 125 nm and 110 nm were obtained when $Zn(NO_3)_2 \cdot 6H_2O$ and glycine, and $Zn(OH)_2$ and carbohydrazide were used respectively. In the case of carbohydrazide, the particle shape was plate-like. On the other hand, in the case of glycine, the particle shape was spherical with uniform size. Using $Zn(OH)_2$ as an oxidant, it was dissolved in nitric acid solution to form zinc nitrate. There might be more nitrate ion (NO_3^-) group in the solution than the case using zinc nitrate as an oxidant. The nitrate ion group acts as an igniter for the combustion. This probably means that more igniter is provided for the combustion process. It seems that this is helpful for the finest particle size.

As shown in Fig. 3, only ZnO peak was observed from the SCM ZnO without dispersant treatment, however, a small extra peak was observed at near 1370 nm in addition to the ZnO peak from the SCM ZnO with dispersant treatment (sodium hexametaphosphate). The extra peak was not correspondent to any peak from zinc compound. It probably came from the dispersant that is on the ZnO powder surface. This indicates that there was no chemical reaction between the ZnO and the dispersant.

As presented in Fig. 4, sodium hexametaphosphate among five dispersants resulted in the highest zeta potential of about −88.2 mV. In this case, the ZnO nanopowder surface was covered by Na^+ ions. Then the positively charged ZnO nanopowders repulse each other. The high
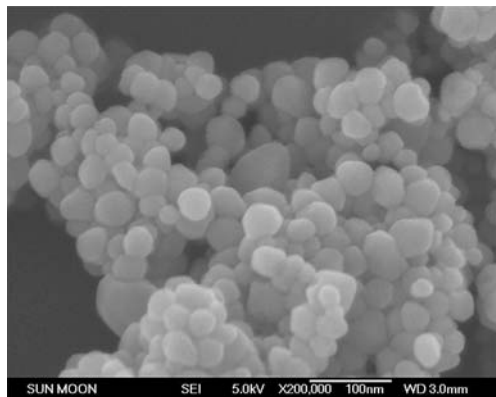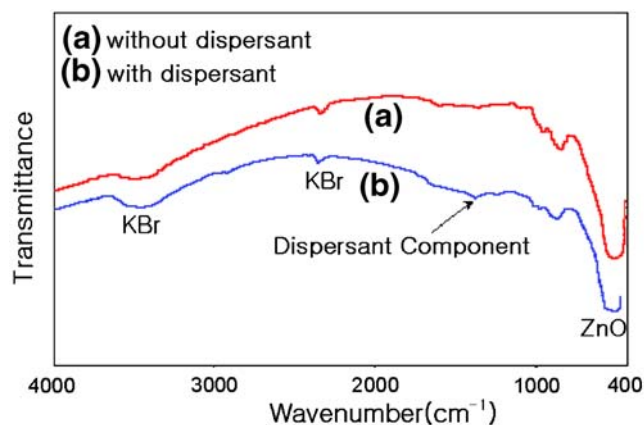

Fig. 3 FT-IR spectra of SCM ZnO powder (*a*) without and (*b*) with dispersant (sodium hexametaphosphate)

zeta potential reflects uniform and high-density surface charge on powder surface. It is proportional to the charged particle mobility. Table 1 presents the particle mobility with different dispersants. ZnO nanopowders with sodium hexametaphosphate showed the highest particle mobility (6.2 cm^2/Vs). This result indicates a good correspondence to the result of zeta potential.

Up to now, P25 TiO_2 is known as the best photocatalyst [3]. However, this is not true any more as shown in Fig. 5. Ag^+ ions of 120 ppm were completely removed in 60 min with the P25 TiO_2 (specific surface area: 55 m^2/g), and the removal rate of Ag^+ ions was about 1.7 µg/g/min. The removal rate of Ag^+ ions, here, was defined as a slope of the curve which represents removed Ag^+ ion concentration as a function of UV irradiation time. It, however, took only 15 min with SCM ZnO (specific surface area: 120 m^2/g), and the removal rate of Ag^+ ions was about 11.9 µg/g/min. The Ag^+ ion removal rate of SCM ZnO powder is 7 folds higher than that of P25 TiO_2 powder. The HPPLT TiO_2 powder and commercial ZnO powder have specific surface
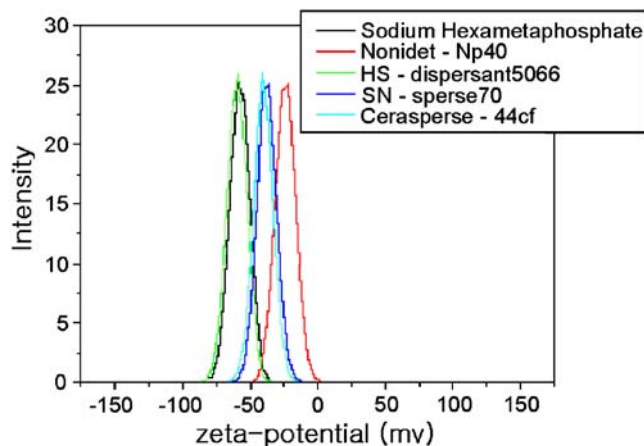

Fig. 2 SEM photograph of ZnO powders synthesized by SCM using $Zn(OH)_2$ and glycine (magnified SEM photograph of above Fig. 1(d))

Fig. 4 Zeta potentials with various dispersants for the ZnO powders synthesized using $Zn(OH)_2$ and glycine

Table 1 Particle mobility with different dispersants.

Dispersant	Mobility (cm^2/Vs)
Sodium Hexametaphosphate	6.2
Nonidet P40	1.0
HS-dispersant5066	3.0
SN-sperse70	1.2
Cerasperse-44cf	3.6

areas of 180–200 m^2/g and 30 m^2/g respectively. It seems that the specific surface area is less critical factor for the high Ag^+ ion removal rate at this point. However, Fig. 6 clearly shows that crystalline quality (defect level) of the photocatalyst powders is more critical factor for the high Ag^+ ion removal rate. The PL spectrum of the SCM ZnO powder was compared with the spectra of commercial ZnO, P25 TiO_2 and HPPLT TiO_2 powders. The SCM ZnO powder showed a single strong band edge peak in the vicinity of 380–390 nm. The commercial ZnO powder showed primary as well as secondary peaks. The secondary peak was near the vicinity of 500–520 nm while the primary one was not intense. The secondary peak may have been arisen from the transition of electrons between conduction band edge and zinc vacancy level. This result shows that while commercial ZnO powder has so many defect structures, the SCM ZnO powder is free of defects. The defects may have been removed during its short exposure at a high temperature of around 1500–1800°C during its synthesis. On the other hand, both the TiO_2 powders showed weak PL intensity at band edge (near ~380 nm). This PL intensity at band edge is proportional to the number of electrons generated by UV irradiation. This implies that the electron generation efficiency of SCM ZnO
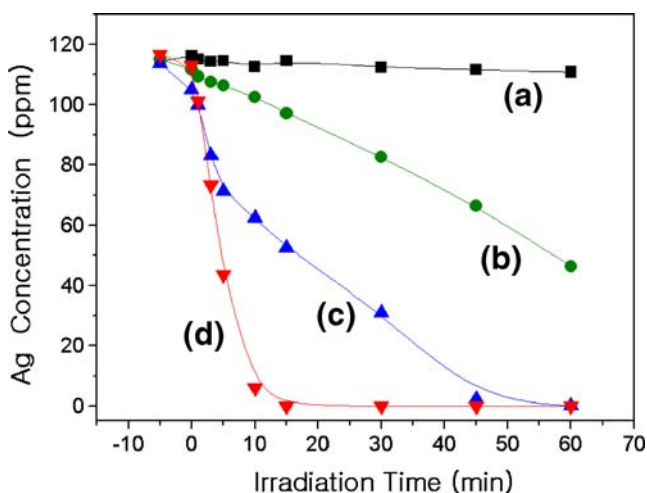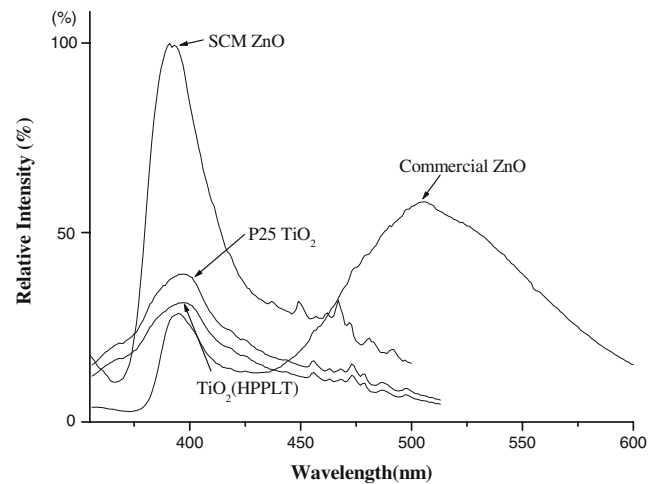

Fig. 6 Comparison of photoluminescence (PL) spectra of different photocatalytic powders

powder is highest among them and led to highest photocatalytic efficiency.

To examine the effect of oxidant and fuel combinations, the SCM ZnO powders were synthesized on four different conditions. These SCM ZnO powders were then treated with most effective dispersant, sodium hexametaphosphate. Figure 7 shows the remained Ag^+ ion concentration as a function of UV irradiation time using SCM ZnO powders with different synthesis conditions. Figure 7(a) shows almost no photocatalytic reaction even though the ZnO powder was dispersant-treated. It seems that this is not the problem of dispersion but the problem of crystalline quality. The commercial ZnO powder has been reported to have a large quantity of defect levels (also shown in Fig. 6) [4, 5].
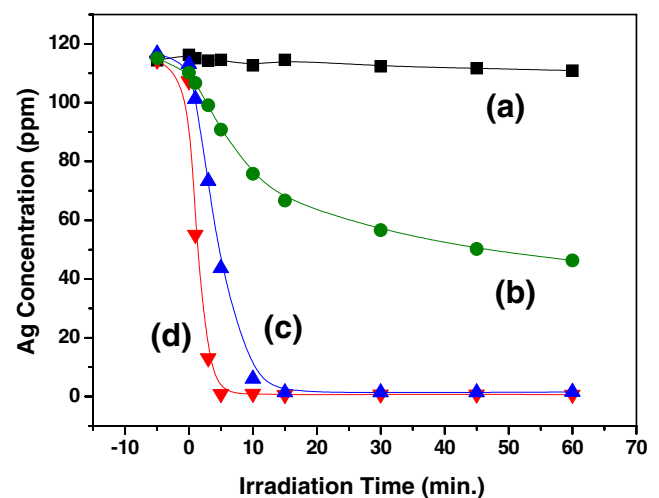

Fig. 5 Ag^+ ion recovery rate by photocatalytic reaction without dispersant treatment: (*a*) commercial ZnO powder (Junsei, Japan), (*b*) HPPLT TiO_2, (*c*) P25 TiO_2, (*d*) ZnO powder synthesized using Zn(OH)$_2$ and glycine

Fig. 7 Ag^+ ion recovery rate by photocatalytic reaction with dispersant treatment: (*a*) commercial ZnO powder (Junsei, Japan), (*b*) ZnO powder using Zn(NO$_3$) · 6H$_2$O and carbohydrazide, (*c*) ZnO powder using Zn(NO$_3$) · 6H$_2$O and glycine and (*d*) ZnO powder using Zn(OH)$_2$ and glycine

When the ZnO powder was synthesized using $Zn(OH)_2$ and glycine and treated with the dispersant (Fig. 7(d)), the Ag^+ ion removal rate was higher (21.5 μg/g/min) than other two SCM ZnO powders (Fig. 7(b) and (c)). Again the crystalline quality of ZnO powders is considered as a dominant factor to determine the photocatalytic reaction rate.

This Ag^+ ion removal rate is about 2 folds higher than that of SCM ZnO powders without dispersant. According to Riddick, zeta potential values more electronegative than −81 mV represent extremely high stability of a colloid system [6]. This high Ag^+ ion removal rate might be due to the extremely high dispersion effect.

This result is more remarkable compared with that of P25 TiO_2 powder. It is about 13 folds higher than that of P25 TiO_2 powder even though P25 TiO_2 powder has also dispersant on the surface. It is known that P25 TiO_2 surface is covered by Cl^- ions that came from its fabrication process [7]. This means that the Cl^- ions act as a dispersant for P25 TiO_2 powder.

4 Conclusions

ZnO nanopowders were synthesized by SCM with four sets of oxidant-fuel combinations. Five different dispersants were tried to treat the SCM ZnO nanopowders. Their dispersion characteristics were analyzed through mobility and zeta potential. Sodium hexametaphosphate was the most effective dispersant among them. The photocatalytic reactions were performed to remove Ag^+ ions from used photographic developing solutions. The Ag^+ ion removal rates by the dispersed SCM ZnO nanopowders were then compared with those by other photocatalyst powders such as commercial ZnO powders, commercial TiO_2 powders and TiO_2 powders prepared by HPPLT. The dispersion of SCM ZnO nanopowder in the solution enhanced the removal rate up to about 13 folds compared with P25 TiO_2 nanopowder and 2 folds to SCM ZnO nanopowders without dispersion.

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