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Photocatalytic ZnO nanopowders prepared by solution combustion method for noble metal recovery

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Nano-sized ZnO powder was synthesized by solution combustion method (SCM). Using this ZnO nanopowder as a photocatalyst, it was tried to recover silver from the silver-plating wastewater that was discharged by noble metal plating industries. The photocatalytic efficiency of ZnO nanopowder, as one of optical properties, was compared with other photocatalysts such as commercial TiO_2 and commercial ZnO. The ZnO nanopowder showed three folds higher photocatalytic efficiency than any other commercial photocatalysts. Other electro-optical measurements such as photoluminescence (PL) measurement, electrical resistivity and carrier concentration measurement also showed very consistent results. The recovery of gold from gold plating wastewater was also tried. The recovery efficiency was improved by about 25% by adding methanol as a scavenger to the gold plating wastewater. It took 45 min to completely recover gold from the wastewater.

1. Introduction

Recently the removal of heavy metal cations from industrial effluents is drawing much interest, since the heavy metals are one of major water pollutants and some of them are fatal for human body.

Industrial effluents containing high metal concentration are usually discharged from metal plating, mining and tanneries industries. Several methods such as precipitaion, reverse osmosis and ion-exchange have been commonly used to remove these metal cations from wastewater [1–4]. When the wastewaters contain considerable amounts of various metal ions, the primary consideration would be the ability of the techniques in recovering the metal ions in a reusable form in order to offset the costs of treatment. While all the techniques mentioned above are capable of recovering the metal ions in reusable form, the economic aspects are much different. The capital costs for chemical precipitation can be expected the least and very high for reverse osmosis and ion-exchange. This might be the reason that the precipitation is employed as the most common method for heavy metal removal from wastewater [5–8].

The photocatalytic method could remove wider range of heavy metals compared to other methods because it could provide electrons that are required to reduce metal cations to neutral metal atoms rather than forming stable chemical compounds such as precipitates. The photocatalytic method is, therefore, more effective to obtain reusable form of metal ions.

In this study, nano-sized ZnO powder was used as a photocatalyst to remove metal cations from plating wastewater. When ultra violet (UV) light is exposed on the ZnO powder surface, electron-hole pairs are generated. The ZnO is a more like n-type semiconductor. Its n-type conductivity is due to oxygen vacancies. This results in a non-stoichiometric compound and structural disorder [9]. This means that electrons are primarily trapped on surface trap sites and contribute to provide electrons to the metal cations. These electrons result in the reduction of the metal cations to metal atoms.

The efficiency of photocatalysts primarily depends on the characteristics of the photocatalytic powder. That is why it is important to understand the characteristics of the photocatalytic powder. In this study, the properties of ZnO nano-powder were investigated to understand its photocatalytic activity.

Nano-sized particles possess different physical and chemical properties compared to bulk materials. High catalyst activity may be expected because of their large

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surface area and different surface properties such as surface defects. Many researchers tried to synthesize ZnO powders. Their particle size is ranging from 200 nm to 150 μm [10–14]. However, the smaller particle size is required to obtain high photocatalyst activity because of their large surface area. In this study, nano-sized ZnO particles with smaller than 30 nm were synthesized. The ZnO nano-powder was synthesized by SCM that was proposed by authors' research group [15–20].

Especially, in this study, it was tried to remove the silver and gold from plating wastewater using this ZnO nano-powder. The removed metals could be reused because they are expensive noble metal. That is why the word "recovery" was used instead of the word "removal" in this paper. The electrical and optical properties of ZnO nano-powder were examined to understand its photocatalytic activity.

2. Experimental

The starting materials selected for this experiment were zinc hydroxide powder [$Zn(OH)_2$] [Junsei (Japan)] dissolved in nitric acid and glycine (H_2NCH_2COOH) [Yakuri Pure Chemicals Co. Ltd. (Japan)]. Here, zinc nitrate formed after the reaction between zinc hydroxide and nitric acid acts as oxidant while glycine on the other hand acts as a fuel. The oxidant solution was then diluted with distilled water in a beaker. Glycine was then added to the starting solution in the beaker. The mixing ratio of fuel and oxidant was changed in the range from 0.75 to 1.3. The solution mixture in the beaker was then heated on a hot plate with stirring as shown in Fig. 1. The heating temperature was about 80–100°C. As the distilled water was evaporated, the solution became viscous with the generation of air bubbles. The nitrate ions (NO_3^-) reacted with the fuel and intense heat was generated (about 1500–1800°C). This high temperature resulted in high pressure. This instantaneous pressure led to the explosion. The ZnO powder was formed in this high temperature and pressure environment. At this point the powder was collected by a filter, which was placed above the fan. Here, all of the experiment was performed inside a stainless steel chamber for the safety.

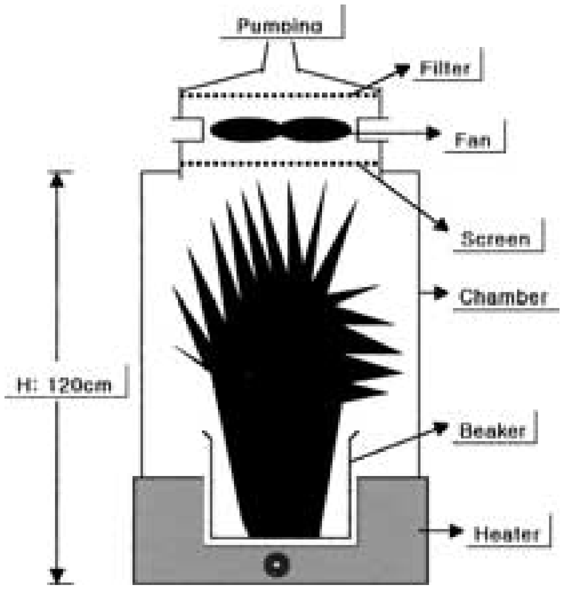

Figure 1 Schematic diagram of SCM ZnO powder synthesizing chamber.

X-ray diffractometer (XRD) (SIMAZ D-1) was used to confirm the crystalline phase of synthesized ZnO powder. Scanning electron microscope (SEM) was also used to investigate the powder size and shape. The powder was then used as a photocatalyst to recover Ag and Au from wastewater. It consisted of tubular cylindrical reactor with centrally mounted UV lamp (24 W). Jacketed cooling system was used for the temperature control. Silver and gold industrial wastewaters were prepared. The silver wastewater contained about 115 ppm of $Ag(NO_3)$ and the gold wastewater contained about 80 ppm of $Na_3Au(SO_3)_2$. Prior to using it as a photocatalyst, the above prepared ZnO nanopowder was mixed with alcohol and treated ultrasonically for 2 h. The remaining alcohol was evaporated at the SEM image Fig. 3 of the powder showed agglomerates of nanoparticles. This process of post-treatment assisted in efficient dispersion of the powder. The wastewaters were mixed with the ZnO nanopowder using magnetic stirrer and the solution mixtures were circulated in the reactor where reaction took place in order to recover silver and gold, respectively. The recovery rates of silver and gold ions using the above-prepared ZnO nanopowder were compared with other photocatalytic powders to see their catalytic efficiency. Photoluminescence (PL) measurement was also performed to investigate the UV sensitivity of photocatalytic powders. On the other hand, the carrier concentration and electrical resistivity of the above-prepared ZnO nanopowder were measured in order to examine its electrical properties.

3. Results and discussion

For the preparation of ZnO nanopowder, zinc nitrate was used as an oxidant and glycine was used as a fuel. When the fuel reacted with nitric acid group ($NO_{x=1,2,3}$), the temperature shot up to 1500–1800°C instantaneously with flame and combustion. This instantaneous heat was utilized to synthesize the powder.

Zinc oxide powders were synthesized adding the fuel in equilibrium state (oxidant: fuel = 1), fuel lean or fuel rich state by the degree of explosion about self-combustion, calculating oxidation number of oxidant and fuel. Different ZnO powders were prepared varying the fuel/oxidant ratio (F/O = 0.75–1.3). Single-phase ZnO powders were obtained in all the cases regardless of the ratio. Especially the ZnO powder with fuel/oxidant ratio of 0.8 showed highest XRD peaks as shown in Fig. 2 indicating its best crystalline properties among different powders.

The average particle size of the above-prepared powder was calculated from SEM images shown in Fig. 3. Finest particles (30 nm) were obtained when zinc nitrate and glycine as an oxidant and a fuel (F/O = 0.8) were used, respectively. Here, the powder was uniform nanometer sized and spherical in shape. At the same time, the specific surface area of the powder was

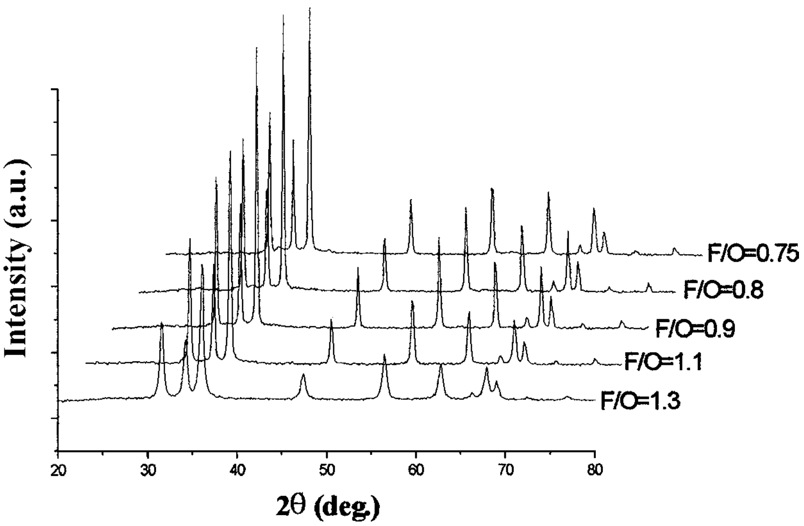

Figure 2 XRD pattern of SCM ZnO powder with fuel/oxidant ratio.

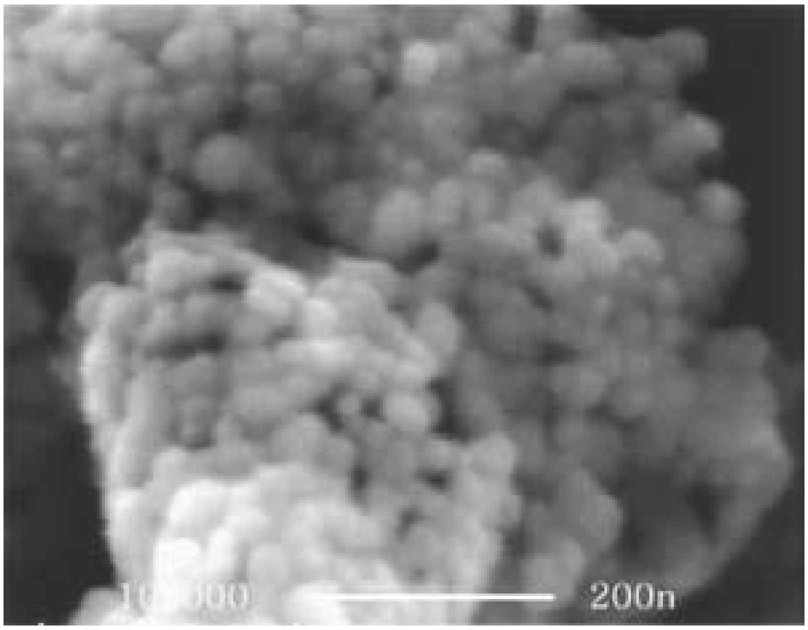

Figure 3 SEM image of SCM ZnO powder synthesized at fuel/oxidant ratio of 0.8.

obtained to be 120 m^2/g. During the preparation process of this powder, $Zn(OH)_2$ was dissolved in nitric acid. Therefore, there would be nitrate (NO_3^-) groups in the solution. The (NO_3^-) group acts as an igniter for combustion, which presumably would be helpful for the fine particle size.

TiO_2 synthesized by conventional HPPLT (homogeneous precititation process at low temperature) process [21], commercial TiO_2 (P-25 Degussa, Germany), commercial ZnO (Junsei, Japan) and the above-prepared ZnO powder were used as photocatalytic powders to see their catalytic efficiency. Each powder was mixed with the wastewater containing silver and irradiated by ultraviolet light to investigate the recovery performance of silver by photocatalytic effect. As shown in Fig. 4, the commercial ZnO did not show any photocatalytic effect. HPPLT TiO_2 recovered about 60% of silver in 60 min. It took 45 min to completely recover silver from the wastewater in the case of commercial TiO_2, known as the best photocatalyst among conventional metal oxides. However, for the case of the above-prepared ZnO powder, it took only 15 min to completely recover silver from the wastewater. This means that the above-prepared ZnO powder showed three times better performance than the conventional best powder.

To see the effect of scavenger on the gold recovery, 10% of methanol was added to the mixture solution containing gold wastewater and the above-prepared ZnO powder. As shown in Fig. 5, it took 60 min to completely recover gold from the wastewater without methanol. However, it took 45 min when the methanol was added to the mixture solution as a scavenger. This result indicates that the scavenger enhanced the recovery rate by 25%. The methanol has (OH^-) groups. These (OH^-) groups would combine with holes that were generated on the surface of ZnO powder during the irradiation of UV. This would decrease the recombination of electrons and holes on the surface of ZnO powder. Eventually, more electrons would contribute to the reduction of gold ions in the mixture solution.

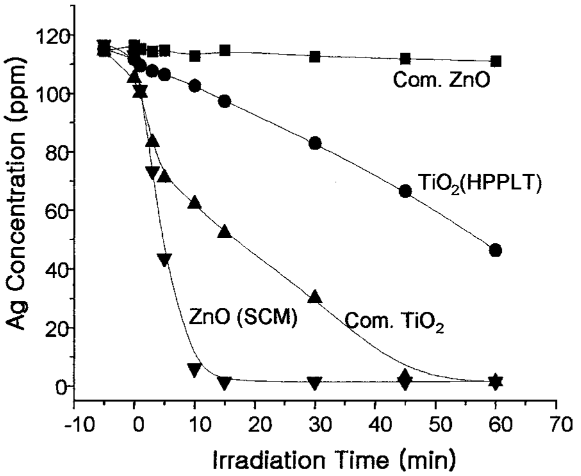

Figure 4 Comparison of Ag recovery efficiency of SCM ZnO powder (at fuel/oxidant ratio of 0.8) with other commercial powders in the photocatalytic process.

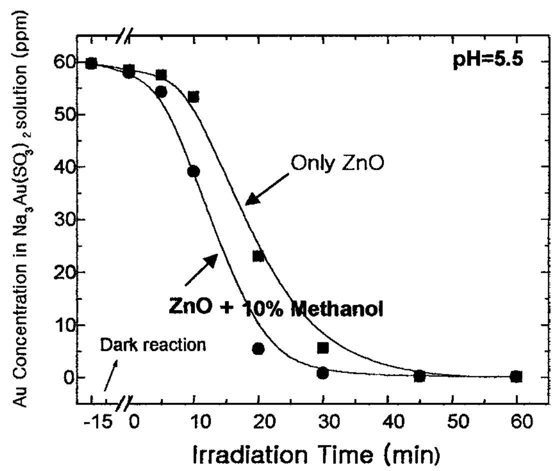

Figure 5 Comparison of Au recovery efficiency of SCM ZnO powder (at fuel/oxidant ratio of 0.8) with and without methanol in the photocatalytic process.

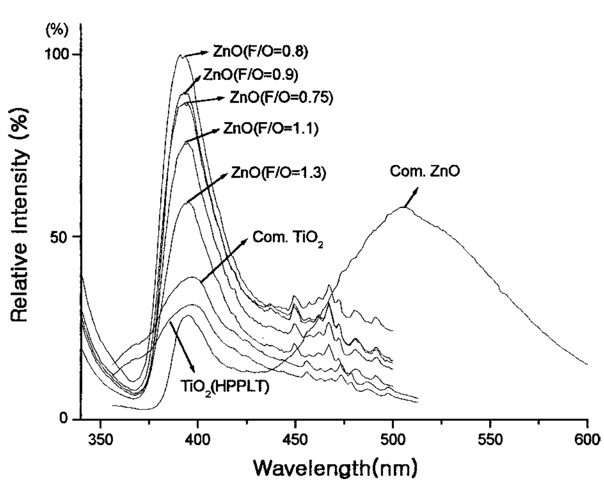

Figure 6 Photoluminescence spectra of commercial ZnO, HPPLT TiO_2, commercial TiO_2 and SCM ZnO powder.

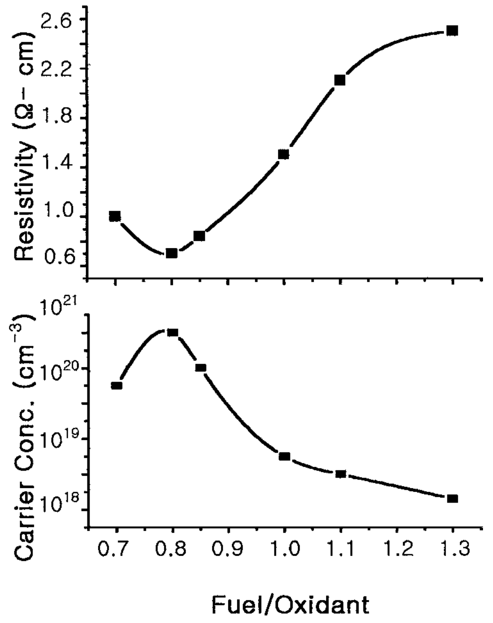

Figure 7 Carrier concentration and electrical resistivity of SCM ZnO powder with fuel/oxidant ratio.

Fig. 6 represents PL spectra of commercial ZnO, HPPLT TiO_2, commercial TiO_2 and above-prepared ZnO powder. The commercial ZnO powder showed two peaks: one is in the vicinity of 500 nm, and the other one is near 400 nm. The peak near 500 nm was probably from the energy transition between O vacancy level and Zn vacancy level. The UV peak near 400 nm might be from band to band transition. Here, the ZnO powder prepared from SCM showed single sharp peak near 390 nm. The peak is slightly shifted to UV side. This peak is equivalent to the energy gap of ZnO (~3.2 eV). There was no second peak near 500 nm region indicating that the ZnO powder synthesized by SCM was free from defects energy levels inside the energy gap. The defects were probably annealed out due to the high temperature during the synthesis process. Again, the powder showed higher PL intensity at UV than other ZnO and TiO_2 powders and highest intensity was obtained at the fuel/oxidant ratio of 0.8. This result suggests that the above-prepared ZnO nanopowder absorbs more UV than the other powders like commercial ZnO powder and different TiO_2 powders.

The above-mentioned PL result was strongly supported by electrical measurement data as shown in Fig. 7. Here, the carrier concentration was obtained by Hall measurement. It showed that the carrier concentration was highest at the fuel/oxidant ratio of 0.8. The same result was obtained from the electrical resistivity measurement. It also showed that the electrical resistivity was lowest at the fuel/oxidant ratio of 0.8. It seems that the surface sites of ZnO nanopowder were properly modified to have high carrier concentration on the surface at the fuel/oxidant ratio of 0.8. The reason is not clear at this stage. The above optical and electrical results led us to select the ZnO nanopowder synthesized with glycine/zinc nitrate ratio of 0.8 for the photocatalytic experiment.

4. Conclusions

In this investigation, nanometer sized ZnO powder was synthesized using SCM. Single-phase ZnO powder could be obtained easily using this method. Using glycine and zinc nitrate at the fuel/oxidant ratio of 0.8, the synthesized ZnO powder showed the best characteristics, such as highest XRD peak, average grain size of 30 nm, the specific surface area of 120 m^2/g, highest UV absorption, highest carrier concentration and lowest electrical resistivity. This high quality of the ZnO powder might be due to the defect removal by the high temperature and pressure generated during the synthesis process. When this ZnO powder was used as a photocatalyst to recover silver from wastewater, the level of silver ions in the wastewater was reduced to zero within 15 min.

This result confirms the outstanding photocatalytic activity of ZnO nanopowder synthesized using SCM. The rate of recovery was three folds faster than other commercially available powders. This result was strongly supported by the PL measurement data showing that the PL intensity of the ZnO powder was much higher than that of the commercial TiO_2 and ZnO powders. This result was also confirmed by electrical measurement data that showed highest carrier concentration. In this case, more carriers will be involved in the photocatalytic reaction. In scavenger study, the added methanol acts as a hole killer. This probably enhanced the carrier lifetime of electrons by decreasing electron and hole recombination. It eventually made more electrons contribute to the reduction of gold ions.

It could be concluded that the photocatalytic activity is strongly dependent on the electro-optical properties of photocatalytic powder as well as its particle size and specific surface area.

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