Collection of high purity gold from wastewater using ZnO nanopowders synthesized by solution combustion method

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Conventional precipitation method has been most often used to remove heavy metals. Of the few precipitation methods, hydroxide precipitation is the most widely used one. Given that all metal hydroxides do not completely precipitate at a single pH, hydroxide precipitation cannot ensure awkward for the various metals present in the wastewater. Thus, researchers are driven to study photocatalysts.

Photocatalysts have the unique capability of not only seperating and converting heavy metal ions from aqueous solution to their less toxic, readily collectable metallic forms, but also destroying the toxic organic contaminants. Photocatalysis using titanium dioxide (TiO_2) has been extensively studied for oxidation and is known to be effective for eliminating organics. Work on photocatalytic metal removal has been much less extensive. Development of a noble process that can simultaneously remove metal ions and destroy organics would provide a significant progress of the cleaning process for heavy-metal-contaminated waters. Besides, metals deposited on the photocatalyst particle surface can be collected and re-used. Being able to collect the heavy metals in metallic form means that the heavy metal toxicity can be minimized and the number of steps required for collection can be reduced. It was reported that metal ions such as lead, chromium, copper, silver and mercury could be removed/collected from dilute aqueous solutions using TiO_2 [1–16]. However, few studies have been conducted to collect metal ions using ZnO since TiO_2 is believed the best photocatalyst [17].

As previously reported, Park *et al*. proposed solution-combustion method to synthesize highly pure and ultra-fine ceramic powders [18–21]. Surprizingly, the silver ions in the used photo-film developing solution were completely removed in just 15 min using the aboved-prepared ZnO powder. This powder showed three times better performance than other commercially available powders. It was reported that the photocatalytic activity was strongly dependent on the electro-optical properties of photocatalytic powder-highest UV absorption, defect removal, highest carrier concentration as well as its particle size and specific surface area.

In this study, gold metal ions was collected from real plating wastewater, not simulated wastewater.

Zinc hydroxide powder [Junsei Chemicals Ltd. (Japan)] was dissolved in nitric acid to form zinc nitrate solution, which acts as an oxidant while glycine [Yakuri Pure Chemicals Co. Ltd. (Japan)] was taken as a fuel. 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 distilled water evaporated, the solution became viscous, producing a large number of air bubbles. At this point, the oxidant reacted with the fuel generating intense heat (about 1500–1800 °C). This heat leads to a high pressure, which created an explosion. The zinc oxide nanopowder was formed at this high-temperature and pressure environment. Here, it must be noted that the experiment, in its entirety, was performed inside a stainless steel chamber for safety reasons.

For the purpose of comparing the photocatalytic collection rates, commercial TiO_2 (Degussa, Germany) and ZnO (Junsei, Japan) powders were purchased. The powders were then used as a photocatalyst for removing metal ions from the aqueous solution. The reaction was carried out in a 100 ml batch-type quartz reactor with a diameter of 37 mm and height of 120 mm. A high-pressure mercury arc lamp served as an external UV source. Plating wastewater containing 60 ppm of gold ions was 3.0 g/L of the photocatalyst powder was mixed in plating wastewater and mixed ultrasonically for 5 min and left for 15 min in the dark for adsorption/desorption equilibrium, stirring it magnetically. Then the UV light was turned on for the photocatalytic reaction. The concentrations of gold ions remaining in the plating wastewater during different time intervals were detected using an AA spectrophotometer (Perkin-Elmer 5100 PC). Prior to detecting the metal ions, the solution was passed through a syringe filter having pore size of 0.2 um for the removal of any photocatalyst particles. Scanning electron microscope (SEM) was used to investigate the materials remaining after the water evaporated. EDX (Energy Dispersive X-ray Spectrometer) was used to confirm the composition of collected materials. Optical microscope was also used to examine the collected gold after removing the ZnO powder.

Fig. 1 shows the gold recovery rate of commercial ZnO(Junsei), commercial TiO_2 (Degussa, Germany)

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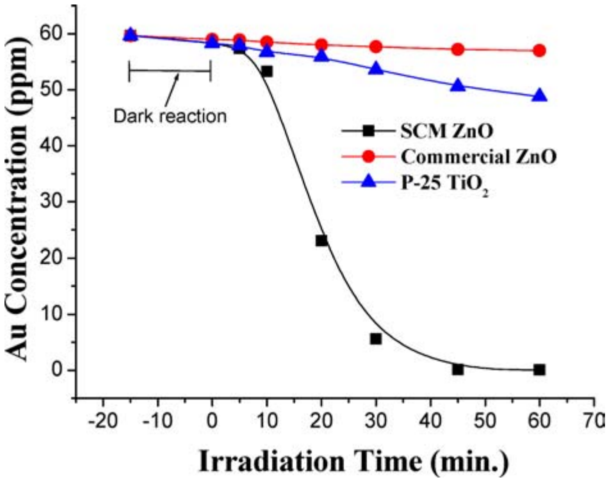

Figure 1 Au collection rate by photocatalytic reaction of commercial ZnO (Junsei, Japan), commercial TiO_2 (P-25 Degussa, Germany) and the SCM ZnO powders synthesized in this study.

and ZnO powders synthesized by SCM. As shown in Fig. 1, commercial ZnO powder did not show detectable photocatalytic reaction, whereas SCM ZnO nanopowder showed remarkable photocatalytic reaction. The powder synthesized by SCM completely collected the gold ions within 45 min of UV irradiation. However, the photocatalytic reaction using the commercial TiO_2 (P-25 Degussa, Germany) shows that only 17% of the gold ions were collected after identical treatment. The photocatalytic gold collection efficiency of SCM ZnO nanopowder is about 6 times higher compared to that by commercial TiO_2 nanopowder. These results were strongly supported by electro-optical measurement data reported previously [30]. Furthermore, the gold ions were completely collected after 30 min of UV irradiation when 10% of methanol (CH_3OH) was added to the solution. Here the methanol acts as hole scavenger. This hole scavenger improved the photocatalytic efficiency by 33%. This is a surprising result, given that TiO_2 is known as the best photocatalyst of all its kind.

As shown in Fig. 2, large particles were observed after a photocatalytic reaction, but no particle was observed before one. Furthermore, the color difference was observed. Gold and gray colors before photocatalytic reaction turned to pure gold color after the reaction. Fig. 3 shows the schematic representation of photocatalytic reaction in this work. At first, the gold ions and ZnO nanopowders were mixed together (Fig. 3a). Then the gold ions were adsorbed on the ZnO nanopowder surfaces (Fig. 3b). Eventually, the positive gold ions were reduced to a neutral gold metal by receiving electrons that were generated on ZnO nanopowder surfaces by UV irradiation (Fig. 3c). The SEM photograph of Fig. 2a represents the state of the gold ions and ZnO nanopowders when mixed together as shown in Fig. 3a. The SEM photograph of Fig. 2b represents the state of the gold ions when neutralized to gold metal on ZnO nanopowder surfaces as shown in Fig. 3c.

EDX measurement was performed to confirm if this collected metal was actually gold. Fig. 4 showed weak gold peaks before photocatalytic reaction, and strong and sharp gold peaks after it. This leads to the conclusion that photocatalytic reaction by SCM ZnO nanopowder produces gold particles from gold ions in solution. The calculation based on EDX measurement data showed that the purity of collected gold was about 99.6% in wt% and 98.8% in at%.

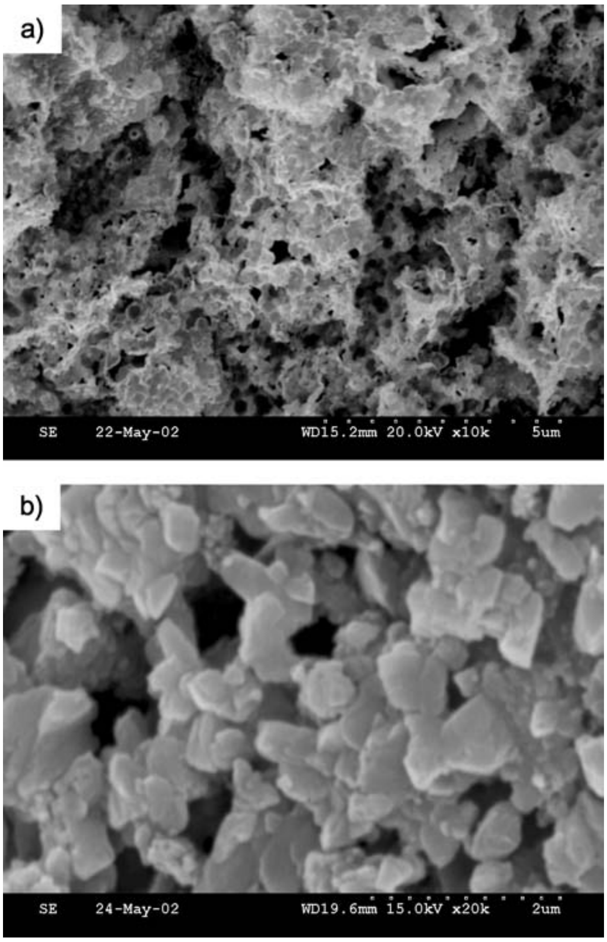

Figure 2 SEM photographs (a) before and (b) after photocatalytic reaction.

Finally, the optical photograph of the collected gold powder was obtained. Fig. 5 clearly shows the collected gold powders. The color is that of pure gold.

In this study, ZnO nanopowders were synthesized by SCM. The photocatalytic gold collection efficiency of this SCM ZnO nanopowder was about 6 times higher compared to that by commercial TiO_2 nanopowder.

Photocatalytic reactivity seems to depend on the preparation method of the photocatalytic powders rather than the crystalline phase, specific surface area or even the nature of the material. The preparation methods affect surface properties such as the surface defect levels. Generally it is known that the smaller particle size results in a greater number of surface defects. In the present SCM ZnO case, however, the extent of surface defects seemed to be minimized despite the fact that the powder was synthesized in nano-size. This might be due to the high synthesis temperature that rose to approximately 1500—1800 °C.

The purity of collected gold was about 99.6% in wt% and 98.8% in at%. The ZnO nanopowder method of synthesis and gold collection process addressed in this work are very cost-effective. This technology is a viable for obtaining high purity gold from plating wastewater.

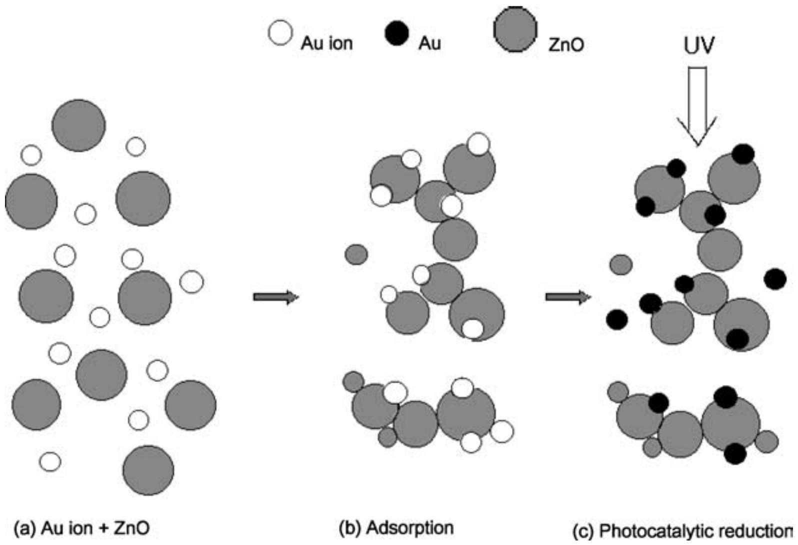

Figure 3 Schematic representation of photocatalytic reaction.

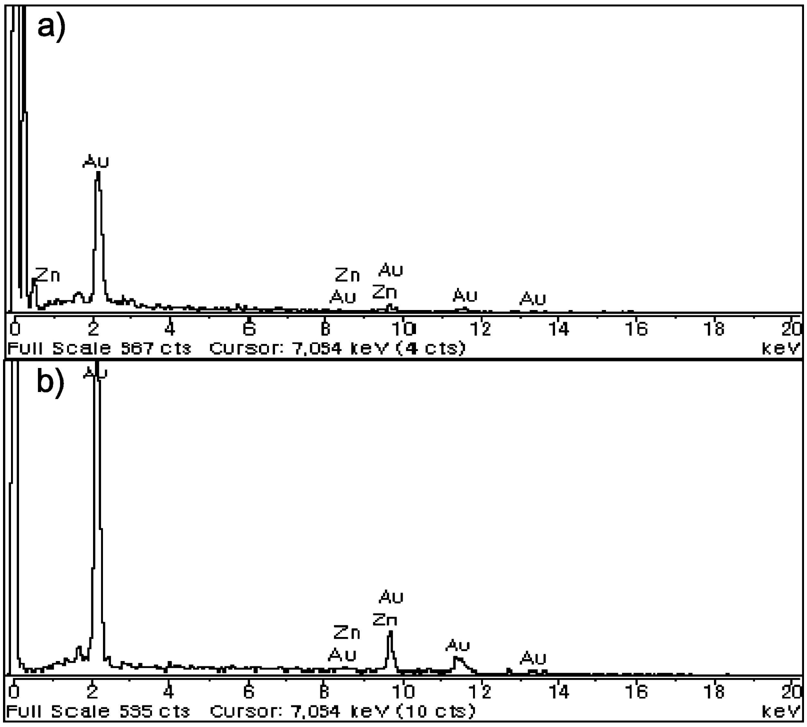

Figure 4 EDX patterns (a) before and (b) after photocatalytic reaction.

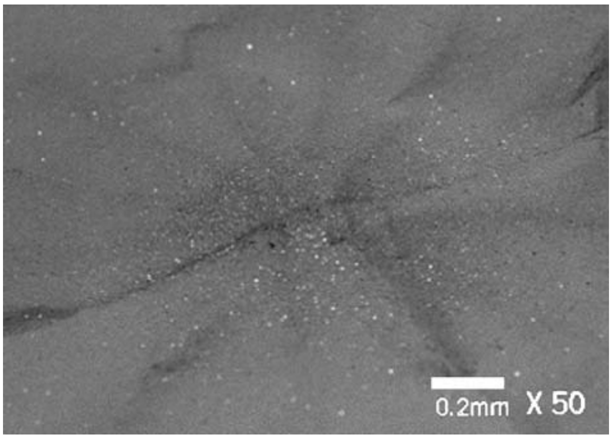

Figure 5 Optical photograph of collected Au after photocatalytic reaction.

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