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Photoreaction of gold ions from potassium gold cyanide wastewater using solution-combusted ZnO nanopowders

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Abstract

Photoreduction of gold ions from potassium gold cyanide wastewater was tried using the ZnO nanopowder which was synthesized by a unique solution combustion method (SCM). The SCM produced instantaneous high pressure and high temperature (1500–1800 °C) conditions which are desirable to obtain high quality ZnO nanopowders, even though it was not intentionally heated at higher than 100 °C during the synthesis reaction. The high crystalline quality of the ZnO nanopowder seemed to result in high efficiency of gold recovery compared to other commercial photocatalysts such as P-25 TiO_2 nanopowder (Degussa). The wastewater contains many kinds of ions such as K, P, Au, Na, Ni, Cu and Zn ions. Only the gold ions were selectively recovered out of these ions. The gold recovery efficiency of the SCM ZnO nanopowder was about 8.6 folds higher than that of the P-25 TiO_2 nanopowder. The very high selectivity of Au^{3+} ions could be explained by the reduction potential which is placed near the edge of valence band.

Keywords: Solution combustion method; ZnO; TiO_2; Chemical properties; Functional applications

1. Introduction

Photocatalysts have the unique capability of both separating and converting heavy metal ions from aqueous solution to their less toxic, readily recoverable metallic forms. Photocatalysis using titanium dioxide (TiO_2) has been extensively studied for oxidation and is known to be effective for destruction of organics. Work on photocatalytic metal removal has been much less extensive. The particular aspect of being able to recover the heavy metals in metallic form reduces the number of steps required for recovery. It was reported that metal ions such as lead, chromium, copper, silver and mercury could be removed/recovered from dilute aqueous solutions using TiO_2.[1–10] However, few studies were conducted to recover metal ions using ZnO since it is well-known that TiO_2 is the best photocatalyst.[11]

The cyanide process is a mining technique for extracting gold from low-grade ore via the use of cyanide compounds. It is at present the most important and most-often used process for this purpose. The process was developed in 1887 by J.S. MacArthur and others. Due to the highly toxic nature of cyanide, the process is controversial. A brief description about the cyanide process might be necessary to understand the property of the wastewater. First of all, the ore is ground to a fine powder in a revolving cylinder with steel balls, and may be further concentrated by flotation. It is combined with a dilute solution of potassium cyanide while bubbling air through it. The negatively charged cyanide anions release the gold cations from the ore as a metal complex. The gold oxidizes to form the soluble aurocyanide metallic complex, $KAu(CN)_2$. The chemical reaction is

$$4Au + 8KCN + O_2 + 2H_2O \rightarrow 4KAu(CN)_2 + 4KOH$$

The solution is separated from the ore by methods such as filtration, and then the gold is displaced by adding zinc dust, which precipitates the gold: zinc has a higher affinity for the cyanide ion than gold.

The wastewater from this process is still containing gold ions. In this study, the selective photocatalytic gold recovery from the gold mining wastewater, potassium gold cyanide wastewater

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was tried using the solution combustion method (SCM) ZnO nanopowder.

2. Experimental

Zinc hydroxide powder [$Zn(OH)_2$, Junsei (Japan)] was used for the starting material. Glycine [H_2NCH_2COOH, Yakuri pure chemicals co. Ltd (Japan)] was used for the fuel. Here the zinc hydroxide powder was dissolved in nitric acid before using, to form zinc nitrate. Each starting material was then dissolved in distilled water in each beaker. Glycine was then added to the starting solution in each beaker. 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 group (NO_3^-) reacted with the fuel and intense heat was generated (about 1500–1800 °C). This intense heat resulted in instantaneous high pressure, which 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, which was placed above the beaker. The prepared ZnO powder was examined by transmission electron microscope (TEM).

For the purpose of comparison of photocatalytic recovery rate, P-25 TiO_2 nanopowder (Degussa, Germany) was purchased. The powder was then used as photocatalysts for the removal of gold ions from the potassium gold cyanide wastewater. The potassium gold cyanide wastewater was received from a gold mining industry and the concentration of metal ions in the wastewater was measured by inductively coupled plasma-atomic emission spectrophotometer (ICP-AES). It was then diluted with deionized water to make the final concentration of Au^{3+} ions at 60 ppm. The prepared ZnO photocatalyst powder of 0.3 g was mixed with 100 ml of the diluted potassium gold cyanide wastewater and it was subjected to ultrasonic mixing for 5 min and then left it 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 gold concentration in the solution during photocatalytic reaction was measured by atomic absorption spectrophotometer. Energy dispersive X-ray (EDX) was used to examine the kinds of materials formed during the photocatalytic reaction.

3. Result and discussion

In this study, zinc hydroxide dissolved in nitric acid was used for the starting material (oxidant), and glycine was used as a fuel, in order to synthesize the ZnO powder. The fuel reacted with nitric acid group ($NO_{x=1,2,3}$) and resulted in combustion. At this point, temperature shot up to 1500–1800 °C instantaneously with flame and combustion. The ZnO powder was synthesized with the aid of this heat. Fig. 1 shows the synthesized ZnO powder whose average size is about 30 nm. The particles have the spherical shape which is most effective for surface reaction.

Fig. 2 shows the concentration of metal ions in potassium gold cyanide wastewater before photocatalytic reaction. The measurement was performed twice and the mean value was obtained. It contains many kinds of ions such as K, P, Au, Na, Ni, Cu and Zn ions.

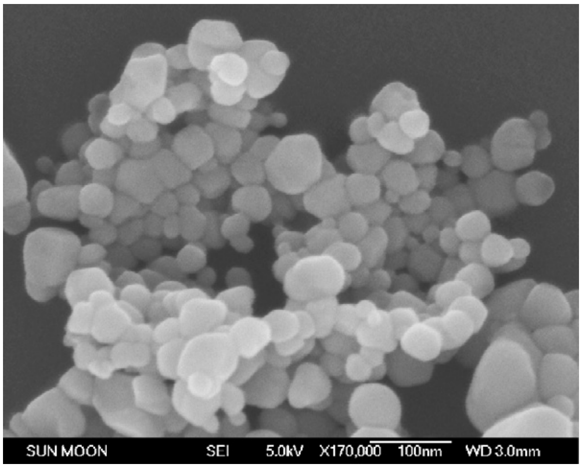

Fig. 1. SEM image of the prepared ZnO nanopowder.

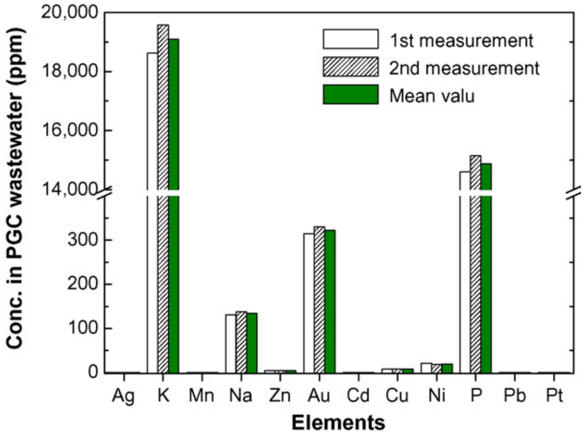

Fig. 2. Compositional elements of potassium gold cyanide (PGC) wastewater by ICP-AES.

As shown in Fig. 3, the photocatalytic reaction using the SCM ZnO nanopowder completely recovered the gold ions after irradiating UV for 45 min, while the photocatalytic reaction using the P-25 TiO_2 recovered only 17% of the gold ions. This is a remarkable result considering that, as well-known, the TiO_2 is

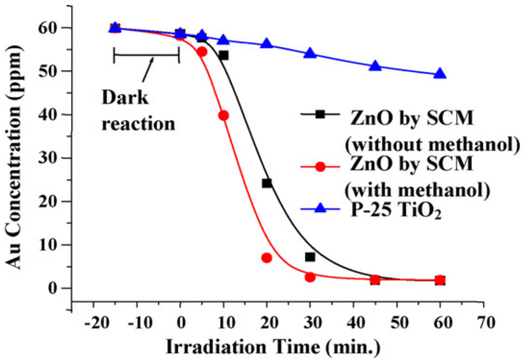

Fig. 3. Au recovery rate by photocatalytic reaction using the commercial TiO_2 and the SCM ZnO powder, and scavenger effect on Au recovery rate.

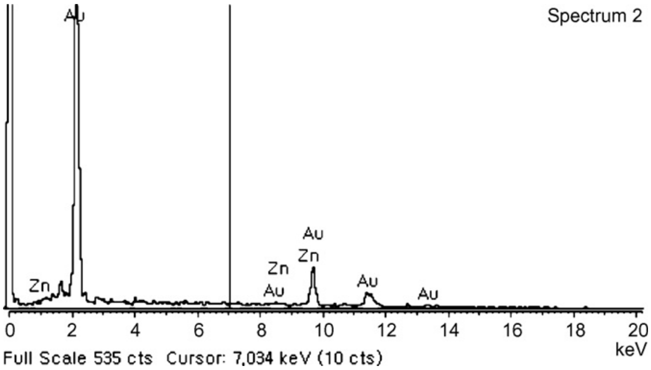

Fig. 4. EDX patterns after photocatalytic reaction.

the best photocatalyst out of all available photocatalytic materials. Furthermore, the gold ions were completely recovered after irradiating UV for 30 min when methanol (CH_3OH) of 10% (v/v) was added to the potassium gold cyanide wastewater. Here the methanol acts as hole scavenger. This hole scavenger improved the photocatalytic efficiency by 33%. The photocatalytic gold recovery efficiency by the SCM ZnO nanopowder is about 8.6 folds higher compared to the case by the P-25 TiO_2 nanopowder since only 11.7% of the gold ions was recovered by the P-25 TiO_2 nanopowder.

Fig. 4 shows EDX patterns of the remained material which was obtained by drying the solution after photocatalytic reaction. As shown in Fig. 4, the observed gold peaks were strong and sharp. This means that the photocatalytic reaction by the SCM ZnO nanopowder effectively produced gold metal particles from gold ions in potassium gold cyanide wastewater. The calculation based on EDX measurement data showed that the purity of recovered gold was about 99.6 wt.%. The recovered gold has the same purity as the one which is called pure gold in gold mining industries. As shown in the figure, only gold and zinc peaks were observed. Here, the zinc peaks probably came from the zinc which is in the ZnO powder. Based on this result, only the gold ions were selectively recovered from the potassium gold cyanide wastewater.

In view of reduction potential, only Au^{3+}, Ni^{2+} and Cu^{2+} ions among the ions in the wastewater could be reduced by ZnO since the reduction potentials of these three ions are within energy gap of the ZnO (+2.40 V for Au^{3+}, +0.34 V for Cu^{2+}, −0.26 V for Ni^{2+} vs NHE).[12] The reduction potentials for other ions are K ($K^+ + e^- \rightarrow K$: −2.93 V), P ($HPO_3^{2-} + 2H_2O + 3e^- \rightarrow P + 5OH^-$: −1.71 V), Na ($Na^+ + e^- \rightarrow Na$: −2.71 V) and Zn ($Zn^{2+} + 2e^- \rightarrow Zn$: −0.76 V). The reduction potentials of all of these ions are outside ZnO band gap as shown in Fig. 5. This means that these ions are not likely to be reduced to form metal atoms. As shown in Fig. 5, the driving force for the reduction (reduction potential) of Au^{3+} ions is the highest among these three ions because the reduction potential of Au^{3+} ions is more positive than the others. The closer the position of reduction potential is to the edge of the valence band, the easier the reduction could occur, since the reduction requires electrons which were excited from the valence band. The positions of reduction potential for Au^{3+}, Cu^{2+} and Ni^{2+} are +2.40 V, +0.34 V and −0.26 V respectively. The top edge of the valence band is at +2.90 V. The energies required for the reduction of Au^{3+}, Cu^{2+} and Ni^{2+} are, therefore, 0.5 eV, 2.56 eV and 3.16 eV respectively. The smallest amount of energy is required for the reduction of Au^{3+} ions. This means that Au^{3+} ions have highest possibility of reduction. The Au^{3+} ions are therefore selectively reduced.

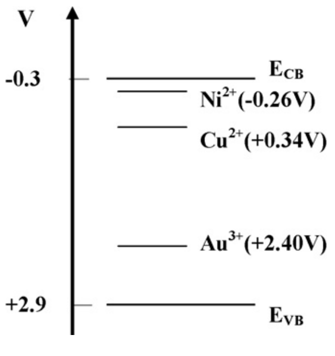

Fig. 5. Positions of metal ion reduction potentials within ZnO semiconductor energy gap (potential vs NHE).

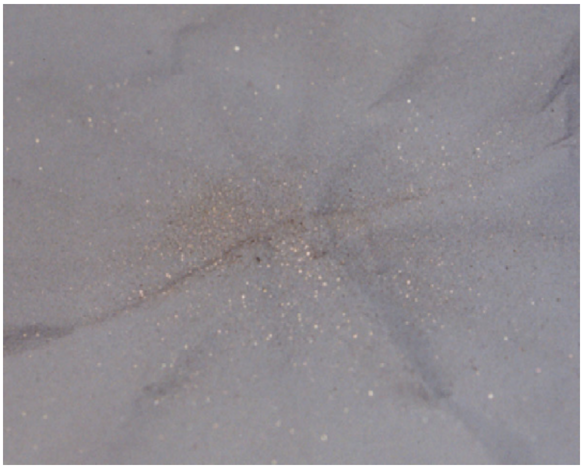

Fig. 6. Optical photograph of recovered Au powder after photocatalytic reaction.

Fig. 6 shows the optical photograph of the recovered gold powder. It clearly confirms the recovered gold powder with pure gold color. The recovered gold powder has a flake shape.

4. Conclusion

Only the Au^{3+} ions in the potassium gold cyanide wastewater were selectively and completely recovered within 45 min when the SCM ZnO nanopowder was used for photocatalytic reaction. Furthermore, the gold ions were completely recovered just within 30 min when methanol (CH_3OH) of 10% (v/v) was added to the wastewater. The photocatalytic gold recovery efficiency by the SCM ZnO nanopowder was about 8.6 folds higher compared to the case by the P-25 TiO_2 nanopowder. The very high selectivity of Au^{3+} ions could be explained by the reduction potential which is placed at near the edge of the valence band. This is a clean process and makes it possible to reuse the cyanide. This technology is therefore very viable for gold mining industries.

Acknowledgement

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