Photodeposition of Au nanocatalysts onto CuCrO₂ powders

Te-Wei CHIU,[†] Yu-Te LIN and Yi-An CHEN

Department of Materials and Mineral Resources Engineering, National Taipei University of Technology,
1, Sec. 3, Zhongxiao E. Rd., Taipei, 106 Taiwan

In this research, Au nanocatalysts were deposited on CuCrO₂ powders using photodeposition to investigate the catalytic activity. Delafossite-type CuCrO₂ porous powders were prepared using a glycine nitrate process. Au nanoparticles were photodeposited onto the CuCrO₂ surface by irradiating light into pH adjusted HAuCl₄ solution. The crystal structure, composition, and micromorphology of the derived Au/CuCrO₂ powders were characterized by X-ray diffraction, X-ray fluorescence, scanning electron microscopy, and transmission electron microscopy (TEM), respectively. TEM observation determined that the diameters of the Au nanoparticles photodeposited on CuCrO₂ powder with UV irradiation at pH = 10 were approximately 4 nm. The differential scanning calorimetric measurement indicated that Au/CuCrO₂ has a catalytic activity of carbon monoxide conversion.

©2014 The Ceramic Society of Japan. All rights reserved.

Key-words : Delafossite, CuCrO₂, Au nanoparticle, Catalyst, Photodeposition

[Received January 29, 2014; Accepted February 17, 2014]

1. Introduction

Haruta et al. discovered that gold nanoparticles deposited on metal-oxide supports show a strong catalytic activity of oxidizing carbon monoxide at temperatures as low as -73°C .¹⁾ Since bulk gold is chemically inert and expresses poor catalytic activity, this novel finding opened up a new field of catalyst. Later studies revealed that the catalytic activity depended on the size of the gold clusters, support materials, and contact structures. Au nanoparticles express a higher catalytic activity at diameters of 2 to 4 nm,²⁾⁻⁴⁾ but they show a lower activity at diameters of less than 2 nm, at which it tends to agglomerate.²⁾ To maximize the catalytic activity, it is essential to control the diameter of Au particles and provide a large surface area on the support.

Delafossite-type CuBO₂ (B=Al, Cr, Y) materials have the potential for application in p-type transparent semiconductors.⁵⁾ It has also been reported that these materials show antibacterial and photocatalytic activities for removing heavy metals and generating hydrogen.⁶⁾⁻⁸⁾ CuCrO₂ is a p-type semiconductor with a direct band gap of 3.1 eV.⁹⁾ In our previous study, we prepared porous and homogeneous CuCrO₂ powders using a glycine nitrate process.¹⁰⁾ The measured surface area of CuCrO₂ powders was 30.92 m²/g, which made them a potential candidate for the catalytic support. In this paper, we report our investigations of the preparation conditions of Au nanoparticles deposited on CuCrO₂ powders by light irradiation and of the catalytic activity of the resulting material.

2. Experimental procedure

2.1 Photodeposition of Au nanoparticles onto CuCrO₂

The CuCrO₂ nanopowder was prepared according to reference.¹⁰⁾ HAuCl₄ solution was used as an Au precursor. First, HAuCl₄ powder was dissolved in deionized water to make 100 mL 0.5 mM solution. Then 0.5 g of CuCrO₂ powder was added to

the solution with rapid stirring to disperse the CuCrO₂ powders effectively into the HAuCl₄ solution. The pH of the resulting dispersion was adjusted by adding a diluted ammonia solution. A 100 W tungsten lamp and a 250 W high-pressure mercury lamp (365 nm) were used as the sources of visible light and UV light for photodeposition, respectively. After being irradiated for 10 min, the slurry was filtered, washed, and dried overnight at 80°C in an oven. Finally, the Au/CuCrO₂ powder was annealed at 300°C for 4 h in atmosphere and subsequently stored in a desiccator in the dark.

2.2 Characterization of samples

The crystal structure was examined by X-ray diffraction spectroscopy (XRD) (Rigaku Dmax 2200 diffractometer), which involved CuK α radiation ($\lambda = 1.540 \text{ \AA}$). The chemical composition of as-prepared Au/CuCrO₂ powder was determined by X-ray fluorescence spectroscopy (XRF) (SII SEA6000VX). The microstructure of the CuCrO₂ powder and Au/CuCrO₂ catalyst were investigated by scanning electron microscopy (SEM) (HITACHI S-4700) at 15 kV. The size of Au particle and the structure were analyzed by high-resolution transmission electron microscopy (TEM) (JEOL FE2100, 200 kV). The carbon monoxide oxidation activity was determined by differential scanning calorimetry (DSC).

3. Results

3.1 XRD analysis

Figure 1 shows XRD patterns of as-prepared CuCrO₂ nanopowder and the Au/CuCrO₂ catalyst prepared by photodeposition. The as-prepared CuCrO₂ powder exhibited typical CuCrO₂ diffraction peaks, corresponding to the delafossite phase (JCPDS 39-0247). The broader peaks were mainly attributed to the nano-sized CuCrO₂. Clear gold patterns (JCPDS 04-7084) were obtained after photodeposition of Au particles onto CuCrO₂ powder both by irradiation of visible light from a tungsten lamp at pH = 10 and by UV light from a mercury lamp at various pH values. The XRD spectrum indicates that the gold particles were successfully deposited onto the CuCrO₂ support without

[†] Corresponding author: T.-W. Chiu; E-mail: tewei@ntut.edu.tw

[‡] Preface for this article: DOI <http://dx.doi.org/10.2109/jcersj2.122.P4-1>

Fig. 1. XRD patterns of as-prepared CuCrO_2 powder and Au/ CuCrO_2 catalyst.

Table 1. XRF analysis results of Au/ CuCrO_2 catalyst

Sample	Cu	Cr	Au
Visible-pH 10	45.9%	34.3%	2.0%
UV-pH 6	46.1%	34.7%	1.9%
UV-pH 7	46.1%	34.5%	2.3%
UV-pH 8	45.8%	34.6%	2.3%
UV-pH 9	46.1%	34.4%	2.4%
UV-pH 10	46.2%	34.4%	2.0%

any chemical interaction. XRD peaks attributed to Au particles prepared by visible light irradiation were higher and narrower than those prepared by UV light irradiation. The photodeposition was carried out at room temperature, and no chemical reaction between Au and CuCrO_2 occurred, as indicated in the XRD analysis in Fig. 1.

3.2 XRF measurement

Table 1 lists a summary of the XRF results for photodeposited Au/ CuCrO_2 . In samples obtained by visible light irradiation and those obtained by UV light irradiation, the compositions of Au/ CuCrO_2 were similar. The Au content in the Au/ CuCrO_2 system was about 2%. The Au content, which is related to the particle size and coverage over support, is a critical factor for evaluating the catalytic activity of the Au/support system.

3.3 SEM microstructure

Figure 2 shows the microstructure of the as-prepared CuCrO_2 nanopowder at 15 kV. It was composed of randomly-arranged thin porous membranes. The pores varied in size from nanometers to micrometers, providing a high surface area. **Figure 3** presents an SEM image of Au photodeposited by visible light irradiation at pH = 10. Au particles were dispersed in the CuCrO_2 porous structure. However, the Au particles were relatively large and consistent with the narrow and sharp XRD pattern in Fig. 1. These results did not achieve our goal of depositing nanosized Au particles on the CuCrO_2 surface. Because the direct energy gap of

Fig. 2. SEM image of as-prepared CuCrO_2 powder.

Fig. 3. SEM image of Au/ CuCrO_2 catalyst prepared by visible light irradiation at pH = 10.

Fig. 4. SEM image of Au/ CuCrO_2 catalyst prepared by UV light irradiation at pH = 10.

CuCrO_2 is higher than 3.1 eV, visible light cannot activate it. However, the defect spots in CuCrO_2 could be activated by visible light, and the Au was photodeposited on these sites in agglomerated clusters.

Figure 4 presents an SEM image of Au photodeposited by UV light irradiation at pH = 10. Although several large Au particles can be observed, the basic microstructure was the same as that of the as-prepared CuCrO_2 (Fig. 2).

3.4 TEM observation

We used TEM to determine if the small gold clusters were present on the CuCrO_2 -support. **Figure 5** presents a TEM image of Au photodeposited by visible light irradiation at pH = 10. Large Au particles of about 100 nm can be clearly observed, but no nano-sized Au particles are in evidence. **Figure 6(a)** shows a TEM image of Au photodeposited by UV light irradiation at pH = 10. Figures 6(b)–6(d) are enlargements of the square areas in Fig. 6(a)–6(c), respectively. The gold clusters (tiny darker spots) were evenly distributed on the CuCrO_2 -support [Fig. 6(c)].

Fig. 5. TEM image of Au/CuCrO₂ catalyst prepared by visible light irradiation at pH = 10.

Fig. 7. DSC measurement of catalytic activity of Au/CuCrO₂.

Fig. 6. TEM image of Au/CuCrO₂ catalyst prepared by UV light irradiation at pH = 10.

The average diameter of the gold clusters was approximately 4.0 nm, which is within the range required for optimal catalytic oxidation activity. The high density of the gold clusters on the CuCrO₂ support provided the Au/CuCrO₂ catalyst with a large three-phase interface area, which is necessary to yield high levels of catalytic activity.

3.5 Catalytic activity

We used DSC to measure the catalytic activity of Au/CuCrO₂ toward carbon monoxide. Exothermic peaks in the DSC plot would confirm a reaction between the Au/CuCrO₂ catalyst and carbon monoxide. **Figure 7** shows a DSC plot of the Au/CuCrO₂ catalyst prepared by visible light irradiation at pH = 10 and UV irradiation at various pH values. All samples showed exothermic peaks after carbon monoxide was introduced into the DSC chamber. Au/CuCrO₂ catalyst prepared by visible light irradiation at pH = 10 had an almost flat line, indicating that the catalytic activity was very low. The most likely explanation for this level of activity is that the particle size was too large, as shown in Fig. 3. The observed heat flows are listed in **Table 2**. All of the Au/CuCrO₂ catalyst prepared by UV irradiation

Table 2. Heat flow of Au/CuCrO₂ catalysts reacting with carbon monoxide

Sample	Heat flow (mW/mg)
Visible-pH 10	0.02
UV-pH 6	0.585
UV-pH 7	0.642
UV-pH 8	0.883
UV-pH 9	0.981
UV-pH 10	1.008

showed decreases in heat flow, indicating that the Au/CuCrO₂ catalyst reacted with the carbon monoxide. In this study, the highest catalytic activity was exhibited by the Au/CuCrO₂ prepared by UV irradiation at pH = 10.

4. Discussion

The nano-deposition of Au particles onto CuCrO₂ nanopowder was accomplished with the photodeposition method in HAuCl₄ solution. Since CuCrO₂ is a p-type semiconductor with a direct bandgap of 3.1 eV, it absorbed UV light during the photodeposition process to generate electron-hole pairs. The Au³⁺ ions in the HAuCl₄ solution caught these UV-pumped electrons and precipitated onto the CuCrO₂ surface as Au metal clusters. The atomic ratio of Au:CuCrO₂ was 0.02:1, according to XRF measurement. These deposited Au nanoparticles were approximately 4 nm in diameter and were uniformly deposited onto the CuCrO₂ surface. If the surface area density of the CuCrO₂ powder is assumed to be 30.92 m²/g [5], and the diameter of the Au nanoparticles was 4 nm, it follows that the Au particle density over the surface area was 0.13/nm², according to the 2% Au atomic ratio in the CuCrO₂ support. However, the density of Au nanoparticles observed in TEM images was 0.01/nm², which is one order of magnitude smaller. This result indicates that the process parameters, such as the dispersion degree of solid nanopowder support in the solution, solution concentration, temperature, UV irradiation intensity, and stir speed, might need to be optimized to increase the Au nanoparticle density over the surface area to maximize catalytic activity.

The preliminary results on catalytic activity reveal that the Au/CuCrO₂ system has an oxidation activity against carbon monoxide. The DSC measurement demonstrated an exothermic energy change of 1.008 mW/mg upon the introduction of CO gas into the chamber. The performance of the Au nanocatalyst is determined by the particle size, contact structure, and support materials.¹¹⁾ This is the first study to employ a multicomponent p-type

oxide as the supporting material for an Au nanocatalyst. It is also reported that copper-containing compounds, such as superconducting and pyrochlore,^{12),13)} have certain catalytic activity. We can thus expect a synergistic effect of Au nanoparticles and copper-containing support in certain catalytic chemistry. We believe that the variety of the delafossite group and its tunable band gap will allow expansion of the applications of such materials in the area of catalysis.

5. Conclusion

Gold catalysts supported on CuCrO_2 powder were prepared by photodeposition method. Visible light and UV light were used as light sources for photodeposition. Visible light irradiation caused large Au clusters ($>50\text{ nm}$) to be deposited on CuCrO_2 , and UV radiation caused nanosized Au particles ($\sim 4\text{ nm}$) to be deposited on CuCrO_2 support. The catalytic activity of Au/ CuCrO_2 reacting with carbon monoxide was measured by DSC and thus confirmed. The highest catalytic activity, 1.008 mW/g , was exhibited by the Au/ CuCrO_2 prepared by UV irradiation at $\text{pH} = 10$.

Acknowledgement This work was financially supported by the National Science Council of Taiwan under Contract No. NSC98-2218-E-027-004 and Much Fortune Tech Co Ltd.

References

- 1) M. Haruta, T. Kobayashi, H. Sano and N. Yamada, *Chem. Lett.*, **2**, 405–408 (1987).
- 2) M. Okumura, S. Nakamura, S. Tsubota, T. Nakamura, M. Azuma and M. Haruta, *Catal. Lett.*, **51**, 53–58 (1998).
- 3) T. Hayashi, K. Tanaka and M. Haruta, *J. Catal.*, **178**, 566–575 (1998).
- 4) M. Haruta, N. Yamada, T. Kobayashi and S. Iijima, *J. Catal.*, **115**, 301–309 (1989).
- 5) H. Kawazoe, M. Yasukawa, H. Hyodo, M. Kurita, H. Yanagi and H. Hosono, *Nature*, **389**, 939–942 (1997).
- 6) T.-W. Chiu, Y.-C. Yang, A.-C. Yeh, Y.-P. Wang and Y.-W. Feng, *Vacuum*, **87**, 174–177 (2013).
- 7) W. Ketir, A. Bouguelia and M. Trari, *Water Air Soil Pollut.*, **199**, 115–122 (2009).
- 8) S. Saadi, A. Bouguelia and M. Trari, *Sol. Energy*, **80**, 272–280 (2006).
- 9) T.-W. Chiu, S.-W. Tsai, Y.-P. Wang and K.-H. Hsu, *Ceram. Int.*, **38**, S673–S676 (2012).
- 10) T.-W. Chiu, B.-S. Yu, Y.-R. Wang, K.-T. Chen and Y.-T. Lin, *J. Alloys Compd.*, **509**, 2933–2935 (2011).
- 11) H. Masatake, *Chem. Rec.*, **3**, 75–87 (2003).
- 12) L. B. Khilil, W. E. Mourad and M. W. Rophael, *J. Chem. Technol. Biotechnol.*, **61**, 117–121 (1994).
- 13) Y. Xuan, C. H. He, R. Wang, R. Liu and Y. Q. Jia, *Catal. Lett.*, **46**, 119–121 (1997).