

Nano-gold supported on TiO₂ coated glass-fiber for removing toxic CO gas from air

Chien-Nan Kuo, Huang-Fu Chen, Jiunn-Nan Lin, Ben-Zu Wan*

Department of Chemical Engineering, National Taiwan University, Taipei 106, Taiwan

Available online 23 March 2007

Abstract

A process for coating a layer of TiO₂ on the surface of glass fiber (Pyrex) was developed to support nano-gold on the fiber. The sol–gel method was utilized. The solution was composed of tetrapropyl titanate (TPT), isopropanol (i-PrOH), HCl and H₂O. The XRD pattern indicated that TiO₂ was in its anatase form after the coated fiber was calcined at 450 °C. In the preparation of nano-gold on the fibers (coated with TiO₂), deposition was performed in a pH-adjusted gold chloride solution. The catalytic activities of the resulting fibers were examined by the oxidation of CO in an air stream at room temperature. The gold containing fibers dried at room temperature contained less metallic gold and exhibited poorer CO oxidation activity than did those dried at 60 °C. Moreover, the catalytic activities of the fibers depended on the gold concentration during deposition. Therefore, the gold fibers from the solution with gold concentrations of 2×10^{-4} M exhibited better CO oxidation activity than those from the solutions with concentrations of 1×10^{-3} and 0.7×10^{-4} M. TEM and A.A. analysis show that different concentrations of the gold solution were associated with different particle sizes and different gold loadings on the fibers, and therefore different catalytic activities of the fibers (per unit weight of fibers). 0.1 g of fibers prepared from the 2×10^{-4} M gold solution removed all CO from the air stream (containing 1% CO at a flow rate 110 cm³/min) at room temperature, approximately meeting the European Community EN403 (1993) standard for a qualified CO gas mask material.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Gold; TiO₂; Glass fiber; CO removal; Face mask

1. Introduction

Since Haruta et al. [1] reported the outstanding catalytic activity of nano-gold for oxidizing CO at low temperature, various reactions over nano-gold catalysts have been studied. These include CO oxidation [2–4], preferential oxidation of CO in the presence of excess hydrogen (PROX) [3,5], water gas shift reaction (WGSR) [6,7], hydrogenation [8,9] and oxidation [10]. However, in most investigations, the nano-gold particles (some in the form of gold nanotubes [11]) are supported on metal oxide powders, such as TiO₂, Fe₂O₃, Al₂O₃ and MgAl₂O₄ [12–15], or on porous materials, such as zeolite [4]. However, the powder form of these catalysts may limit their application, because the drop in pressure becomes an important problem when the packing density of the powder is too high. Hence, nano-gold was prepared on glass fiber to widen the range of

applications. This supported gold catalyst is expected to have various applications, one of which is as a packing material in safety gas masks for removing toxic CO gas from air.

For safety face masks, the European standard EN403 (Respiratory Protective Devices For Self-Rescue From Fire), which was first instituted in 1993 and re-issued in 2004, is the best known and most widely accepted of these. This standard was developed by the national standards organizations of 18 European countries. The condition for qualified removing CO from air requested in the EN403 (1993) standard, roughly described (details are presented in Section 2), is that all CO must be continuously converted within 15 min. Nano-gold catalysts have advantages over other catalysts for removing CO, including higher reaction activity at room temperature and higher moisture resistant. The objective of this study is to develop a gold-containing packing material for a qualified CO safety gas mask, which can meet the standard of EN403 (1993). Glass fiber (Pyrex) was chosen as the packing material. This study prepares nano-gold particles on this fiber and characterizes their catalytic activity.

* Corresponding author. Tel.: +886 2 33663021; fax: +886 2 23623040.
E-mail address: bezuwan@ntu.edu.tw (B.-Z. Wan).

2. Experimental

2.1. Preparing catalyst

Nano-gold particles cannot easily be supported directly on glass fiber (Pyrex); however, they can easily be supported on TiO_2 . Therefore, before the preparation of nano-gold in this study, the attempts were made to coat a layer of TiO_2 on the surface of a glass fiber. The sol–gel solution was used for coating. The solution was composed of tetrapropyl titanate (TPT), isopropanol (i-PrOH), HCl and H_2O . Glass fiber was immersed in the solution for a period. Following filtration, drying, calcination, ultrasonic treatment and drying again, a TiO_2 -coated glass fiber (designated as TiO_2 @GF) was obtained. Ultrasonic treatment was employed to remove the TiO_2 clusters that were coagulated between the fibers. SEM images, presented in Fig. 1(a and b), confirm that the treatment markedly reduced the amounts of TiO_2 clusters between fibers. Meanwhile, even under ultrasonic treatment, the TiO_2 film did not peel off from the fiber, indicating that the interaction between TiO_2 and the fiber after the calcination is strong enough to endure the force of ultrasonic vibration.

Nano-gold particles were prepared on TiO_2 -glass fiber via by deposition–precipitation. Sufficient $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (ACROS, 99.99% purity) was dissolved in deionized water and the pH of the solution was adjusted to 6.0 by adding 0.1 M NaOH. The solution was heated to 70°C and then the support was added to the solution. Following continuous stirring for 1 h and cooling to the room temperature, the catalysts were washed with deionized water and dried. The resulting catalyst is designated Au/ TiO_2 @GF.

2.2. Characterizing catalyst

The elemental content in each sample was determined using an AA unit (GBC906) and an ICP-AES unit (Kontro Plasmakon Model S-35). SEM photographs of TiO_2 films coated on the surface of the glass fiber were taken using a Hitachi S-2400

electron microscope operated at 20 kV. The distribution of nano-gold particles was measured by TEM. TEM photographs were taken using a Hitachi H-7100 electron microscope operated at 75 kV. XRD measurements were conducted using a MAC Science Diffractometer (model MXP-3) with Cu $\text{K}\alpha$ radiation at 40 kV and 30 mA. A PHI 1600 ESCA spectrometer, using Mg $\text{K}\alpha$ mono-chromatic X-rays and equipped with a charge-compensating electron gun, was employed to obtain information about the state of gold on catalysts. The vacuum inside the analysis chamber was better than $5 \times 10^{-8} \text{ N/m}^2$. All the measured binding energies referred to the C1s line at 284.6 eV.

2.3. Catalytic activities

The reaction system was a continuous flow type reactor, and CO oxidation was conducted in a quartz-tubular reactor at atmospheric pressure. The EN403 standard for materials that can be applied in CO safety gas masks is as follows. Over 15 min, 1 vol.% CO in air ($30 \text{ dm}^3/\text{min}$ total volumetric flow rate) must be totally eliminated as reactant gas is passed through the testing device (catalyst) with a cross-sectional area of 105 cm^2 ; restated, the total volumetric flow rate per unit cross section area must be $285.7 \text{ cm}^3/\text{min}$ per cm^2 . Based on the same total volumetric flow rate per unit cross-sectional area, the reactor and the reaction conditions herein this study were as follows; 1 vol.% CO in air with a total volumetric flow rate of $110 \text{ cm}^3/\text{min}$ passed through 0.1 g Au/ TiO_2 -glass fibers at 25°C ; the cross-sectional area of the catalyst bed was 0.385 cm^2 . A Shimadzu GC-8A gas chromatograph was used to analyze the composition in the reactor outlet stream. A Carboxy-2000 column was used to separate out the oxygen, the nitrogen, the carbon monoxide and the carbon dioxide. The carrier gas was helium, which was 99.999% pure, and the flow rate was $30 \text{ cm}^3/\text{min}$.

3. Results and discussion

Directly depositing nano-gold in the solution on the surface of glass fibers (without any coating) was difficult. As presented

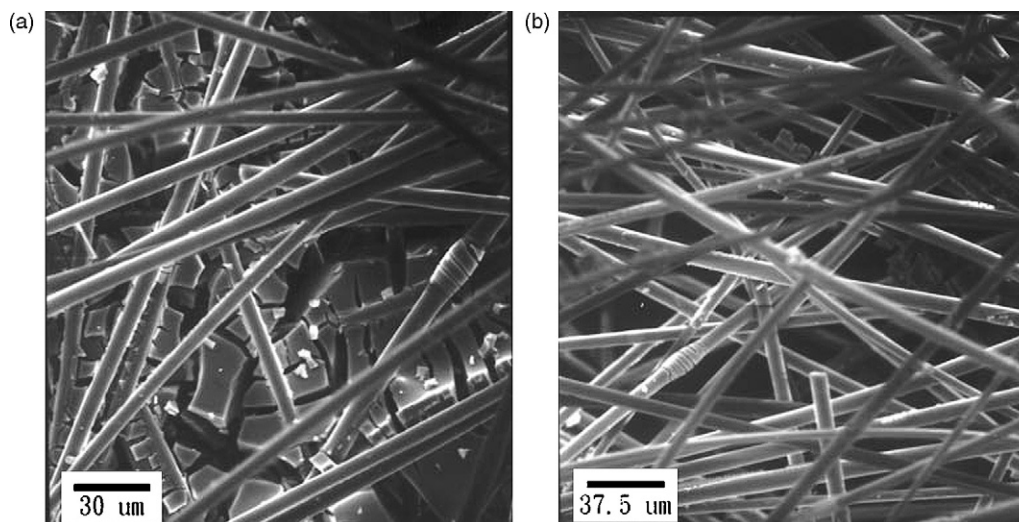


Fig. 1. SEM images of TiO_2 clusters between glass fibers: (a) before ultrasonic treatment and (b) after ultrasonic treatment.

Table 1
Gold loadings on different supports prepared from similar gold colloids and similar procedures

Catalysts	Au [wt.%]
Au/GF	0.12
Au/SiO ₂ ^a	0.17
Au/TiO ₂ ^b	1.70
Au/Y ₁ ^c	1.70
Au/Y ₂ ^d	0.26

^a Data from Ref. [4].

^b Japanese reference catalyst, JRC-TiO-4 [4].

^c Y zeolite with 12.4 wt.% Al [4].

^d Y zeolite with 1.8 wt.% Al [4].

in the first row of Table 1, only 0.12 wt.% of gold was supported on the surface of the glass fiber (sample Au/GF, GF represent the glass fiber (Pyrex)), which proportion is much less than those on the surfaces of Y-type zeolite and TiO₂, presented previously [4]. All of the pH values of the solutions used in the preparation of gold colloid in our laboratory were adjusted to 6 by adding NaOH solution, to reduce the amount of chloride deposited on the supports and to form smaller gold particles. However, the iso-electric points of SiO₂, the major component of glass fiber, is about 2, and that of TiO₂ is about 6 [4]. The solution at pH 6 leaves negative charges on the surface of the glass fiber rather than on the surface of TiO₂. Since numerous gold chloride ions in the solution were negatively charged, if the deposition was the major route for the preparation of gold particles on glass fibers, then only a few gold particles could reasonably be deposited from the solution on the surface. Additionally, the gold particles on the glass fibers exhibited no observed catalytic activity for CO oxidation under the reaction conditions applied in this study. This result is not unusual. Our earlier work [4] has demonstrated that gold particles on SiO₂ surfaces or on Y-type zeolite with few aluminum sites have much lower catalytic activities than those on Y-type zeolite with more aluminum sites or on the TiO₂ surface. Therefore, the direct deposition of gold particles on glass fiber is not effective.

However, since the good performance in CO oxidation for nano-gold catalysts using TiO₂ as support [12] and TiO₂ could be coated on some substrates as a thin film material [19]. Hence, coating a layer of TiO₂ on the surface of glass fibers and depositing gold is the best way to prepare gold-containing glass fibers with high catalytic activity, as it takes advantage of the ease of deposition of the gold particles.

3.1. Preparing TiO₂-coated glass fibers and nano-gold-containing glass fibers

The sol–gel method was employed to coat TiO₂ on the surface of glass fibers. The preparation and the composition of sol on coated TiO₂ films were investigated. Among various preparation procedures, the stirring times for TiO₂ sol–gel, before and after the addition of glass fiber were important. The sol was mixed from two solutions. One was TPT in i-PrOH solvent and the other was HCl in i-PrOH. After each had been stirred for 1 h, the two solutions were mixed together and continued to be stirred for *m* hour(s) before glass fiber was added, and for *n* hours after glass fiber was added. The resulting TiO₂-coated fiber is TiO₂-*m-n*@GF. Following the deposition of nano-gold and various treatments, the resulting samples are designated as Au/TiO₂-*m-n*@GF. The following three molar ratios of TPT/i-PrOH/HCl/H₂O were examined to elucidate the effect of the composition of TiO₂ sol; 2.0/18/1.3/4.7 (as noted as DHC), 2.0/36/1.3/4.7 (as noted as HC) and 2.0/72/1.3/4.7 (as noted as LC). The major difference among these three compositions is in the amount of i-PrOH solvent used in the sol–gel solution. Accordingly, DHC represents the densest TiO₂ sol–gel solution examined herein this study. The gold-containing glass fiber that formed after DHC, 3 h of stirring, the addition of glass fiber and a further 3 h of stirring, is designated as Au/TiO₂(DHC)-3-3@GF.

As presented in Fig. 2, the TiO₂ film can be successfully coated on the surface of the glass fiber. The XRD results, shown in Fig. 3, indicate that TiO₂ crystals with the anatase

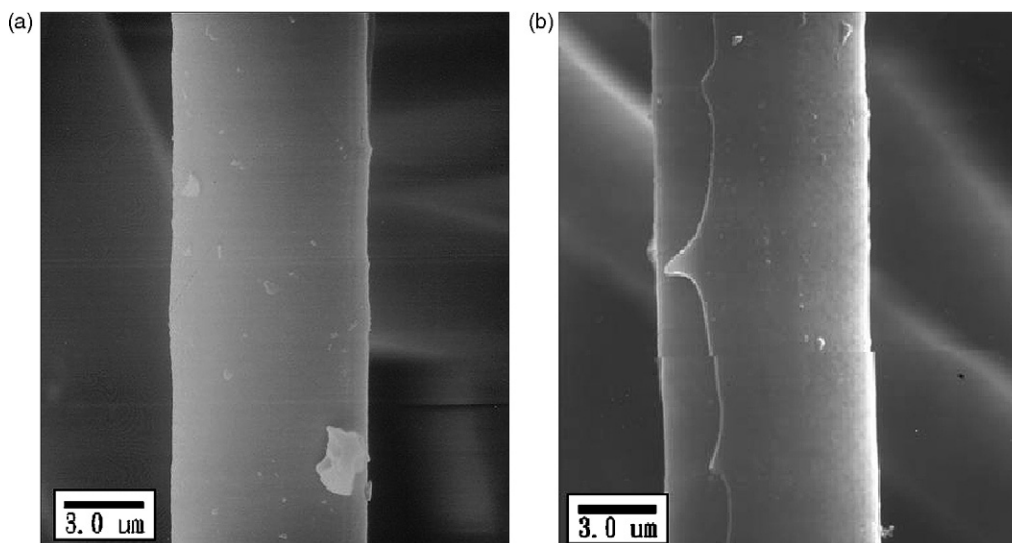


Fig. 2. SEM image of: (a) glass fiber (Pyrex) and (b) TiO₂-glass fiber (Pyrex).

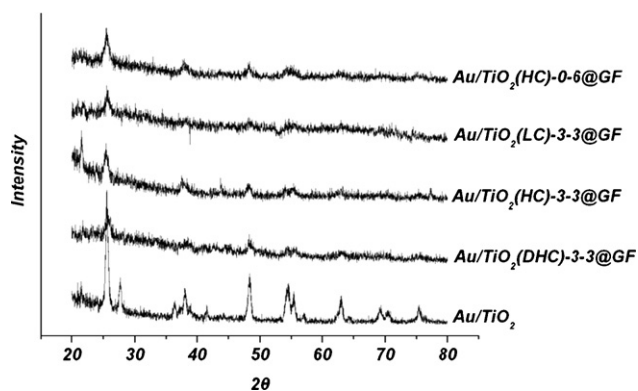


Fig. 3. XRD patterns of various gold containing glass fibers coated with TiO₂.

structure were formed after calcination at 450 °C. Table 2 lists the loadings of titanium and gold in nano-gold containing glass fibers prepared from solutions with various titanium concentrations and after different stirring times. The samples are divided into four groups, each of which involves preparation using a particular stirring time before or after glass fiber was added to the solution. In each of the first three groups, titanium loadings increase with the titanium concentration in the solution, for a given preparation process. For example, in sample series III (Au/TiO₂-3-3@GF series), the titanium loadings in glass fibers increase from 5.66% (solution LC) to 14.45% (solution DHC), because DHC has 4 times more titanium than LC. However, the relationship was not linear. The concentration of titanium in DHC was double that in HC and 4 times that in LC, but the titanium loading in DHC was about 2.2 times that in HC and about 2.6 times that in LC. Stirring of the titanium sol–gel (before the addition of glass fibers) reduced the titanium loadings in Au/TiO₂(HC)-0-3@GF (of series I), Au/TiO₂(HC)-3-3@GF (of series III) and Au/TiO₂(HC)-6-3@GF (of series IV) from 7.94 to 4.25%. All three samples were prepared in titanium sol–gel with the same concentration (HC); however, the stirring time before the addition of glass fibers was increased from 0 to 6 h. Similarly, the titanium loadings in Au/TiO₂(LC)-0-3@GF and Au/TiO₂(LC)-3-3@GF decreased from 6.23 to 5.66%. Therefore, the stirring time for

titanium sol–gel before the addition of fibers does not favor the coating of the fiber surface with TiO₂. As the concentration of titanium and the stirring time of the solution increases, larger TiO₂ particles are formed by TPT hydrolysis and the dehydration between titanium hydroxyl groups. The particle sizes of TiO₂ in the sol–gel increased in the order sample series I, III and IV. Larger TiO₂ particles are simply more difficult to coat onto the surface.

The larger TiO₂ particles may have formed the larger crystals on the fiber surface. The crystal sizes were calculated from XRD data, according to the Scherrer equation, and are presented in Table 2. However, the peak to noise ratios were too small to allow the crystal sizes of sample series I to be calculated. The samples in series II were prepared following the same processes as those in series I (without stirring of the solution before the addition of glass fibers), but the stirring time after the addition of fibers was 6 h (instead of 3 h). TiO₂ particle sizes in sample series II are expected to be larger than those in series I; therefore, the crystal sizes of the samples in series II can be calculated. Table 1 demonstrates that TiO₂ crystal sizes in sample series II are less than 10 nm. They are much smaller than those in samples in series III and IV (which are larger than 10 nm), even though the (6 h) series II samples were stirred longer after the addition of fibers to the solution. These results indicate the importance of stirring time for TiO₂ sol–gel before the addition of fibers, if the formation of TiO₂ crystal on the fiber surface is expected. Furthermore, TiO₂ particles that are too large in the solution cannot be coated on glass fibers. Hence, the crystal sizes of the samples in series III and series IV do not differ greatly, although larger particles were stirred for longer in series IV.

3.2. Catalytic activities of nano-gold containing glass fibers (coated with TiO₂)

Titanium particles that are too small on the surface of glass fibers may not have enough sites for the deposition of nano-gold. Therefore, Table 2 shows that Au loadings in the samples of series I are the lowest, even though the titanium loadings are among the highest. The catalytic activity of

Table 2

Elemental analysis and TiO₂ crystal size of various gold containing glass fibers coated with TiO₂ films, and CO conversion over 0.1 g each of these fibers

Group	Catalysts	Ti [wt.%]	Au [wt.%]	TiO ₂ crystal size [nm] ^a	X [%] ^b
I	Au/TiO ₂ (HC)-0-3@GF	7.94	0.29	–	44
	Au/TiO ₂ (LC)-0-3@GF	6.23	0.24	–	20
II	Au/TiO ₂ (HC)-0-6@GF	7.60	0.61	7.9	35
	Au/TiO ₂ (LC)-0-6@GF	4.29	0.58	8.4	27
III	Au/TiO ₂ (DHC)-3-3@GF	14.45	1.39	11.6	100
	Au/TiO ₂ (HC)-3-3@GF	6.47	0.92	14.9	100
	Au/TiO ₂ (LC)-3-3@GF	5.66	0.86	12.2	100
IV	Au/TiO ₂ (HC)-6-3@GF	4.25	0.50	12.6	100

^a Calculated by Scherrer equation with TiO₂ (1 0 0) peak (at 25.8°).

^b CO conversion over 0.1 g fiber.

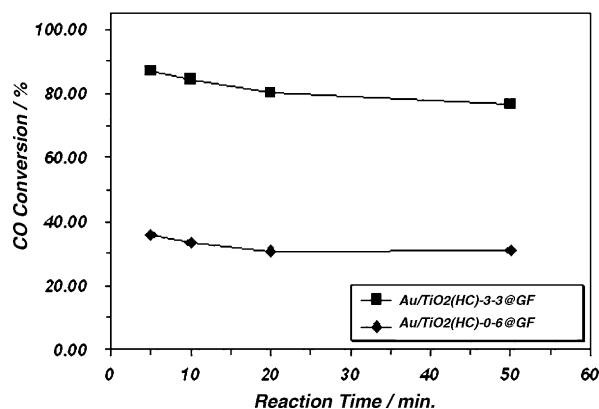


Fig. 4. CO conversion vs. time on-stream over Au/TiO₂-glass fibers with 6.0 × 10⁻⁴ g of gold.

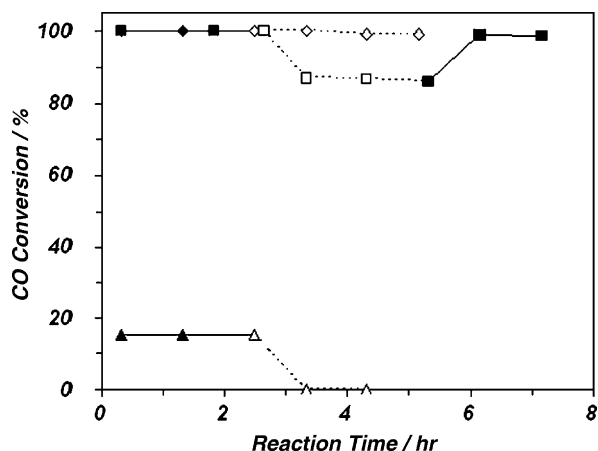


Fig. 5. CO conversion vs. time on-stream over 0.1 g of Au/TiO₂-glass fibers prepared from the gold solutions with gold concentrations of 10×10^{-4} (■, □), 2×10^{-4} (◆, ◇) and 0.7×10^{-4} (▲, △). The total volumetric flow rate of the stream that contained 1 vol.% CO was 110 cm³/min, with (open symbols) and without (filled symbols) saturated moisture. The saturated moisture was turned on (after 2.5 h) and off (after 5 h) during the runs.

nano-gold supported on TiO₂-coated glass fibers also depends on the TiO₂ crystal size. The data on the conversion of CO oxidation reaction listed in Table 2 indicate that the catalytic activities of the samples in series I and II (with smaller TiO₂ crystal sizes) are markedly less than those in series III and IV (with larger crystal sizes). As shown in Fig. 4, using 6.0×10^{-4} g Au to test CO oxidation yielded 80% CO conversion over sample Au/TiO₂(HC)-3-3@GF (14.9 nm TiO₂ crystal size), in contrast to the 35% conversion obtained over Au/TiO₂(HC)-0-6@GF (7.9 nm TiO₂ crystal size). In the figure, based on a 0.1 g sample and a similar amount of Au on the fibers, 100% CO conversion over Au/TiO₂(HC)-6-3@GF (10.4 nm TiO₂ crystal size) can be obtained, in contrast to the 27% obtained over Au/TiO₂(LC)-0-3@GF (8.4 nm TiO₂ crystal size). Hence, nano-gold supported on TiO₂ with larger crystals exhibits higher CO oxidation activity. Stirring TiO₂ sol-gel solution for at least 3 h before adding glass fibers to the solution promotes the coating of larger TiO₂ particles on the fiber surface.

3.3. Effect of chloroauric acid concentration (for the deposition) on the catalytic activity of nano-gold-containing glass fibers

Three catalysts were prepared at various concentrations of chloroauric acid. The concentration of chloroauric acid considerably affects the performance of gold catalysts [16]. The design of the concentration was roughly based on a comparison of the surfaces of the Au/Y catalysts [17].

Although the catalyst with gold concentration of 2×10^{-4} M contained less gold (0.70 wt.%) than the catalyst with a gold concentration of 10×10^{-4} M (1.30 wt.%), it exhibited extraordinary high activity for CO oxidation, even considering the moisture effect, as shown in Fig. 5. During the first 2.5 h of reaction time, 1 vol.% CO in the reactant gas could be completely oxidized to CO₂ by the catalysts with gold concentrations of 10×10^{-4} and 2×10^{-4} M. Under the moist reaction condition, the catalyst with a gold concentration of 2×10^{-4} M also exhibited the best catalytic performance of the three catalysts. The most significant effect of the gold concentration was related to nano-gold particle size: a lower gold concentration was associated with smaller nano-gold particles. In Fig. 6, comparing the sizes of the gold particles in these two catalysts indicated that the catalyst at the higher concentration, 10×10^{-4} M, contained more large nano-gold particles than the catalyst at the lower concentration 2×10^{-4} M. This result verifies the relationship between the nano-gold particle size and the gold concentration. However, the activity of the catalyst with a gold concentration of 0.7×10^{-4} M was much lower than the others. Poor catalytic performance could be attributed to the low loading of gold in the catalyst (0.12 wt.%).

3.4. Effect of drying process (for nano-gold containing glass fibers) on catalytic activity

Another factor which may affect the catalytic activity is the drying procedure utilized in the preparation of the gold catalysts [18]. Two drying procedures are discussed here—one at 60 °C and one at room temperature. After catalytic activity

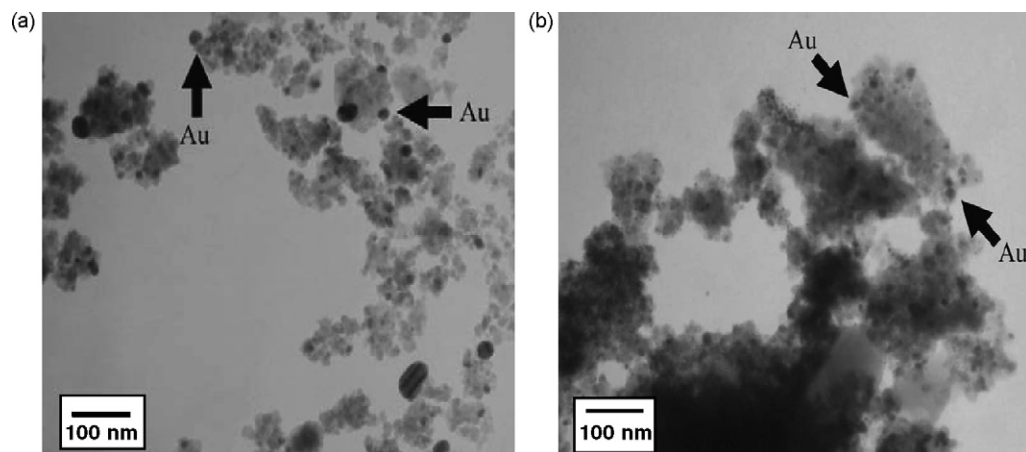


Fig. 6. TEM images of Au/TiO₂-glass fiber, prepared from the solutions with (a) the gold concentration of 10×10^{-4} M (b) the gold concentration of 2×10^{-4} M.

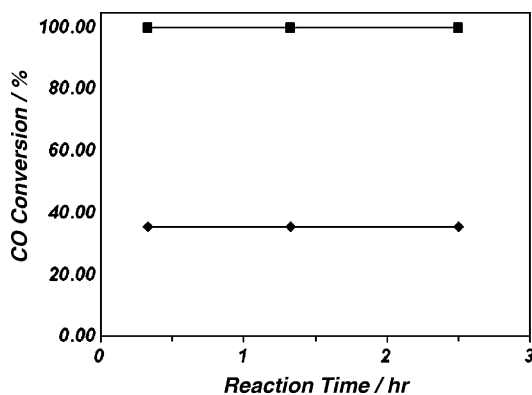


Fig. 7. CO conversion vs. time on-stream over 0.1 g of Au/TiO₂-glass fiber dried at 60 °C (■) and room temperature (◆). The total volumetric flow rate of the stream that contained 1 vol.% CO in, was 110 cm³/min.

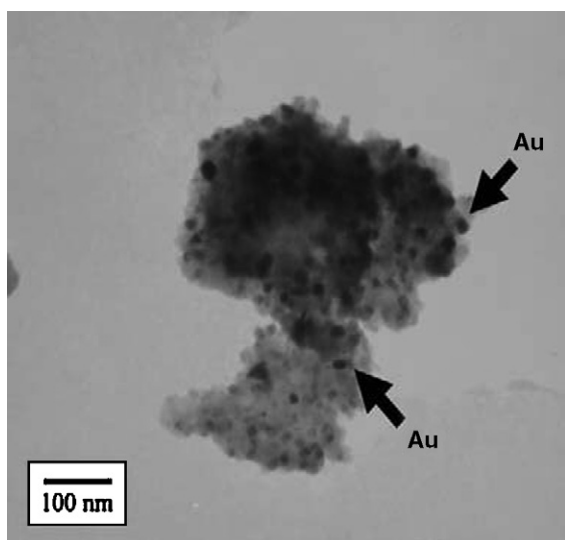


Fig. 8. TEM image of Au/TiO₂-glass fiber dried at room temperature.

was measured, the catalyst that was dried at room temperature exhibited lower CO oxidation activity than the catalyst dried at 60 °C, as presented in Fig. 7. Moreover, as shown in Fig. 8, the size of the nano-gold particles in the catalyst dried at room temperature was similar to that in the catalyst dried at 60 °C, as shown in Fig. 6(b). Therefore, something must have affected catalytic performance, other than gold particle size, during the long contact between catalysts and air. XPS was employed to obtain information of the state of gold in catalysts prepared using different drying procedure, and the gold 4f peaks were deconvoluted to determine the relative fractions of the states of gold. Table 3 presents the results. It indicates differences in only

Table 3
XPS analysis (obtained by deconvolution of gold 4f peaks) of surface composition of Au/TiO₂-glass fiber prepared after using different drying procedures

Dried at	Metallic Au	Au ₂ O ₃	Au(OH) ₃
60 °C	0.74	0.26	0
RT	0.48	0.27	0.25

two factors—the fraction of the metallic gold and the amount of Au(OH)₃ present in the catalyst dried at room temperature. These two differences may explain why the catalyst dried at room temperature was less active than the catalyst dried at 60 °C. Although the cause of the activity of gold nanoparticles may be unknown, the difference between the fractions of the metallic gold implied that the metallic gold might provide the active sites in the gold catalysts, more metallic gold is associated with higher activity. The presence of Au(OH)₃ only in the catalyst dried at room temperature also provides evidence of the formation of Au(OH)₃ in catalysts during the drying procedure when water was not rapidly removed.

3.5. Application of nano-gold containing glass fibers in gas mask

Glass fibers that contain nano-gold particles, prepared as described in this study, can be utilized in CO safety face masks that meet the European Community EN403 (1993) standard. Unlike powder catalysts, fiber form catalysts are flexible. The catalysts studied herein yielded a catalyst bed with a thickness of about 0.5 cm. Therefore, when such catalysts are used as a material in a face mask, the product would be a 0.5 cm thick and flexible material. Nano-gold containing glass fibers are therefore very practical.

4. Conclusions

As a packing material for a qualified CO safety face mask, TiO₂ film was successfully coated on the surface of glass fibers (Pyrex) using the sol-gel method, and can be used to support nano-gold particles, via the deposition-precipitation method. Au/TiO₂-glass fiber catalysts can continuously convert CO to CO₂ for more than 15 min, meeting the EN403 (1993) standard.

Both the preparation procedure of the TiO₂ film coated on the glass fiber, and composition of the sol markedly affect the performance of the catalysts. Stirring TiO₂ sol-gel solution for at least 3 h before adding glass fibers into the solution is an effective way to coat larger TiO₂ crystals on the fiber surface. Titanium loadings increase with the titanium concentration in the solution for a particular preparation process.

The gold fibers prepared from the solution with gold concentrations of 2×10^{-4} M exhibited better CO oxidation activities than those from the solutions with concentrations of 1×10^{-3} and 0.7×10^{-4} M.

However, the trace amount of glass-fiber, TiO₂ or nano-gold from the face mask packed with Au/TiO₂-glass fiber may harm lung, during removing toxic CO gas from air. The safety measure may need to be considered before the practical application.

Acknowledgement

The authors would like to thank the National Science Council of the Republic of China, Taiwan, for financially supporting this research.

References

- [1] M. Haruta, T. Kobayashi, H. Sano, N. Yamada, *Catal. Lett.* (1987) 405.
- [2] G.C. Bond, D.T. Thompson, *Catal. Rev. Sci. Eng.* 41 (1999) 319.
- [3] T.V. Choudhary, D.W. Goodman, *Top. Catal.* 21 (2002) 25.
- [4] J.-H. Chen, J.-N. Lin, Y.-M. Kang, W.-Y. Yu, C.-N. Kuo, B.-Z. Wan, *Appl. Catal. A* 291 (2005) 162.
- [5] W.-Y. Yu, C.-P. Yang, J.-N. Lin, C.-N. Kuo, B.-Z. Wan, *Chem. Commun.* (2005) 354.
- [6] D. Andreeva, V. Idakiev, T. Tabakova, A. Andreev, *J. Catal.* 158 (1996) 354.
- [7] F. Boccuzzi, A. Chiorino, M. Manzoli, D. Andreeva, T. Tabakova, *J. Catal.* 188 (1999) 176.
- [8] J. Jia, K. Haraki, J.N. Kondo, K. Domen, K. Tamaru, *J. Phys. Chem. B* 104 (2000) 11153.
- [9] T.V. Choudhary, C. Sivadinarayana, A.K. Datye, D. Kumar, D.W. Goodman, *Catal. Lett.* 86 (2003) 1.
- [10] J.-N. Lin, B.-Z. Wan, *J. Chin. Inst. Chem. Eng.* 35/2 (2004) 149.
- [11] M.A. Sanchez-Castillo, C. Counto, W.B. Kim, J.A. Dumesic, *Angew. Chem. Int. Ed.* 43 (2004) 1140.
- [12] M. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, M.J. Genet, B. Delmon, *J. Catal.* 144 (1993) 175.
- [13] M. Okamura, S. Nakamura, S. Tsubota, T. Azuma, M. Haruta, *Catal. Lett.* 51 (1998) 53.
- [14] S.-J. Lee, A. Graviilidis, *J. Catal.* 206 (2002) 305.
- [15] J.-D. Grunwaldt, H. Teunissen, *Eur. Patent EP1209121* (2002).
- [16] J.-N. Lin, B.-Z. Wan, *Appl. Catal. B* 41 (2003) 83.
- [17] J.-N. Lin, J.-H. Chen, C.-Y. Hsaio, Y.-M. Kang, B.-Z. Wan, *Appl. Catal. B* 36 (2002) 19.
- [18] S. Su, M.-Y. Lee, S.-D. Lin, *Catal. Lett.* 57 (1999) 49.
- [19] K. Shimizu, H. Imai, H. Hirashima, K. Tsukuma, *Thin Solid Films* 351 (1/2) (1999) 220.