

## Maintaining catalytic activity of Au/TiO<sub>2</sub> during the storage at room temperature

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### Abstract

The preferential oxidation of CO in a hydrogen-rich stream (PROX) at around room temperature was used to test the storage effect on catalytic activity of Au/TiO<sub>2</sub>. It is demonstrated in this study that indoor light is the main cause of the deactivation of the catalyst. UV-vis results suggest that the gold ions on the Au/TiO<sub>2</sub> surface can be slowly reduced to gold metal during exposure to light; moreover, XPS detected a substantial drop in gold content on the TiO<sub>2</sub> surface. However, Raman spectra reveal that the presence of nano-gold on the surface can weaken absorption from the anatase phase of TiO<sub>2</sub>, and exposure to the light during storage can further weaken absorption. Nevertheless, HRTEM has shown no apparent growth of gold particles on TiO<sub>2</sub> under light. This study reveals that storing Au/TiO<sub>2</sub> in a well defined dark environment under ambient conditions for as long as 5 months ensures that its catalytic activity in PROX remains that of the fresh sample.

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**Keywords:** Au/TiO<sub>2</sub>; Deactivation; PROX; Storage; UV-vis; XPS; Raman; HRTEM

### 1. Introduction

Unlike inert bulk gold, supported gold nano-particles are highly active in many reactions [1–3]. Their catalytic activities depend on the support, preparation method and especially size of the Au clusters. Various materials have been examined for supporting nano-gold. Of these, TiO<sub>2</sub> is extremely active, and on this compound, nano-gold can catalyze CO oxidation at very low temperatures and can catalyze the preferential oxidation of CO in a hydrogen-rich stream (PROX) at around room temperature [4]. However, according to literature [5–7], the decay in catalytic activity during storage limits the practical application of this catalyst. Zanella and Louis [6] observed that the sizes of gold particles on TiO<sub>2</sub> (Au/TiO<sub>2</sub>) increased in the pres-

ence of light or in ambient air during storage. Several reports have demonstrated that storing Au/TiO<sub>2</sub> in a refrigerator effectively prevents the sintering of gold particles and preserves its catalytic activity [7,8]. However in some practical applications, storage in a refrigerator may be inconvenient. For instance, when Au/TiO<sub>2</sub> is adopted as a catalyst material in a face mask to remove toxic CO from air, users cannot easily be required to store the mask in a refrigerator before its practical application.

In this study, the characterizations of Au/TiO<sub>2</sub> exposed to and not exposed to the light during the storage under ambient air were carried out by using UV-vis, XPS and Raman spectrometry, and HRTEM. It was found that the indoor light rather than the ambient conditions (i.e., air and temperature) was the major source to deactivate the catalyst. By carefully controlling the dark, maintaining active Au/TiO<sub>2</sub> catalysts after long-time storage can be achieved. The possible mechanism for the deactivation is discussed in this work.

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## 2. Experimental

### 2.1. Catalyst preparation

Au/TiO<sub>2</sub> catalyst was prepared herein study by deposition–precipitation, as described in our previous publication [4]. A suitable amount of chloroauric acid (HAuCl<sub>4</sub> · 3H<sub>2</sub>O, Merck) was dissolved in 230 ml deionized water. The concentration of gold in the solution was  $1.46 \times 10^{-3}$  M. NaOH<sub>(aq)</sub> solution (0.1 M) was added to adjust the pH of the gold solution to 6. The total pH adjustment time was 6 h. During the first 2 h, the pH was increased to 6 by adding NaOH very frequently. Later, the change in pH was slowed down, and the pH of the solution was adjusted back to 6 only every 10 min. Then, 2.0 g TiO<sub>2</sub> powder (mainly anatase, JRC-TIO-4, a Japanese reference catalyst) was added to the solution, which was then heated to 80 °C, at which temperature it was maintained for 1 h. After cooling to ambient temperature, filtration, washing with 500 ml de-ionized water and drying at 60 °C in air, the resulting grey sample of Au/TiO<sub>2</sub> was obtained.

### 2.2. Catalytic reaction

PROX reaction was used to evaluate the catalytic activity of Au/TiO<sub>2</sub>. The reaction was performed in a packed bed tubular quartz reactor (7 mm i.d.) at atmospheric pressure. The temperature of the reactor was maintained between 0 and 80 °C by a thermostatic fluid that circulated around the shell of the reactor. Au/TiO<sub>2</sub> (0.04 g), mixed with 0.2 g silicon carbide (SiC, Strem Chemical), was used in the reaction tests. The reactant feed ratios were CO/O<sub>2</sub>/H<sub>2</sub>/N<sub>2</sub> = 1/1/50/balance in vol%. The total volumetric flow rate at the reactor inlet was 110 ml min<sup>-1</sup>. The concentrations of CO, CO<sub>2</sub> and O<sub>2</sub> in the effluent gas were analyzed by two gas chromatographs (Shimadzu GC-8A with Carboxen™ 1000 column and Shimadzu GC-14A with Molecular sieve 5A column).

### 2.3. Characterizations

Atomic absorption (GBC 906) revealed that the gold loading in Au/TiO<sub>2</sub> was 1.3 wt%. The HRTEM (Philips/FEI Tecnai 20 G2 S-Twin Transmission Electron Microscope) images, used to determine the sizes of the gold particles, were obtained at 200 kV. The gold plasmon bands from different samples were identified using a Hitachi U3410 UV–vis spectrometer. XPS spectra, used to determine the metal loadings on the catalyst surface, were obtained with a PHI 1600 ESCA spectrometer with Mg K $\alpha$  mono-chromatic X-rays and equipped with a charge-compensating electron gun. The working pressure was under  $2 \times 10^{-8}$  N/m<sup>2</sup>; the pass energy was 23.5 eV; the step size during the measurement was 0.1 eV, and the expected resolution was 0.1–0.8%. All measured binding energies were referred to the C<sub>1s</sub> line at 284.6 eV. Moreover, the

TiO<sub>2</sub> structures of Au/TiO<sub>2</sub> were characterized using a Nicolet ALMEGA XR Dispersive Raman spectrometer.

## 3. Results and discussion

One sample of Au/TiO<sub>2</sub> was spread to a thin layer on a Petri-dish and exposed to indoor light (intensity = 1.6  $\mu$ W/cm<sup>2</sup>) from fluorescent lamps, and the other sample from the same batch was in a capped glass vial, which was wrapped with black tape and stored in a desk drawer, to investigate the effect of light. Five months later, the color of the former sample changed to purple, whereas that of the latter sample remained grey, like the fresh sample. Fig. 1 plots the CO conversions in the PROX reaction over the fresh sample and those over the samples that had been stored for 5 months. The sample that was wrapped with black tape had the same activity as the fresh one; therefore, CO conversions at various temperatures were almost identical. In contrast, the sample that had been exposed to light, except at a reaction temperature of 80 °C, exhibited much lower reaction activities than the fresh sample at various temperatures, suggesting that the indoor light can deactivate Au/TiO<sub>2</sub> catalyst after long storage, as has been indicated in the literature [6].

The catalysts were characterized by HRTEM, UV–vis reflectance, Raman and XPS spectrometry to determine why the Au/TiO<sub>2</sub> that was prepared herein work exhibited low catalytic activity after exposure to light. Fig. 2 reveals that the UV–vis reflectance spectrum of the sample after exposure light had a strong band around 570 nm, which is the surface plasmon resonance band of nano-gold metal [9]; however, that of the sample that had not been exposed was only a weak surface plasmon band, suggesting that nano-gold clusters were reduced to metal during exposure

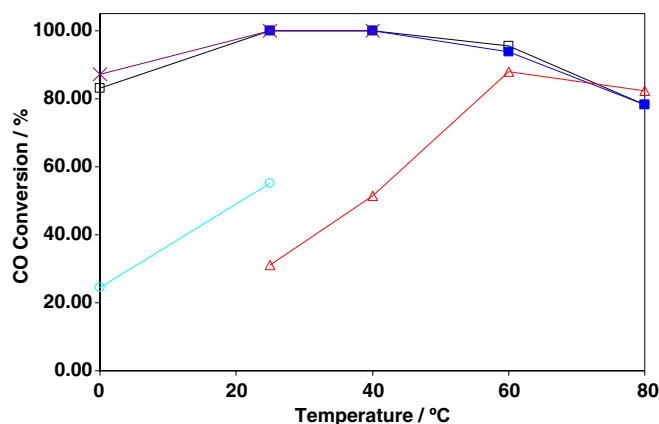


Fig. 1. Preferential oxidation of CO over 0.04 g Au/TiO<sub>2</sub>: fresh catalyst (□), sample stored in a glass vial wrapped with black tape and stored in a drawer for 5 months (■), sample exposed to the light (1.6  $\mu$ W cm<sup>-2</sup>) for 5 months (△), sample changed to purple color in a glass vial and stored in a drawer for 2 months (○), and that still retaining grey color after 12 months storage in a drawer (×). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

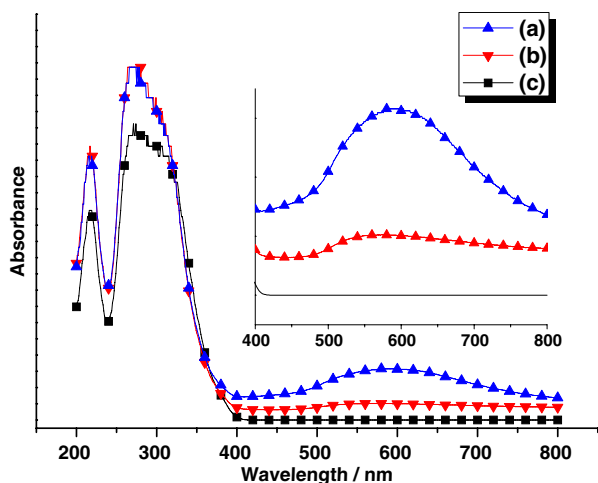


Fig. 2. UV-vis spectroscopy of (a) Au/TiO<sub>2</sub> exposed to the light ( $1.6 \mu\text{W cm}^{-2}$  intensity) for 5 months, (b) Au/TiO<sub>2</sub> not exposed to the light (wrapped with black tape and stored in a drawer for 5 months), and (c) TiO<sub>2</sub>. The absorbance value was calculated by using Kubelka–Munk relation (K–M theory) [13].

to light, and that the surfaces of catalysts that had not been exposed had less gold metal. However HRTEM analysis, as displayed in Fig. 3, indicated no apparent difference between the sizes of the gold particles on exposed and the unexposed samples. Therefore, the HRTEM results show that light has no effect on the growth of gold particles on the surface of TiO<sub>2</sub>. Restated, the growth of gold particles that has been reported in the literature [6] may have other causes, such as the remaining of chloride on the support surface [10].

Fig. 4 presents Raman spectra of Au/TiO<sub>2</sub> samples exposed and unexposed to light after storage for 5 months. The figure also displays the spectrum of a pure TiO<sub>2</sub> support. Since the Au/TiO<sub>2</sub> samples were prepared in a gold solution at pH 6 and were heated to 80 °C, as described in Section 2, the processes used to prepare Au/TiO<sub>2</sub> were

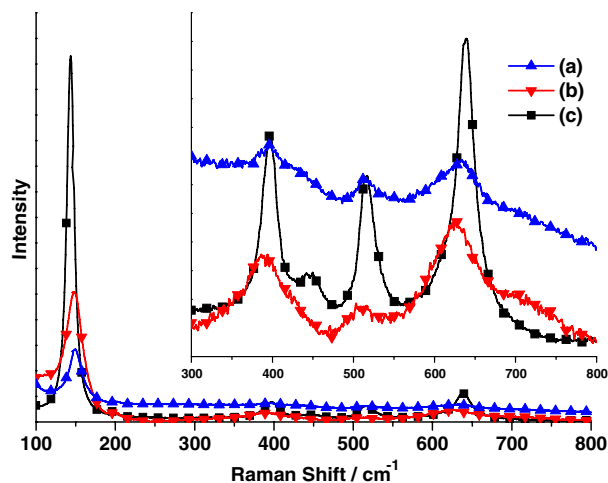


Fig. 4. Raman spectroscopy of (a) Au/TiO<sub>2</sub> exposed to the light ( $1.6 \mu\text{W cm}^{-2}$  intensity) for 5 months, (b) Au/TiO<sub>2</sub> not exposed to the light (wrapped with black tape and stored in a drawer for 5 months), and (c) TiO<sub>2</sub>.

also used to prepare pure TiO<sub>2</sub>. TiO<sub>2</sub> was therefore prepared in a solution that had been adjusted to pH 6 and heated to 80 °C, but no chloroauric acid was added to the solution. Fig. 4 reveals that the intensity of Raman spectrum of TiO<sub>2</sub> is much stronger than that of the Au/TiO<sub>2</sub> samples. The Raman lines at 145, 395, 510 and 635 cm<sup>-1</sup> are assigned to the Eg, B1g, A1g and B2g modes of the TiO<sub>2</sub> anatase phase, respectively [11]. The presence of gold nano-particles on the TiO<sub>2</sub> surface reduced the intensity of the strongest Eg mode at 145 cm<sup>-1</sup>, arising from the extension vibration of the anatase structure. Scurrell obtained similar results [11]. This observation together with the drops in the intensities of the other modes, B1g, A1g and B2g, shown in Fig. 4, indicate that gold affects the surface properties of TiO<sub>2</sub>. Moreover, when Au/TiO<sub>2</sub> was exposed to light, the intensity of the Raman spectrum decreased below that of Au/TiO<sub>2</sub> that had not been

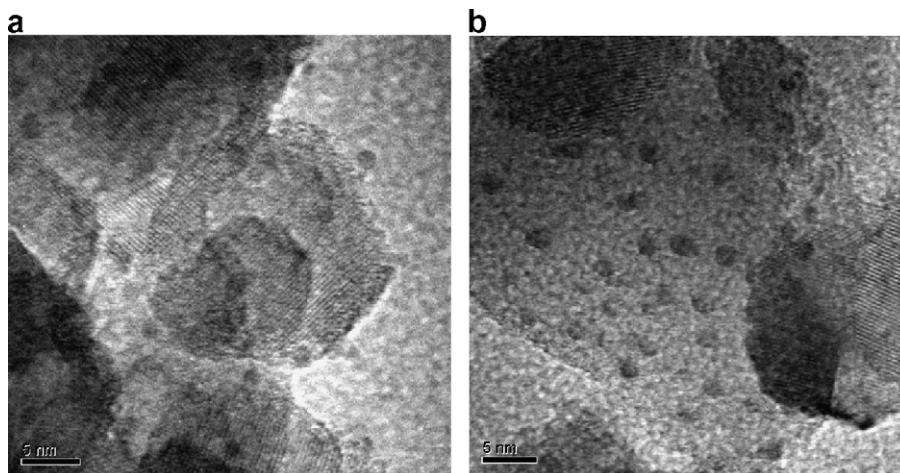


Fig. 3. HRTEM images of Au/TiO<sub>2</sub>, (a) exposed to the light ( $1.6 \mu\text{W cm}^{-2}$ ) for 5 months, and (b) not exposed to the light (wrapped with black tape and stored in a drawer for 5 months).

exposed to the light, suggesting that light increases the capacity of gold to modify the surface of TiO<sub>2</sub>.

The difference between the samples exposed and unexposed to light was also studied by XPS, which was conducted to analyze the amounts of elements on the solid surface. Fig. 5 and Table 1 present the results. It can be found that the amount of gold on the exposed TiO<sub>2</sub> surface was substantially less than that of the sample that had been stored in the dark. Additionally, as displayed in Fig. 5, the slightly lower binding energies of gold on the sample that had been exposed to light for 5 months may be suggesting that more gold metal was formed thereon, which finding is consistent with the stronger gold metal plasmon band revealed by the UV–vis results shown in Fig. 2. Since the unexposed sample exhibited the same reaction activity as the fresh one, the active species on the surface of this sample are assumed to be similar to those on the fresh sample. The XPS and UV–vis results indicate that following exposure to light during storage, the gold on the TiO<sub>2</sub> surface was slowly reduced to gold metal. The drop in the total gold content on the surface reveals that either gold ions or gold metal on the surface may slowly migrate into TiO<sub>2</sub> solid during storage and thus no longer be detectable by XPS. Accordingly, the less gold on the exposed surface is one of the main reasons for the lower activity of Au/TiO<sub>2</sub> following storage.

Since the deactivation of Au/TiO<sub>2</sub> during the storage under the influence of light is associated with the reduction of gold, a color change from grey to purple can be observed by the naked eye. For instance, when the Au/TiO<sub>2</sub> samples in glass vials (not wrapped with black tape) were stored in a desk drawer (with a light intensity of less than 0.01  $\mu\text{W}/\text{cm}^2$ ), the powder on the top or that on the edge of the vial wall turned purple indicating that gold ions were reduced. Carefully selecting the purple sample from the vial that had been stored for just 2 months and testing for PROX revealed that the catalytic activity had decayed, as presented in Fig. 1. This finding indicates that a very little light was present in the drawer, even though such an environment is generally thought to be dark. Therefore, as the storage time increased, the amount of purple powder in

Table 1  
XPS results of Au/TiO<sub>2</sub>

Catalysts	Atom%		
	O	Ti	Au
No exposure to the light and stored for 5 months	72.34	26.47	1.19
Exposed to the light (1.6 $\mu\text{W}/\text{cm}^2$ ) for 5 months	72.06	27.47	0.47

the glass vial increased and spread toward the inner parts of the samples. However, the powder that was shielded in the center of vial remained as grey as the fresh samples. When the grey powder in the vial that had been stored in the desk drawer for one year was carefully separated from the purple powder and tested for PROX, the catalytic activity was found to be as high as that of the fresh sample, which result is also presented in Fig. 1. This result suggests again that light is the main cause of the deactivation of the Au/TiO<sub>2</sub> catalyst. The top layer of the sample in the glass vial stored in the drawer is typically the first to be exposed to light and is deactivated first. The deactivation of catalytic CO oxidation of the Au/TiO<sub>2</sub> catalyst will be found after storage without differentiating the Au/TiO<sub>2</sub> from different portions in the glass vial, even under very weak illumination, as in a drawer.

The mechanism of the deactivation of Au/TiO<sub>2</sub> under light is probably related to the photo-catalytic property of TiO<sub>2</sub>, which is a semiconductor. Photo-catalysis over a semiconductor is initiated by the absorption of a photon with energy equal to or greater than the band gap of the semiconductor (3.2 eV for TiO<sub>2</sub>), generating electron-hole ( $e^-/h^+$ ) pairs [12]. The  $e^-/h^+$  pairs then act as either an electron donor or an acceptor to or from the substance close to them. Under irradiation by light, the electrons in the conduction band of TiO<sub>2</sub> reduce gold ions to form gold metal. The interaction between gold ions and the TiO<sub>2</sub> surface, as well as the formation of gold metal may cause the migration of gold from the exterior layer of solid TiO<sub>2</sub> into its interior, and may also perturb anatase phase of TiO<sub>2</sub>. The exact mechanism of gold migration must be investigated in the future.

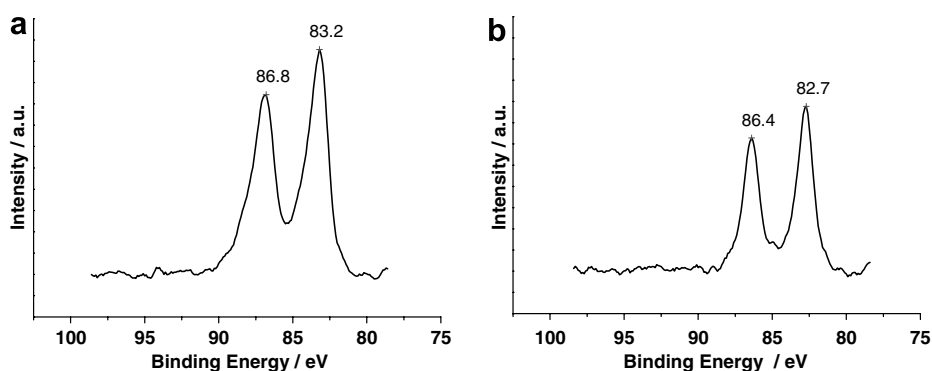


Fig. 5. XPS spectra of Au/TiO<sub>2</sub>, (a) not exposed to the light (wrapped with tight black tape and stored in a drawer for 5 months), and (b) exposed to the light (1.6  $\mu\text{W}/\text{cm}^2$ ) for 5 months.

#### 4. Conclusions

Indoor light is the main cause of the deactivation of the catalytic activity for PROX of Au/TiO<sub>2</sub> prepared herein after the long storage. Light as weak as that in a desk drawer (which supposedly represents a dark environment), with an intensity of less than 0.01 μW/cm<sup>2</sup>, can slowly deactivate Au/TiO<sub>2</sub>. However, if Au/TiO<sub>2</sub> is stored in a darker environment (such as in a sample glass vial wrapped with black tape and stored in the drawer) under ambient conditions, even for as long as 5 months, the catalytic activity can remain that of the fresh sample. XPS reveals that light causes the migration of gold on the Au/TiO<sub>2</sub> surface into TiO<sub>2</sub> solid. Therefore, less gold on the surface is associated with less catalytic activity. Moreover, UV–vis reflectance shows that gold ions are reduced to gold metal during the exposure to light. Raman spectra indicate that nano-gold on TiO<sub>2</sub> perturbs the absorption from the anatase phase of the TiO<sub>2</sub> surface, weakening the Raman bands. After Au/TiO<sub>2</sub> was exposed to light for 5 months, the band was even weaker. Nevertheless, HRTEM images displayed no growth of gold particles during storage under light.

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