

## Preparation of TiO<sub>2</sub> supported gold nano-clusters by photo-deposition

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**Abstract** TiO<sub>2</sub> supported gold clusters are prepared by photo-deposition method. The effect of preparation parameters on the size and morphology of gold clusters are investigated. The as-prepared Au/TiO<sub>2</sub> samples are characterized by means of ICP, XRD and TEM. Au/TiO<sub>2</sub> samples with different gold cluster sizes are studied as possible catalysts in the selective oxidation of benzyl alcohol to benzaldehyde and smaller gold clusters are observed to exhibit higher catalytic activity.

### Introduction

Supported metal clusters have drawn more and more attention for their wide application in heterogeneous catalytic reactions, *e.g.* refining of petroleum, conversion of automobile exhaust, hydrogenation of carbon monoxide, and so on [1-9]. For supported metal clusters, the smaller the metal clusters are, the larger the number of metal atoms is exposed at surfaces, where they are accessible to reactant molecules and available as active sites [10]. Besides, the cluster size may influence the exposed facets of supported metals, which are essential to their catalytic activities. Therefore, great efforts have been paid on the preparation of supported metal clusters with controllable morphology and cluster sizes [11].

Up to now, a number of techniques, including but not limited to co-precipitation [12], deposition-precipitation [13], chemical vapor deposition [14], laser vaporization [15], modified wet impregnation [16] and photo-deposition [17], have been developed for the preparation of supported metal clusters. Amongst them, photo-deposition method is especially suitable to coat noble metal clusters on semi-conductor support. Compared to other methods, photo-deposition shows its advantages in the following aspects. First, photo-deposition process is very simple and no surfactant is needed throughout the process. Thus, the possible introduction of impurities during preparation can be completely avoided. Second, photo-deposition is highly efficient and the utilization factor of metal precursor is approaching 100%. Third, the morphology and size of coated clusters can be controlled simply by adjusting the preparation parameters.

In our previous work, TiO<sub>2</sub> supported metal clusters, *e.g.* silver [18], platinum [19] and palladium [20], have been successfully prepared by a pH-controlled photo-deposition process and the morphology and size of clusters can be well controlled. The supported clusters, *e.g.* Ag/TiO<sub>2</sub> [21] and Pt/TiO<sub>2</sub> [22], have shown remarkable catalytic activity in important catalytic reaction. Supported gold clusters have been extensively studied in recent years and gold catalysts are widely applied in numerous reactions [23]. It is generally accepted that activity of gold catalysts is strongly dependent on the size of gold clusters and excellent catalytic activity can only be obtained on small gold clusters of below 5 nm [24]. The preparation of supported gold clusters below 5 nm and with homogeneous dispersion becomes a hot topic both in materials science and in catalysis research.

In this study, a series of TiO<sub>2</sub> supported gold clusters have been prepared by photo-deposition method. The preparation parameters in photo-deposition process have been investigated and the as-prepared Au/TiO<sub>2</sub> samples have been characterized by a couple of techniques. As for catalysis, the Au/TiO<sub>2</sub> has been studied as possible catalysts for the selective oxidation of benzyl alcohol to benzaldehyde, a new environmentally benign reaction in synthetic chemistry [25]. The effect of gold

cluster sizes on the catalytic activity has been discussed based on the characterization and catalytic results.

## Experimental

### Preparation of samples

TiO<sub>2</sub> (P25, Degussa, Japan; anatase 79%, rutile 21 %) supported gold clusters were prepared by a pH-controlled photo-deposition process. A typical photo-deposition was carried out in a 250 mL round-bottom flask using a 250 W high-pressure mercury light with the main wavelength of 365 nm as the light source. Certain amount of 2 mM HAuCl<sub>4</sub> solution, 1g of TiO<sub>2</sub> and 10mL of ethanol were added. The initial pH value of the slurry was adjusted to the desired value by 10% ammonia solution or 2M NaOH solution. The suspension was purged with high-purity N<sub>2</sub> atmosphere to remove oxygen. The slurry was vigorously stirred throughout the process. After 2 h of irradiation, the particles were filtered, washed, and dried in desiccators overnight. The products are labeled as Au/TiO<sub>2</sub>-px, where x indicates the initial pH value for photo-deposition. For reference, the TiO<sub>2</sub> supported gold clusters with similar gold loading were also prepared by wet impregnation and labeled as Au/TiO<sub>2</sub>-i. All Au/TiO<sub>2</sub> samples were calcined in flowing air at 200 °C for 2 h and stored in the desiccator for catalytic application.

### Characterization of samples

Powder X-ray diffraction (XRD) measurements were carried out on the samples using a Rigaku D/max 2500 diffractometer, equipped with a graphite monochromator and using Cu K $\alpha$  radiation. Transmission electron microscopy (TEM) images of TiO<sub>2</sub> supported metal clusters were acquired on a Tecnai G<sup>2</sup> 20 S-TWIN transmission electron microscope at an accelerate voltage of 200 kV. The actual gold loading content in as-prepared Au/TiO<sub>2</sub> was analyzed by inductively coupled plasma-atomic emission spectra (ICP-9000, Thermo Jarrell-Ash Corp).

### Catalytic evaluation

The catalytic oxidation of benzyl alcohol to benzaldehyde was carried out in a three-necked round bottom flask with reflux condenser at 90 °C under atmospheric pressure. Typically, 25ml of 0.55mol/L K<sub>2</sub>CO<sub>3</sub> aqueous solution, 1.0 ml benzyl alcohol and 0.1g Au/TiO<sub>2</sub> catalyst were mixed inside the flask and stirred at a speed of 500 rpm. After reaction for 2h, the unconverted substrate and the products were extracted from the reaction mixture by diethyl ether and analyzed by gas chromatography (Tianmei 7890F) with a flame ionization detector using a FFAP column.

## Results and discussion

### Sample characterization

The XRD patterns of Au/TiO<sub>2</sub> samples are displayed in Fig. 1. Typical diffraction peaks of TiO<sub>2</sub> support corresponding to anatase (JCPDS 21-1272) and rutile (JCPDS 21-1276) phase are easily observed, as marked in the figure. Besides, unobvious peaks of gold at  $2\theta = 44.5^\circ$  and  $64.6^\circ$  are observed. The peak corresponding to gold at  $2\theta = 38.2^\circ$  should also be observed, however, it is overlapped by the peak corresponding to anatase phase. From the intensity and width of peak at  $2\theta = 44.5^\circ$ , it can be concluded that the size of the gold clusters on TiO<sub>2</sub> decreases with increasing initial pH value from 7.5 to 11.5.

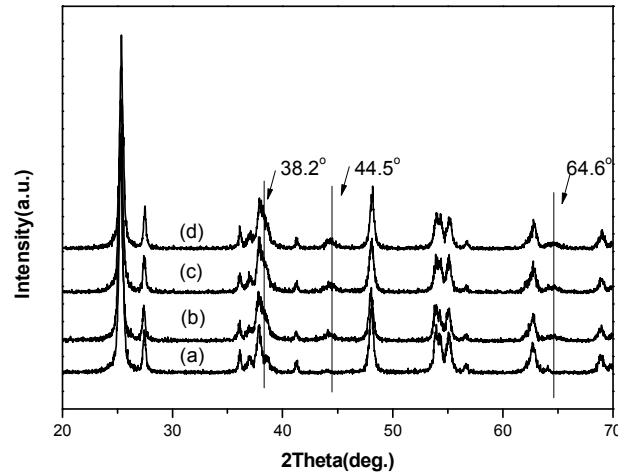
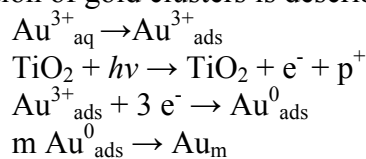


Fig. 1 XRD patterns of TiO<sub>2</sub> support (a), Au/TiO<sub>2</sub>-p7.5 (b), Au/TiO<sub>2</sub>-p9.5 (c) and Au/TiO<sub>2</sub>-p11.5 (d)

The TEM images of Au/TiO<sub>2</sub> prepared by photo-deposition are shown in Fig. 2 and it is seen that the size of gold clusters on TiO<sub>2</sub> decreases with increasing initial pH value, in consistent with XRD results. The average size of gold clusters is *ca.* 7.5nm at initial pH value of 7.5 (Figure 2a), while the average size is as small as *ca.* 3.5 nm at initial pH of 11.5 (Figure 2c). Undoubtedly, the size of gold clusters can be controlled to some extent by adjusting the initial pH value with ammonia solution during photo-deposition. In our previous work, the pH-controlled photo-deposition route has been developed to prepare metal clusters, *e.g.* silver [18] and platinum [19], on TiO<sub>2</sub>. The key issue for photo-deposition is controlling the deposition rate of metal precursor, which is realized by adjusting the initial pH value with NaOH solution. As for Au/TiO<sub>2</sub>, the addition of NaOH solution cannot control the deposition rate efficiently and so the gold clusters deposited are rather large and not homogeneous (see Figure 2d). To solve the problem, we use ammonia solution instead of NaOH solution in the present work. On one side, the addition of ammonia solution ensures the necessary conditions for photo-deposition, *i.e.* pH > 6.25 (isoelectric point of TiO<sub>2</sub>). On the other side, the ammonia can form complex compound with gold precursor and thus greatly reduces the local concentration of gold ions. With reduced concentration of gold ions, the photo-deposition and reduction rate is correspondingly reduced, leading to the formation of homogeneous small clusters. A simple scheme for the formation of gold clusters is described as follows.



The actual gold loading content and the visualized color of different Au/TiO<sub>2</sub> samples are summarized in Table 1. The actual gold loading contents of all Au/TiO<sub>2</sub> are quite similar and approaching theoretical value of 5%, indicating the high efficiency of photo-deposition. According to literature reports [26], the color of Au/TiO<sub>2</sub> can reflect the existence state of gold species. Color purple indicates that the deposited gold is metallic (Au<sup>0</sup>), while color blue indicates that the deposited gold is ionic (Au<sup>+</sup> or Au<sup>3+</sup>). As we can see from Table 1, the color of Au/TiO<sub>2</sub> changes from purple to purple blue as initial pH value increases from 7.5 to 11.5 (the gold cluster size decreases from *ca.* 7.5 nm to *ca.* 3.5 nm). That is, more ionic gold species are present in small gold clusters. It should be noted that all the gold clusters, no matter larger or smaller, are quite stable. The visualized color of each sample can be well preserved after calcination in air and catalytic reaction.

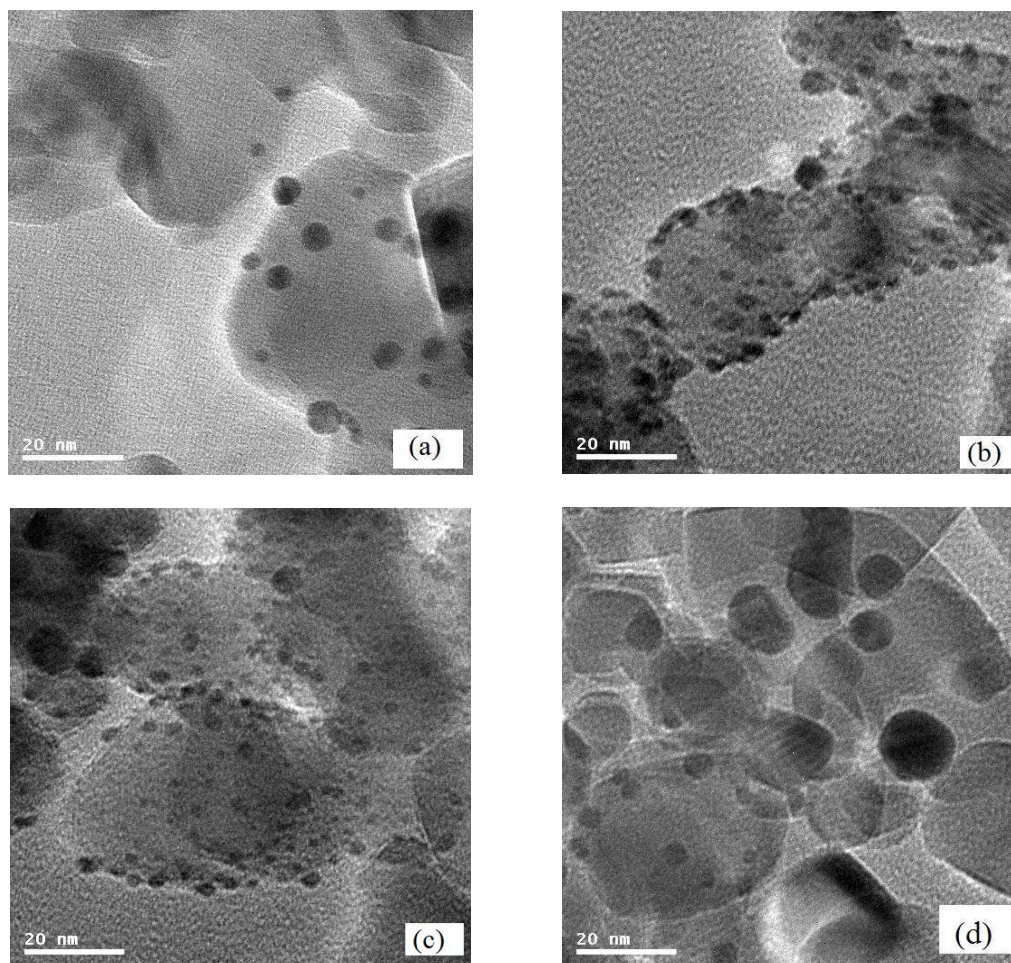


Fig. 2 TEM images of Au/TiO<sub>2</sub>-p7.5 (a), Au/TiO<sub>2</sub>-p9.5 (b), Au/TiO<sub>2</sub>-p11.5 (c) and Au/TiO<sub>2</sub> prepared by photo-deposition with NaOH at initial pH of 11.5 (d)

Table 1 Gold loading and visualized color of Au/TiO<sub>2</sub> samples prepared by photo-deposition

Sample	Cluster size <sup>a</sup>	Gold loading <sup>b</sup>	Sample Color <sup>c</sup>	Sample Color <sup>d</sup>	Sample Color <sup>e</sup>
Au/TiO <sub>2</sub> -p11.5	3.5 nm	4.93 %	purple blue	purple blue	purple blue
Au/TiO <sub>2</sub> -p9.5	4.5 nm	4.97 %	light purple	light purple	light purple
Au/TiO <sub>2</sub> -p7.5	7.5 nm	4.86 %	purple	purple	purple

<sup>a</sup> Average gold cluster size from TEM

<sup>b</sup> Actual gold loading content measured by ICP, theoretical gold loading content = 5%

<sup>c</sup> as-prepared; <sup>d</sup> after calcination at 200 °C in air; <sup>e</sup> after reaction at 90 °C

### Catalytic oxidation of benzyl alcohol

The catalytic performances of benzyl alcohol oxidation over Au/TiO<sub>2</sub> catalysts are shown in Fig. 3. Au/TiO<sub>2</sub>-i exhibits quite low activity and the conversion of benzyl alcohol is below 1%. In contrast, production of benzaldehyde from benzyl alcohol (selectivity > 99%) is clearly observed over Au/TiO<sub>2</sub> prepared by photo-deposition, and the activity is strongly dependent on the initial pH value for photo-deposition. Typically, low benzyl alcohol conversion of 1.23% is obtained on Au/TiO<sub>2</sub>-p7.5. While benzyl alcohol conversion on Au/TiO<sub>2</sub>-p11.5 can reach 15.36%, *ca.* 12 times higher than that on Au/TiO<sub>2</sub>-p7.5. The activity difference can be attributed to the different sizes of gold clusters and/or the different existence states of gold clusters.

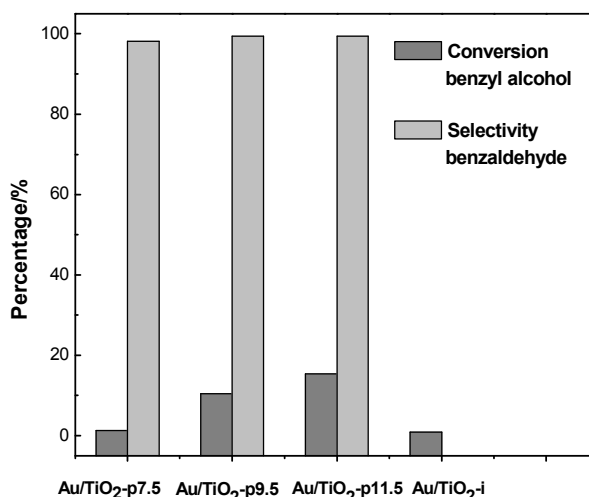


Fig. 3 The reactivity of Au/TiO<sub>2</sub> catalysts in selective oxidation of benzyl alcohol

## Conclusion

TiO<sub>2</sub> supported gold clusters are prepared by photo-deposition process and the size of gold clusters can be controlled by adjusting the initial pH value for photo-deposition with ammonia solution. The size of gold clusters on TiO<sub>2</sub> decreases from 7.5 nm to 3.5 nm with increasing initial pH value from 7.5 to 11.5, and correspondingly more ionic gold species are observed in smaller clusters. Au/TiO<sub>2</sub> with smaller cluster size exhibits higher activity for the oxidation of benzyl alcohol to benzaldehyde.

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