

# Size/Shape Controlled Synthesis of Au/TiO<sub>2</sub> Nano-Composites

Pandian Lakshmanan, Vadivel Saravanan and Chennan Ramalingan.

**Abstract:** In order to control the size of titania supported gold nanoparticles, a new strategy of liquid phase chemical reduction has been demonstrated. It involves on-site reduction of gold phase by glycerol due to thermal treatment. In the first step DPU process is performed prior to chemical reduction. The results show that, this method offers many size-control parameters including mainly reduction temperature and catalyst to glycerol ratio. This paper analyzes various aspects of the different approaches attempted to control the size/shape of the titania supported gold.

**Keywords:** Gold nanoparticles, Titania, chemical reduction, glycerol, selective oxidation, size-controlled synthesis.

## I. INTRODUCTION

Titanium dioxide-gold combination has emerged as a powerful catalytic material in view of its potential applications towards energy and environmental sectors. The catalytic activity of Au/TiO<sub>2</sub> catalysts depends strongly on the preparation method [1-4]. Mainly the size and shape are very important. This is the current problem that, gold can be present as isolated atoms, small clusters, small/medium sized nanoparticles and larger particles on oxide support. Only the weighted average size for gold has been used to correlate the results. But such a size-controlled synthesis is a current challenge in the field of nano-catalysis. The LSPR properties are influenced by the shape [5], size [6-8] and gold loading [9]. Several approaches have been applied to control the size/shape of gold nanoparticles supported on titania including loading change [10-11], sol-immobilization [12-14], pore confinement [15] self assembly [16]. In the loading change approach, it did not work properly. This is because, the histogram simply shifted to higher size areas without narrowing. Furthermore, always smaller particles less than 5 nm is present even though the average size increases. Another problem in high loadings is that, amount of gold increases along with the average gold size. This makes comparison difficult. The activity contribution of small particles present in the sample is masked. In sol-immobilization method, gold sol is formed prior to contact with support. The use of stabilizers/spacers during the

sol-immobilization size-control must have to be removed as well. Any additional thermal treatment may alter the characteristics of gold.

Pore confinement strategy is good in the sense that, the upper size limit is strictly fixed that is equal to the pore diameter. Note that, below that level, smaller particles can be formed as well. Therefore, careful procedure to obtain the porous support oxide is must in this approach. Another possible problem would arise from the sensitivity of porous material towards acidic nature of gold precursor like HAuCl<sub>4</sub>.

Self assembly approach has been demonstrated. Gold nanoparticles are covered by organic binders which can connect the other end to the surface of the metal oxide support or another gold nanoparticle. Such a molecule ends with thiol and carboxylic groups and act as spacer between nanoparticles. Obviously two problems arise now. The gold particles are not in direct contact with support and their removal problems.

In a recent study, we have demonstrated an on-site growth approach to control the size of ceria supported gold [17, 18]. In this method, gold is loaded by DPU method in a first step. In general, the as prepared DPU samples are either calcined or reduced under flowing gas accompanied by thermal treatment. On the contrary, the possibility of liquid phase thermal reduction with only pure glycerol has been demonstrated. One of the attractive physical properties of glycerol is its high boiling point (290 °C). Furthermore, its high viscosity (1.412 Pa.s) [19] can prevent fine particles from settling down.

A relationship between average size and catalyst to glycerol ratio could be found. Particularly, at low glycerol amounts, larger gold size obtained. It was also observed that, reduction temperature had profound effect on the on-site growth of gold over titania. These papers analyzes various approaches and discuss the positive points involved in the chemical reduction method. This study exposes the size-control factors that are available in the reduction .

## II. EXPERIMENTAL SECTION

### A. Chemicals and Techniques

HAuCl<sub>4</sub>.4H<sub>2</sub>O (SHOWA, 99.9%), glycerol (Aldrich, 99%), TiO<sub>2</sub> (Degussa, 50 m<sup>2</sup>g<sup>-1</sup>), and urea (Aldrich, 98%) were used as received. The glassware used in the synthesis was cleaned with aqua-regia and then rinsed with deionized water and dried overnight prior to use. Chemical analyses were performed by duo inductively coupled plasma atom emission spectroscopy (ICPAES) with Thermo Scientific iCAP 6500 instrument. The Au loadings were expressed as wt%.

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The TEM analysis was performed using a TECNAI G2 microscope. UV-Vis spectroscopic measurements were carried out with SHIMADZU UV-1800 equipment..

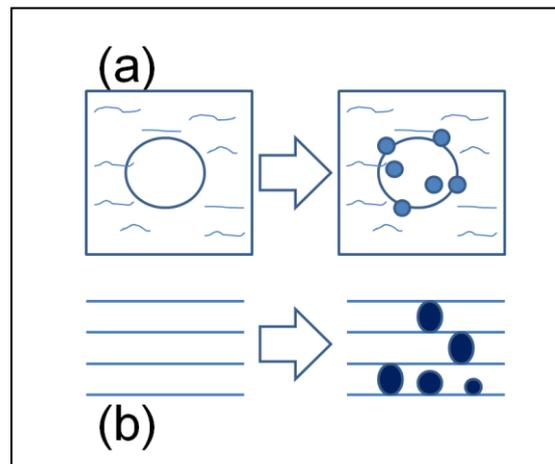
### B. Preparation of Catalysts

TiO<sub>2</sub> was dispersed in distilled water and the slurry temperature was kept at 80°C. A solution of HAuCl<sub>4</sub>.4H<sub>2</sub>O was added followed by the addition of urea. The resulting mixture was stirred at 80 °C for 12 hours. Centrifugation was performed to recover the solid, washed 3 times with distilled water and dried in a desiccators. The aliquots of .dried (*as prepared*) samples were treated in glycerol at different temperatures to obtain reduced gold catalyst. In a typical process, 150 mg of finely powdered *as prepared* samples was and mixed with 30 g of pure glycerol in a closed 50 mL vial and stirred vigorously. The catalyst mixed well with the glycerol due to the presence of residual moisture in the *as prepared* catalyst and hygroscopic nature of glycerol. The reaction mixture was stirred at 100 °C in an oil bath for 12 h. The progressive reduction of gold could be followed with changes in color (which is not possible with conventional gas-phase catalyst activation). After stirring for 12 h, the reaction mixture was removed from oil bath, cooled and diluted with excess of water. Centrifugation was performed to recover the catalysts, followed by washing (3 times with deionizer water) and finally mixed with the reaction mixture immediately.

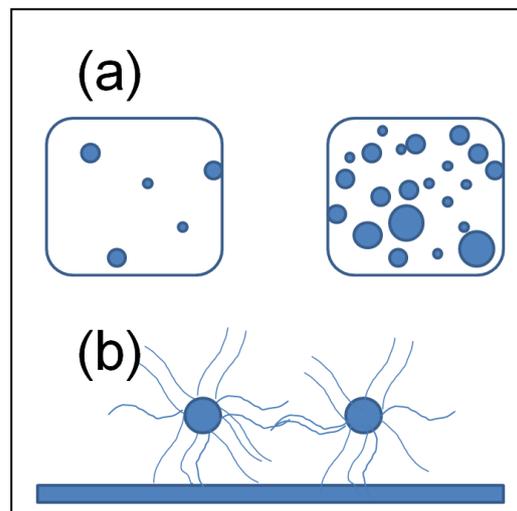
### III. RESULTS AND DISCUSSION

The problems associated with the various approaches are illustrated in the Scheme-1 &2. As can be seen from the Scheme-2, in the loading change method, the number of particles/nm<sup>2</sup> increases. This can facilitate the process of sintering that is not favorable to size control. Furthermore, the width of the histogram did not change significantly due to loading change (simply the histogram shifts its spreading on the X axis). One more point is that, if the surface area is low, this loading change approach will face the problem of high population density (facile surface migration and sintering).

In the case of sol-immobilization Scheme-1-(a), it involves the size control of unsupported gold particles first in the liquid phase reduction. It is followed by the deposition of reduced particles on the surface of metal oxide. The main point in this case is about the nature of metal-support interaction. The particles if round shaped, then the contact with the support is not strong. Again the problem of sintering may become a serious problem against size-control. Due to poor contact between metal and support, surface migration is facilitated in such systems, which gets worse at higher temperatures. First step involves reduction of gold precursor in solution in the presence of capping/stabilizing agents like polyvinyl alcohol to form surface stabilized gold nanoparticles. In the second step, the stabilized metal nanoparticles are immobilized onto the metal oxides. For example, acidification of gold suspension (pH= 2.5) followed by addition of titania support. Rogers et al used Polyvinylalcohol stabilized gold sols to immobilize on titania [20]. Mingming Du et al used plant extract (Cinnamomum camphora) to stabilize gold sols [21]. Jan-Dierk et al utilized tetrakis(hydroxymethyl)phosphonium chloride tetrakis(hydroxymethyl)phosphonium chloride [22].



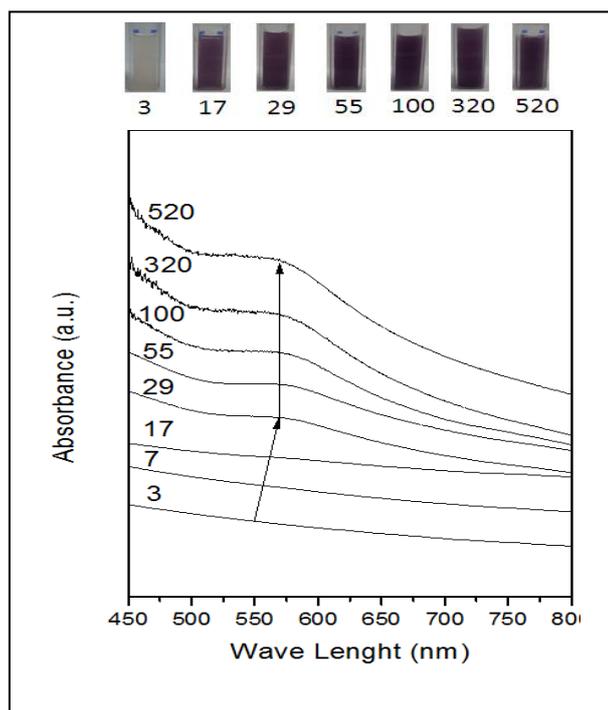
**Scheme-1. Approaches for size-controlled synthesis of titania supported gold nanoparticles: Sol-immobilization (a) and pore confinement techniques (b).**



**Scheme-2. Approaches for size-controlled synthesis of titania supported gold nanoparticles: loading change (a) self assembly strategy (b).**

In the pore-confinement technique Scheme-2-(b), the main advantage is that, the maximum size is strictly limited to the pore diameter. However, all particles may not fit exactly to the pore diameter of support material. The sensitivity of porous support to the acidic/basic conditions involved in the next step of gold loading is another issue. Niu et al [23] used carbide derived carbon with pores so that, gold particles capable of entering into the pores can only loaded onto the carbon support. Datta et al used mesoporous carbon nitride [15] to obtain an average size of 7 nm for gold. The main drawback of this method is formation of only small particles below 7 nm. Obviously, for non-porous metal oxides this method cannot be applied. As can be seen from the Scheme-2-(b), again there is poor surface to surface contact between gold and support as they are separated by spacers. Removal of spacer molecules will need a thermal treatment during which the Ostwald ripening process may occur. Therefore,

poor contact and the stabilizer/spacer/linker molecules are appearing to be the unwanted factors.



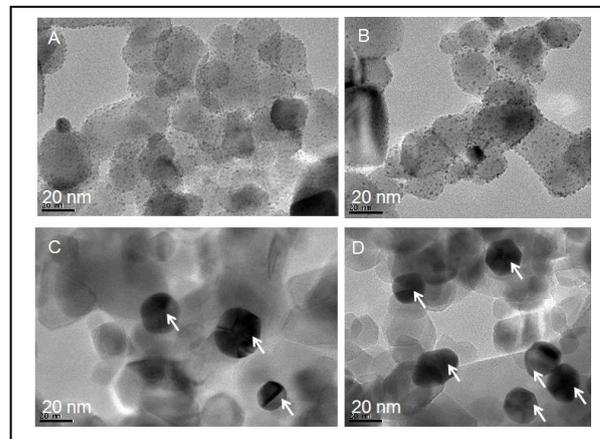
**Figure 1. Time dependant UV-Vis. analysis of 6.4% Au/TiO<sub>2</sub> catalyst during chemical reduction process.**

Let us consider the chemical reduction with glycerol method. Basically it is an on-site growth method. The gold precursor is highly dispersed on titania surface by DPU process in the first step. Glycerol reduces gold on titania surface during thermal treatment. The growth process is controlled directly by temperature in addition to other parameters including amount of glycerol. A spectacular advantage of the chemical reduction method is that, no any stabilizing and capping agents are needed. Because, gold is not reduced even after loaded on the support. Another plus point is the possibility of size control above 10 or 15 nm scale, which has not been reported according to the best of our knowledge. This method can be applied wherever gold is deposited by DPU method.

The 6.36% Au/TiO<sub>2</sub> sample was reduced by CRG method. The progress of the chemical reduction process at different time points were monitored with the techniques of UV-vis. absorption spectroscopy (Fig. 1) and TEM analysis (Fig. 2).

Initially the sample in glycerol appeared yellow. But the rapid disappearance of yellow color was observed with time and after 17 minutes, the sample turns violet, which indicates the formation of metallic gold nanoparticles. The continuation of the stirring process did not show significant difference in the color of the sample, except darkening of the violet color followed by gray color. The rapid color changes indicate that, the growth of gold particles must be fast. However, the informations that can be derived from the color changes after a short period of time is limited (after 30 min) as the changes in color is not significant and spectacular. Interestingly, the corresponding UV-vis. spectra of the

samples measured at different time points provide additional informations. As can be seen from the Fig. 1, the first spectra measured after 3 minutes appears as a featureless spectrum. After 7 minutes, the left hand side of the spectra moves upwards and the appearance of the surface plasmon resonance (SPR) signal starts from the spectra measured after 17 minutes. A well defined SPR peak could be obtained after 29 minutes.

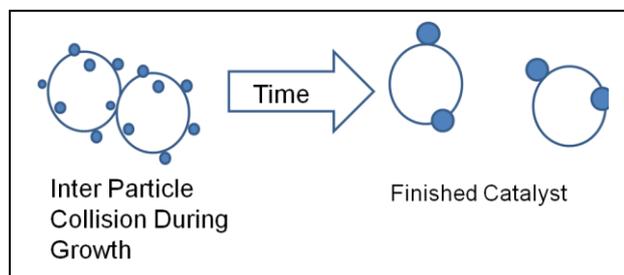


**Figure 2. Time dependant TEM analysis of 6.4% Au/TiO<sub>2</sub> catalyst during chemical reduction process.**

The observed SPR peak continues to gain intensity up to the spectrum measured at 320 minutes. All spectrum, measured after 320 minutes appeared similar. Such changes in the shape and intensity of the SPR peak indicate stepwise changes during the chemical reduction process. The total time period could be divided into 3 parts. The first part is from the beginning up to 7 minutes. The second part could be located in between 7 and 29 minutes. The rest of the time corresponds to the third part. As no clear SPR peak could be detected up to 7 minutes, it could be related to the nucleation step. From the time period of 7 minutes to 29 minutes, the evolution of clear SPR peak occurs which can be attributed to the completion of nucleation step and steady progress of the growth part. After 29 minutes, as only the gain in the intensity of the SPR peak observed, it could be attributed to the progress of growth. After 320 minutes, all spectra measured appear similar, indicating the completion of the growth. Note that, with only the color changes, it is difficult to get conclusion after 17 minutes. However, the progressing SPR peak after 17 minutes up to 320 minutes suggests that, the changes in the dimension of the gold nanoparticles during growth, have not stopped. In order to support the conclusions derived from the color changes and UV-vis spectra, TEM analyses were performed with the corresponding samples. The TEM images measured after different time intervals during the chemical reduction process is presented in the figure 2. These images clearly reveal the rapid growth of the gold particles over the surface of titania during the CRG process. The Fig. 2(A) corresponds to the sample removed after 7 min while, Fig. 2(B) corresponds to the sample at 17 min.

The small aggregates appearing in Fig. 2(A) shows that already the nucleation has started. The Fig. 2(B) corresponding to 17 minutes shows that, the evolution of small particles has occurred during this period after nucleation. However, Fig. 2 (C) corresponding to 320 minutes shows the presence of large gold particles (indicated by white arrows) accompanied with the absence of smaller particles revealing a rapid growth of gold particles which is in agreement with the results of UV-vis. spectra. In order to check the leaching of gold in glycerol during the chemical reduction method, aliquots of the reaction mixture were removed at different time intervals to perform the elemental analyses. After different time intervals (3, 7, 320 and 520 minutes) aliquots from the reaction mixture were removed and analyzed by ICPAES analysis. In all the cases, gold was not detected in glycerol. These results show that, titania supported gold particles can be synthesized by chemically reducing the as prepared Au/TiO<sub>2</sub> DPU samples with glycerol.

From the above results, it can be concluded that, there are many size-controlling parameters available in the chemical reduction process. The reduction temperature is one of the very important size-controlling parameter. The catalyst to glycerol weight ratio is another strongly influencing parameter. Other parameters include the nature of support, reducing agent, other reagents and stirring aspects, which need further detailed investigations in the chemical reduction process aimed to control the size and shape of the gold nanostructures supported on titania.



**Scheme-3: Growth of gold particles over titania surface during chemical reduction process.**

Note that, the gold size distribution is entirely in different ranges for these samples. TEM images of chemically reduced sample were carefully examined and it was found that, the smaller gold particles below 7 nm were clearly absent (Fig. 2-D). These results indicate that, the growth of large particles with low gold loading is possible with CRG method [Scheme-3], which is not possible with the conventional method of reducing under flowing H<sub>2</sub>. Furthermore, the present study reveals the efficacy of glycerol as a reducing agent. It may appear quite different approach. When the as prepared DPU sample was mixed with glycerol, it was observed that, the fine powders mixed very well with glycerol by stirring. The driving force for such an observation could be related to the hygroscopic nature of glycerol and the residual moisture present in the as prepared DPU samples. In order to understand the growth of gold nanoparticles during chemical reduction method, sample drawn in between beginning and finished catalyst was examined [Fig. 5]. As

could be seen from the figure, first small clusters appear and later, they merge to form larger particles, which is in line with the absence of smaller gold particles.

### IV. CONCLUSIONS

The various aspects of size/shape controlled synthesis of titania supported gold nano-composites have been analyzed with different approaches. A chemical reduction strategy that uses pure glycerol as reducing agent for Au/TiO<sub>2</sub> has been described. The advantages and disadvantages of this new method has been discussed. With many size-controlling parameters and scope of extending to alloys, this method appears to be interesting towards the size/shape controlled synthesis of titania supported gold nano-composites via DPU method.

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**Chennan Ramalingan** profile which contains their education details, their publications, research work, membership, achievements, with photo that will be maximum 200-400 words.