

# D-Glucose-Derived Polymer Intermediates as Templates for the Synthesis of Ultrastable and Redispersible Gold Colloids

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A two-stage hydrothermal process was developed for the synthesis of highly dispersed Au colloids. In the first stage, a novel glucose-derived polymer template was prepared by the hydrothermal treatment of glucose at 160 °C. This template was then further used in the next step to synthesize highly dispersed gold (Au) colloids by hydrothermal treatment with HAuCl<sub>4</sub>. The templates treated at 160 °C with changing reaction times had different templating effects toward Au species. The 3-h treated template was able to tightly adhere to the Au colloids. As a result, an unusual stability was observed for the prepared Au particles that could be repeatedly precipitated and redispersed with the template in H<sub>2</sub>O and were also stable against heating (below 160 °C) and aging. Meanwhile, the 5-h and 7-h treated templates had much poorer templating effects to Au species, leading to severe aggregation of the Au colloids immobilized on them. The various templating effects were correlated to the different structural features of the templates. Compared to the 5- or 7-h treated templates that were deeply carbonized, the 3-h treated template was only slightly carbonized, thus possessing a lot of functional and hydrophilic O-containing groups that could bind to Au species. These differences in templating ability were also observed in the Au samples prepared by the sonication-assisted method. The highly dispersed Au colloids immobilized on the 3-h treated template were tested for CO oxidation, and a good catalytic activity and stability for CO oxidation was observed.

## Introduction

Gold (Au) nanostructures have rich optical and electronic characteristics, excellent compatibility with biomolecules, and unique catalytic performance. Moreover, these properties can be tuned by changing the size and shape of the Au nanostructures.<sup>1–4</sup> For example, it is well-known that the catalytic performance of Au catalysts is highly dependent on the Au-particle size.<sup>4,5</sup> When the Au particle becomes very small (usually ≤ 5 nm), high activities for a number of reactions under mild conditions are reported.<sup>6</sup> Haruta et al.<sup>7</sup> reported that for CO oxidation, the optimum Au particle size should be ca. 3 nm, and Goodman et al.<sup>5</sup> reported that a bilayer of Au islands on the Mo/TiO<sub>2</sub> support exhibited the highest activity. Therefore, in recent years, intensive research has been focused on the synthesis of various gold (Au) nanostructures and the organization of these structures into various assemblies for application in nanodevice fabrication, biology, and catalysis.

The synthesis of Au nanoparticles and their assembly by wet chemical methods usually involve the use of ligand molecules

to cap the Au nanoparticles. These ligands include many sulfur-containing organic molecules, phosphine, peptides,<sup>1</sup> polymers,<sup>2</sup> and amino acids,<sup>8</sup> etc. By further equipping the sulfur- or amine-containing ligand molecules with certain functional groups that are able to conjugate specific biomolecules, and then using them to cap Au particles, a number of biomedical applications can potentially be developed.<sup>2,3</sup> Unfortunately, in most cases the ligand molecules limit the access of other reactant molecules to the Au colloids and endow them with a hydrophobic/hydrophilic surface, depending on the polarity of the tail of the ligand molecules. Therefore, the prepared Au colloids are either immiscible in H<sub>2</sub>O when the ligand molecule has a long hydrophobic tail or are difficult to be harvested from solutions when the ligand molecules have a high affinity to polar solvents. In other words, it is difficult for these capped Au colloids to achieve a repeated dispersion and precipitation in the solvent. Moreover, when Au colloids are subjected to high temperature heating and long-term aging, severe aggregation will usually occur, thus limiting their application in many areas. Some inorganic templates, such as porous anodic alumina (AAO), have been used for the synthesis of Au nanorods.<sup>9</sup> However, these nanorods are neither stable without the protection of the template nor well dispersed in solvents such as H<sub>2</sub>O without functionalizing their surface.

Herein, we report on a two-stage hydrothermal process that can be used for the synthesis of highly stable and redispersible Au colloids. These organic–inorganic templates originate from the hydrothermal treatment of glucose, a kind of carbohydrate

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(1) Daniel, M. C.; Astruc, D. *Chem. Rev.* **2004**, *104*, 293–346.  
(2) (a) Storhoff, J. J.; Mirkin, C. A. *Chem. Rev.* **1999**, *99*, 1849–1862. (b) Zhong, Z.; Male, K. B.; Luong, J. H. T. *Anal. Lett.* **2003**, *36*, 15, 3097–3118.  
(3) Tong, L.; Zhao, Y.; Huff, T. B.; Hansen, M. N.; Wei, A.; Cheng, J. X. *Adv. Mater.* **2007**, *19*, 3136–3141.  
(4) (a) Haruta, M.; Kobayashi, T.; Sano, H.; Yamada, N. *Chem. Lett.* **1987**, 405. (b) Valden, M.; Lai, X.; Goodman, D. W. *Science* **1998**, *281*, 1647.  
(5) Chen, M. S.; Goodman, D. W. *Science* **2004**, *306*, 252.  
(6) (a) Fu, Q.; Saltsburg, H.; Flytzani-Stephanopoulos, M. *Science* **2003**, *301*, 935. (b) Kim, W. B.; Voith, T.; Rodrigue-Rivera, G. J.; Dumesic, J. A. *Science* **2004**, *305*, 1280. (c) Enache, D. I.; Edwards, J. K.; Landon, P.; Solsona-Espriu, B.; Carley, A. F.; Herzog, A. A.; Watanabe, M.; Kiely, C. J.; Knight, D. W.; Hutchings, G. J. *Science* **2006**, *311*, 362.  
(7) Haruta, M.; Tsubota, S.; Kobayashi, T.; Kageyama, H.; Genet, M. J.; Delmon, B. *J. Catal.* **1993**, *144*, 175.

(8) (a) Zhong, Z.; Luo, J.; Ang, T. P.; Highfield, J.; Lin, J.; Gedanken, A. *J. Phys. Chem. B* **2004**, *108*, 18119. (b) Zhong, Z.; Subramanian, A. S.; Highfield, J.; Carpenter, K.; Gedanken, A. *Chem.—Eur. J.* **2005**, *11*, 1473–1478. (c) Zhong, Z.; Chen, F. C.; Subramania, A. S.; Lin, J.; Gedanken, A. *J. Mater. Chem.* **2006**, *16*, 489–495.

(9) Moon, J. M.; Wei, A. *J. Phys. Chem. B* **2005**, *109* (49), 23336–23341.

that extensively exists in many biological systems.<sup>10</sup> The prepared Au colloids are tightly adhered to these organic templates, and thus they are stable against heating, aging, and even the high concentration of electrolytes and can be precipitated by centrifugation and redispersed in H<sub>2</sub>O easily without severe aggregation.

### Experimental Section

All the chemicals were purchased from Aldrich and had an analytical purity. The templated synthesis of Au particles was carried out by a two-stage hydrothermal process. In the first stage, the D-glucose-derived polymer template was synthesized according to Li's elegant hydrothermal method.<sup>11</sup> In the second-stage reaction, the Au particles were deposited on the template by the hydrothermal reduction of HAuCl<sub>4</sub> or by microwave and/or ultrasonic irradiation (second reaction). Typically, 2.5 g of D-glucose was dissolved in 20 mL of DI H<sub>2</sub>O. The mixture was transferred to a 45 mL screw-capped autoclave lined with a Teflon vessel, which was then placed in an oven and maintained at 160 °C for 1–7 h (first-stage reaction). After that, the mixture was cooled to room temperature, and 1.0 mL of a 0.01 M aqueous solution of HAuCl<sub>4</sub> was added. The autoclave was returned to the oven and maintained at 160 °C for 1 h (second-stage reaction).

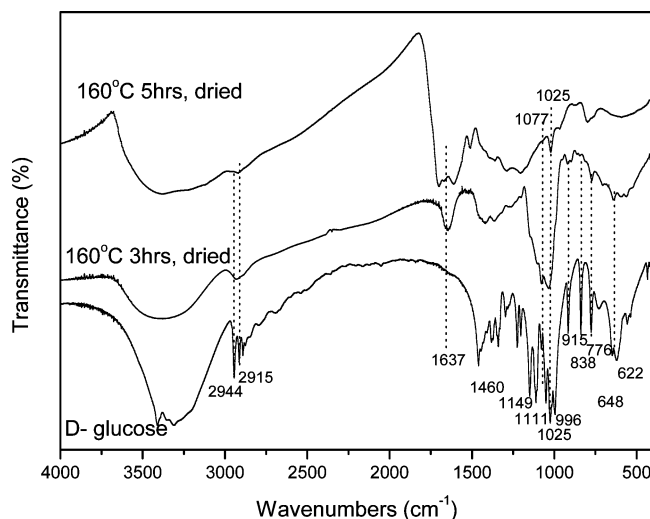
Two other alternative approaches were also tested for depositing Au particles on the above glucose-derived polymer template (after the first-stage reaction), including microwave-assisted and ultrasound-assisted methods. For the microwave-assisted synthesis of Au particles, the mixture after the first-stage reaction was blended with HAuCl<sub>4</sub> in a special Teflon container, which was then placed in a microwave oven (Milestone Micro-Synth Microwave Labstat) and subjected to 0.5 h microwave irradiation with a controlled reaction temperature (160 °C). For ultrasound-assisted synthesis, the mixture after the first-stage reaction was blended with lysine and HAuCl<sub>4</sub>, and the pH value was adjusted to 5 with 0.1 M NaOH. The suspension was then subjected to ultrasonication (20 kHz, Vibracell 500 W ultrasonic processor) for 20 s. During the sonication, NaBH<sub>4</sub> was injected instantly to reduce HAuCl<sub>4</sub>. In this sonication-assisted synthesis, the lysine molecules acted as a capping agent that could reduce the growth opportunity of Au particles.<sup>12</sup>

The catalytic activity of the prepared Au colloids was demonstrated by a CO oxidation reaction, which was used to model the purification process of air. The reaction was carried out at room temperature (23 °C). A 20 mL amount of the Au colloidal solution was put in a glass vial, and 1% CO in air was bubbled in at a flow rate of 20 mL/min. The outlet gas was analyzed on-line with a GC (Shimadzu-14B).

The morphology and size of the products were observed employing a transmission electron microscope (TEM, Tecai TF20 Super Twin, 200 kV). The UV–vis spectra of the suspension were recorded on a UV-2550 spectrophotometer (Shimadzu). The infrared spectra (FTIR) for dried samples were recorded on a Bio-Rad Excalibur spectrometer employing a KBr disc method.

### Results and Discussion

**1. Synthesis of Glucose-Derived Polymer Template.** The glucose-derived polymer template was synthesized by hydrothermal treatment at 160 °C, a temperature higher than that of glycosidation.<sup>13</sup> Such treatment resulted in a complicated structural evolution for the glucose molecules, including a series of polymerization, aromatization, and carbonation reactions.<sup>13–15</sup>



**Figure 1.** FTIR spectra of D-glucose and its derived polymerized intermediates that were hydrothermally treated at 160 °C for various times. The polymer intermediates were centrifuged, precipitated, and dried at 100 °C for 3 h prior to the FTIR measurement.

During the process, the O–H, C–O, and C–H groups in the glucose molecules were gradually lost and increasingly more C–C bonds were formed. Finally, the individual glucose molecular structure ceased to exist and a polymerized carbonlike template or organic–inorganic hybrid was obtained instead. The density and distribution of the O–H, C–O, and C–H functional groups in these templates were determined as a function of the progress of the above-mentioned reactions. A higher reaction temperature and a longer reaction time led to fewer remaining organic functional groups. Figure 1 presents the FTIR spectra of D-glucose and its derived polymer intermediates. For the spectrum of D-glucose, the absorbance peaks at 2915, 2944, 837, and 622 cm<sup>−1</sup> are assigned to C–H vibrations, the peaks in the range of 1200–1460 cm<sup>−1</sup> to  $\delta$ CH +  $\delta$ OCH +  $\delta$ CCH +  $\delta$ OH vibrations, and the peaks in the range of 915–1111 cm<sup>−1</sup> and the peak at 776 cm<sup>−1</sup> to  $\nu$ CO +  $\nu$ CC and  $\delta$ CCO +  $\delta$ CCH vibrations, respectively.<sup>16</sup> After the hydrothermal treatment at 160 °C for 3 h, the C–H vibration near 2944 and 622 cm<sup>−1</sup> still existed but with a much weakened intensity. The same peak could be found even after hydrothermal treatment at 160 °C for 5 h. A similar phenomenon was observed for the other absorbance peaks. Though it is difficult to identify the detailed structure evolution process, it is clear that after hydrothermal treatment at 160 °C for 3 h, there were still a lot of functional groups remaining, especially in the range of 995–1200 cm<sup>−1</sup> (the  $\nu$ CO +  $\nu$ CC +  $\delta$ OH vibrations), within the polymer intermediates. As shown later, these groups are the sites that can bind the Au particles. It should be pointed out that a suspension was formed for this sample, even though it had looked almost transparent, and it was quite stable. The suspension could be precipitated via a high speed ( $\geq 10000$  rpm) and a long-term centrifugation ( $> 10$  min) and redispersed in H<sub>2</sub>O.

**2. Templated Synthesis of Au Particles by the Hydrothermal Method.** Figure 2 presents the TEM images of the Au particles prepared by the two-stage reaction, in which three glucose-derived templates obtained by the hydrothermal treatment at 160 °C for 3, 5, and 7 h were used, respectively. The 3-h treated template had a spongelike structure and an irregular morphology (Figures

(10) (a) Galgali, P.; Agashe, M.; Varma, A. J. *Carbohydr. Polym.* **2007**, *67*, 576–585. (b) Maki-Arvela, P.; Holmbom, B.; Salmi, T.; Murzin, D. Y. *Catal. Rev.* **2007**, *49*, 197–340.

(11) Sun, X.; Li, Y. D. *Angew. Chem., Int. Ed.* **2004**, *43*, 597–601.

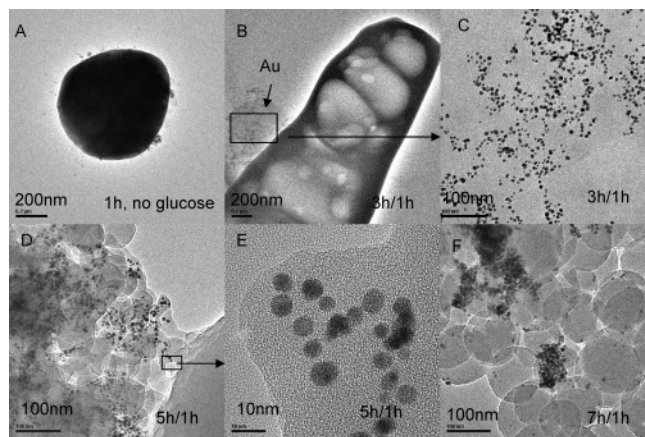
(12) Zhong, Z.; Lin, J.; Teh, S. P.; Teo, J.; Dautzenberg, F. *Adv. Funct. Mater.* **2007**, *17*, 1402–1408.

(13) Sakaki, T.; Shibata, M.; Miki, T.; Hirose, H.; Hayashi, N. *Bioresour. Technol.* **1996**, *58*, 197–202.

(14) Luijckx, G. C. A.; Van Rantwijk, F.; Van Bekkum, H.; Antal, M. J., Jr. *Carbohydr. Res.* **1995**, *272*, 191–202.

(15) Wang, Q.; Li, H.; Chen, L. Q.; Huang, X. J. *Solid State Ionics* **2002**, *152–153*, 43–50.

(16) Ibrahim, M.; Alaam, M.; El-Haes, H.; Jalbout, A. F.; Leon, A. *Ecl. Quim São Paulo* **2006**, *31* (3), 15–21.



**Figure 2.** Preparation of Au particles in the absence/presence of glucose templates. In A, 1 mL of a 0.01 M  $\text{HAuCl}_4$  solution was diluted with 10 mL of  $\text{H}_2\text{O}$  and was hydrothermally treated at 160 °C for 1 h. In B, C, D, and F, 2.5 g of glucose was dissolved in 10 mL of  $\text{H}_2\text{O}$ , and the solution was hydrothermally heated at 160 °C for 0.5 to 7 h. The mixture was then cooled to room temperature, and 1 mL of a 0.01 M  $\text{HAuCl}_4$  solution was added. The mixture was hydrothermally treated again at 160 °C for 1 h. The heating time at 160 °C at the two-stage reaction is marked at the right corner of each TEM image.

2B and 2C), while the 5-h treated template showed a carbon-sphere contour but was still somewhat irregular in shape (Figures 2D and 2E); for the 7-h treated template, similar to Li's results,<sup>11</sup> carbon spheres in the range of 100–130 nm in diameter were formed (Figure 2F). These templates were further used to prepare small Au particles via the second-stage hydrothermal reaction with  $\text{HAuCl}_4$ . For all three templates, very small Au particles were obtained (5–10 nm) but with different dispersions. Highly dispersed and small size Au particles were generated and immobilized onto the 3-h template (Figures 2B and 2C), but more severe aggregation was observed in the case of the 5- and 7-h treated templates (Figures 2D, 2E, and 2F). As previously mentioned, the increase in the hydrothermal treatment time at 160 °C will greatly reduce the quantity of the organic functional groups, such as the C–O and O–H in the glucose-derived templates. Probably the 3-h treated template provided the proper density and distribution of the functional groups, thus leading to the formation of highly dispersed Au particles.

In order to confirm that the small Au particles were indeed generated due to the templating effect, several control experiments were designed and conducted. One Au sample was prepared under the same conditions of the second-stage reaction but without any glucose-derived template. The prepared Au particles were large in size, ranging from 100 to 300 nm (Figure 2A). In addition, the possibility that the glucose molecules themselves could act as stabilizers to the small Au particles was also excluded, as a one-stage process by the direct hydrothermal treatment of the mixture of glucose and  $\text{HAuCl}_4$  led to the formation of very large Au particles ( $\geq 100$  nm) (Figure 3). These results clearly indicate that under such high-temperature reactions, the glucose molecules themselves cannot prevent the growth of the small Au particles. Therefore, a two-stage process is necessary to grow the small and highly dispersed Au particles.

Though the detailed chemistry between the Au particles and the templates is not clear, and probably similar to the case of  $\gamma$ -cyclodextrin molecules, the templates have a partial host function that can host and stabilize the small Au particles. Kaifer et al. reported that a  $\gamma$ -cyclodextrin (CD) molecule could trap very small Au particle in its cages.<sup>17</sup> Noting the fact that each

$\gamma$ -CD molecule consists of eight glucose molecules and is actually a kind of “polymerized” glucose molecule, it is reasonable to imagine that during the hydrothermal treatment, the glucose molecules were polymerized, and the formed polymer chains could be folded to form either some cage-like structures, or the spongelike structure shown in the TEM microgram (Figure 2B). Similar to the  $\gamma$ -CD molecules, in the polymerized glucose molecules there are some functional groups that can weakly bind to the Au particles. The binding of Au particles with these O-containing functional groups were probably weak; not as strong as in the case of thiol and amino groups,<sup>18</sup> but similar to the case of weak interaction between Au and carboxylic groups.<sup>19</sup> However, these functional groups are critical in keeping the affinity of the template to the Au precursor molecules. With the assistance of this binding capability, the Au precursor molecules were separately stored in cage-like structures within the template and were decomposed into isolated Au particles upon heating. The prepared Au particles were extremely stable, even under the hydrothermal treatment conditions with a reaction temperature as high as 160 °C. The templating effect is illustrated in Scheme 1.

1. According to this model, it is understandable that glucose molecules themselves are not able to stabilize the small Au particle, as  $\text{HAuCl}_4$  will be hydrolyzed below 100 °C, where the polymerization, aromatization and carbonization of the glucose molecules do not occur. As a result, the Au particles were formed and aggregated prior to the formation of the rigid template and its cage-like structure (Figure 2A). In the case where the hydrothermal treatment of glucose molecules was carried out at 160 °C for above 5 h, the deep aromatization and deep carbonation of the glucose molecules occurred, causing the loss of too many functional groups on the templates. The templates themselves also became too rigid to fold their chains to form the cage-like structure. As a result, the affinity of the templates to  $\text{HAuCl}_4$  or to Au particles was too weak (Figures 2D, 2E, and 2F). In contrast, the hydrothermal treatment at 160 °C for 3 h provided the proper density and distribution of the functional groups and cage-like structures for the template, leading to the templated formation of small and highly dispersed Au particles.

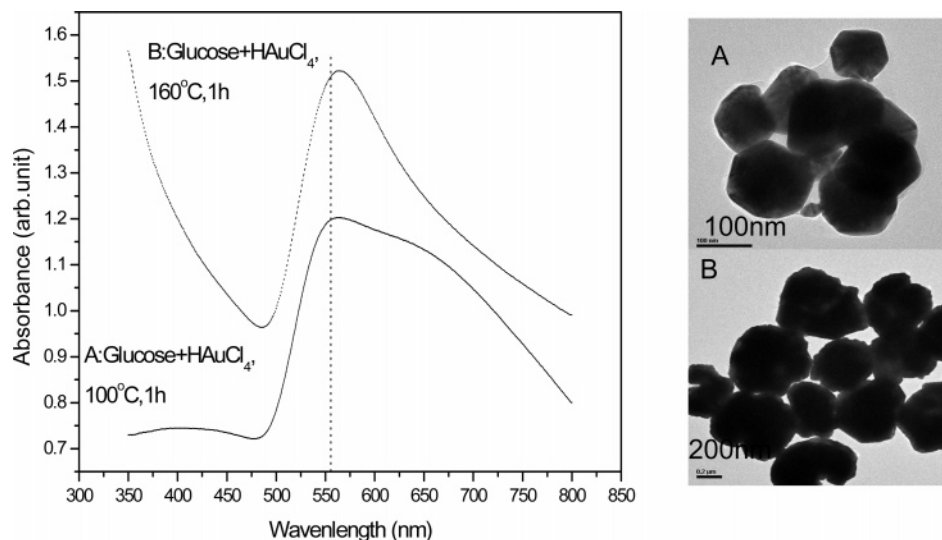
**3. Stability of the Prepared Au Particle Suspension and Its Catalytic Performance for CO Oxidation.** As opposed to most inorganic templates, the glucose-derived polymer template is dispersible and stable in aqueous solutions, as it possesses a lot of O-containing organic functional groups. As mentioned above, the affinity of the glucose-derived templates toward water depends on the quantity of the O-containing functional groups in them, which is determined by the time and temperature of the hydrothermal treatment to which the glucose molecules are subjected. A longer reaction time or a higher reaction temperature led to the lower affinity of the prepared templates to water. Figure 4 presents photographs of the Au particle suspensions and their UV–vis spectra. The two suspensions were prepared using the glucose-derived templates that were hydrothermally treated for 3 and 7 h, respectively (denoted as 3-h and 7-h samples). The 3-h sample had a deep red color, and was stable for at least 3 months, while the 7-h sample was brownish in color because of the formation of large carbon colloids in it, and also had a shorter life span (precipitated after 2 days). The measured UV–vis spectra for the 3-h sample had a strong absorbance at 534 nm, and no shifting for this peak was observed within 3 months (Figure 4,

(17) Liu, J.; Alvarez, J.; Ong, W.; Kaifer, A. E. *Nano Lett.* **2001**, *1*, 57.

(18) Zhong, Z.; Patskovsky, S.; Bouvrette, P.; Luong, J. H. T.; Gedanken, A. *J. Phys. Chem. B* **2004**, *108*, 4046–4052.

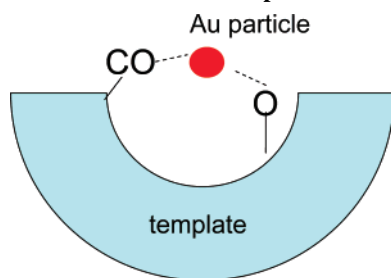
(19) Paik, W. K.; Han, S. B.; Shin, W.; Kim, Y. S. *Langmuir* **2003**, *19* (10), 4211–4216.





**Figure 3.** Au colloids were prepared by hydrothermally treating the mixture of D-glucose and  $\text{HAuCl}_4$  at 100 °C (A) and 160 °C (B) for 1 h (one-stage hydrothermal process).

**Scheme 1. Illustration of the Templating Effect: Au Colloids Are Hosted in the Cages in the Template and Are Anchored by the O-Containing Functional Groups on the Wall of the Template**



right). Meanwhile, the 7-h sample had a weak absorbance peak at ca. 620 nm, indicating a much more severe aggregation of the Au particles in it. In addition, unlike the Au colloids capped by many other ligand molecules, the 3-h sample had a good thermal stability against heating. In the second -stage reaction, we varied the reaction temperature from 80 to 160 °C, and no obvious difference in Au particle size and dispersion was observed, indicating that the Au colloids were formed at a temperature as low as ca. 80 °C, but they were fixed on the template and were stable in the range of 80 to 160 °C.

In addition to the high stability against the long-term aging for the 3-h sample, it is also redispersible in water and resistant to electrolytes. Figure 5 shows the UV-vis spectra for the 3-h sample before and after being repeatedly precipitated, washed, and redispersed in  $\text{H}_2\text{O}$  and after the addition of  $\text{NaCl}$  (1.72 M). There was no shift of the absorbance peak at 534 nm after the redispersion, just a continuous decrease in absorption intensity, which was the result of a slight loss of Au during the washing process (usually a 5-min centrifuge at 10000 rpm was used. If the centrifuge time was increased to 10 min, much less Au was lost). In curve d, it showed a good stability for the Au suspension against the concentrated electrolyte (1.72 M  $\text{NaCl}$ ) solution, while in similar case,<sup>18</sup> the Au colloids prepared by sodium citrate showed a much poorer stability. It is easy to understand and explain these experimental results: as the Au particles were tightly fixed on the templates and are not easily separated from the template, even after washing and redispersion, there was no change in the aggregation state of the Au particles. This unique property of the Au nanoparticles that are fixed on highly stable,

hydrophilic, and dispersible templates in  $\text{H}_2\text{O}$  will enable them to have important applications and will be further explored in the future.

The above-mentioned 3-h and 7-h samples were tested directly for CO oxidation, as the Au particles are able to catalyze a number of reactions under mild conditions.<sup>2</sup> When a gas of 1% CO in air at a flow rate of 20 mL/min was passed through the 3-h sample (20 mL), a 5.6% conversion of CO was achieved at room temperature (23 °C), which corresponded to a total removal of 560 ppm CO/min from 20 mL air, or a specific activity of  $4.6 \times 10^{-6} \text{ mol CO} \cdot \text{g Au}^{-1} \cdot \text{s}^{-1}$ . For the 7-h sample, the CO conversion was 3.4% and the specific activity was  $2.8 \times 10^{-6} \text{ mol CO} \cdot \text{g Au}^{-1} \cdot \text{s}^{-1}$  under the same conditions (it should be pointed out this 7-h sample was precipitated after being reacted for ca. 1 h). This specific catalytic activity of the 3-h sample is comparable to that of the solid Au/carbon fiber catalyst,<sup>20</sup> 46 times higher than that of Au powder,<sup>21</sup> but much lower than that of the reference solid catalyst of Au/ $\alpha\text{-Fe}_2\text{O}_3$  from the World Gold Council (WGC), measured at 30 °C in our lab ( $4.9 \times 10^{-4} \text{ mol CO} \cdot \text{g Au}^{-1} \cdot \text{s}^{-1}$ ).<sup>22</sup> As opposed to the two solid catalysts, this solution-based catalyst did not deteriorate within 5 h of the testing. Its relative low catalytic activity, compared to the WGC Au/ $\alpha\text{-Fe}_2\text{O}_3$ , is probably attributed to its larger Au particle size (ca. 5–10 nm) than that in the powder catalysts, and the carbon-based support is inferior to  $\alpha\text{-Fe}_2\text{O}_3$  for CO oxidation.<sup>21</sup> The merit of this catalyst is its long stability, probably because of the sufficient contact between Au particles and CO molecules in the suspension, less aggregation of Au particles as they are fixed on the template, and the sufficient OH groups in the suspension. It is reported that the OH groups are needed to maintain the catalytic activity of supported Au catalysts for CO oxidation.<sup>23</sup>

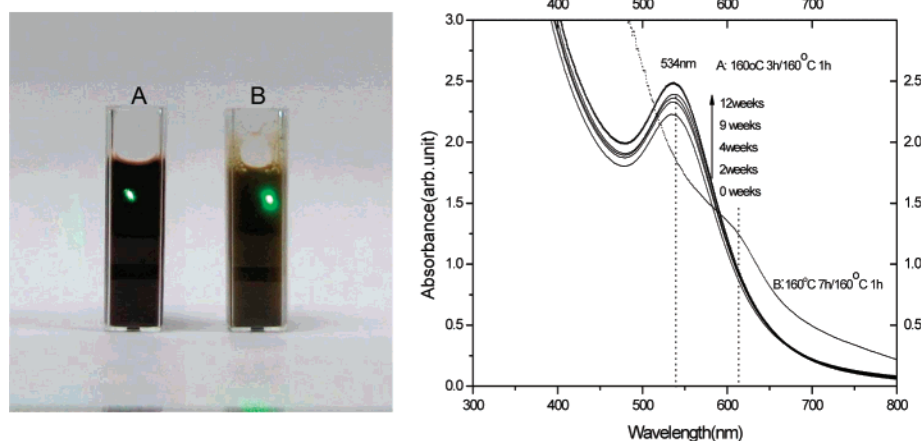
**4. Au Particles Deposited on the Glucose-Derived Polymer Template by Microwave and Ultrasonic Irradiation of  $\text{HAuCl}_4$ , Respectively.** Microwave and ultrasonic irradiation are useful tools for materials synthesis. The microwave irradiation on the mixture of the glucose-derived template and  $\text{HAuCl}_4$  caused a rapid heating, but the prepared Au particles (Figures 6A and

(20) Bulushev, D. A.; Yuranov, I.; Suvorova, E. I.; Buffat, P. A.; Kiwi-Minsker, L. *J. Catal.* **2004**, *224*, 8–17.

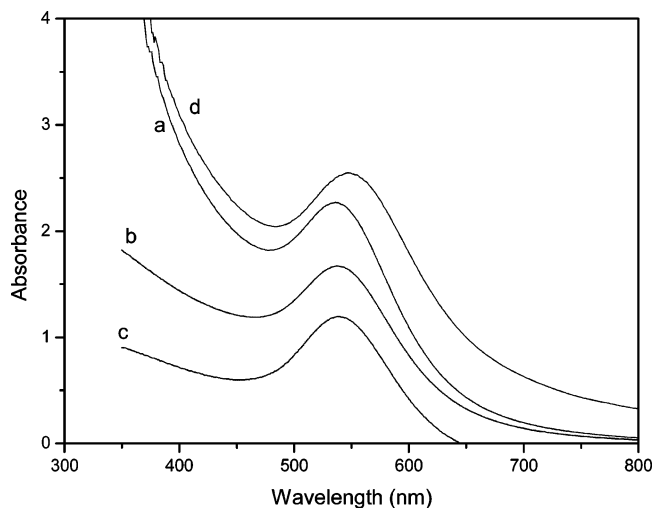
(21) Schubert, M. M.; Hackenberg, S.; Veen, A. C. V.; Muhler, M.; Plzak, V.; Behm, R. J. *J. Catal.* **2001**, *197*, 113.

(22) Zhong, Z.; Ho, J.; Teo, J.; Gedanken, A. *Chem. Mater.* **2007**, *19*, 4776–4782.

(23) Moreau, F.; Bond, G. C. *Topics Catal.* **2007**, *44*, 1–2, 95–101.

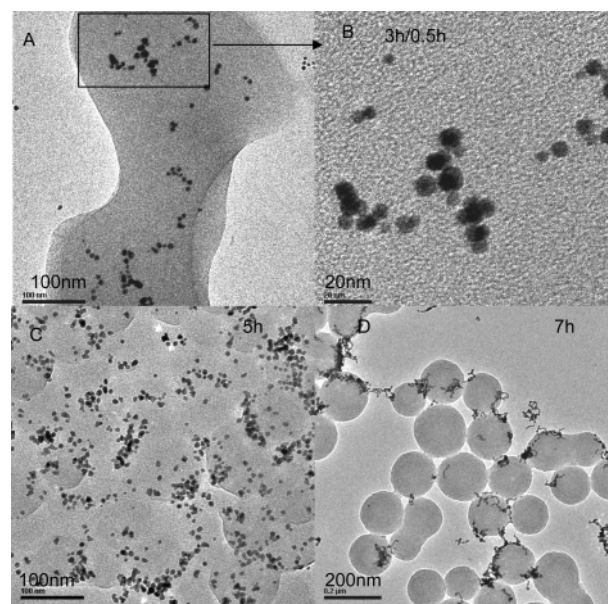


**Figure 4.** (left) Photographs of the prepared Au colloidal solution prepared in the presence of glucose. In A, the glucose solution was previously heated at 160 °C for 3 h and cooled to room temperature, a 1 mL of a 0.01 M  $\text{HAuCl}_4$  solution was added, and the solution was heated again at 160 °C for 1 h (corresponding to the sample shown in Figures 2B and 2C). In B, similar experimental conditions were used, except that the glucose solution was hydrothermally treated at 160 °C for 7 h (corresponding to the TEM image in Figure 2F). In A, the colloidal template was highly hydrophilic, and the Au particles were small and highly dispersed; thus, the green laser was only slightly scattered (Tyndall effect) and a small laser spot was generated. In B, a slurry of larger carbon spheres was formed, and the Au particles were severely aggregated. Thus, the laser was severely scattered and a larger laser spot was generated. Shown on the right are the corresponding UV-vis spectra of the two samples.



**Figure 5.** UV-vis spectra for the sample shown in Figure 4A before and after repeatedly redispersed in water and after the addition of NaCl: (a) original Au suspension; (b) after washing three times and redispersion in  $\text{H}_2\text{O}$ ; (c) after washing five times and redispersion in  $\text{H}_2\text{O}$ ; (d) 0.5 g of NaCl powder was added in 3 mL of the original Au suspension, and after ca. 30 min the UV-vis spectra of the suspension (still not precipitated) were recorded.

6B) were not as uniform as those prepared by the hydrothermal treatment (Figures 2B and 2C). Some of the Au particles were obviously aggregated during microwave irradiation, and probably the very fast decomposition and reduction of  $\text{HAuCl}_4$  caused the instant formation of too many Au nuclei in the solution. Before they were properly trapped by the template functional groups and cage-like structures, these nuclei were capable of moving around and forming aggregates with one another. Differing from the microwave irradiation, with the sonication-assisted method it was possible to prepare highly dispersed Au particles with an Au particle size of 4–6 nm (Figure 6C). However, this method cannot deposit Au particles on the glucose-derived carbon (the 7-h template, Figure 6D), even under strong sonication. It has been proven that sonication could facilitate the deposition of Au particles on a number of catalyst supports.<sup>12</sup> In the case of carbon spheres (Figure 6D), since there were not sufficient functional groups on the surface, some linear aggregates of Au particles



**Figure 6.** (A and B) Au nanoparticles prepared by microwave irradiation. Similar to samples shown in Figures 2B and 2C, the glucose solution was first heated at 160 °C for 3 h before 1 mL of a 0.01 M  $\text{HAuCl}_4$  solution was added, and the mixture was heated in a microwave oven again at 160 °C for 0.5 h. (C and D) Sonication-assisted fast deposition of Au nanoparticles on a glucose-derived polymer intermediate or carbon using  $\text{NaBH}_4$  as the reducing agent and lysine as capping agent. The glucose-derived templates were hydrothermally heated at 160 °C for 5 h in C and at 160 °C for 7 h in D.

were observed, similar to our previous observation in the absence of catalyst supports.<sup>8a</sup> The formation of the linear aggregates was because of the poor reactivity or weak affinity of the carbonlike template toward the small Au particles. Therefore, the formed small Au particles had to stay in the solution for a much longer time, compared to the case where the 3-h or 5-h templates were used. After ceasing the sonication (20 s), the un-deposited Au particles started to form linear aggregates in solution, a phenomenon reported in our previous work.<sup>8a</sup> However, though the Au particles were quite small (Figure 6C), this sample exhibited poor results for CO oxidation, as the Au particle surfaces

were capped with a layer of lysine molecules, which blocked the access of CO molecules to Au particles. In other words, as opposed to these capped Au colloids, the aforementioned Au colloids prepared by the two-stage hydrothermal process are accessible to reactant molecules, but are highly stable. This unique property will enable some special application for them.

### Conclusion

We have successfully synthesized highly dispersed and stable Au colloids deposited on glucose-derived polymer templates employing a two-stage hydrothermal process. The template is first prepared by hydrothermally heating glucose in an aqueous solution at 160 °C for several hours. The template is then cooled to room temperature and mixed with HAuCl<sub>4</sub>, and the mixture is rehydrothermally treated again at 160 °C for 1 h. The 3-h treated template has a proper density and distribution of O-containing functional groups, and probably some cagelike structures, and thus can be used to prepare Au particles with a

high dispersion. The templated Au particles can be easily precipitated and redispersed in H<sub>2</sub>O. A further increase of the hydrothermal treatment in the template preparation leads to overaromatization and deep carbonization, and thus the prepared template is not able to fix the Au particles well and causes their severe aggregation. The microwave- and sonication-assisted synthesis of the Au particles also confirms the difference in reactivity for the templates that are hydrothermally treated at various times. Finally, the highly dispersed Au colloids are used for the CO oxidation reaction, and a good catalytic activity and stability are observed.

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