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## COMMUNICATION

# One-pot fabrication of yolk-shell nanospheres with ultra-small Au nanoparticles for catalysis

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We report a "one-pot" method for the direct synthesis of organosilica-shell/silica core nanoreactor confined with ultrasmall metal (Au, Pd, Ru) nanoparticles. The nano-reactor confined with Au nanoparticles showed high activity towards styrene oxidation using  $O_2$  as oxidant under 1 atm pressure and could be stably recycled without deterioration on both conversion and selectivity. The strategy could be adapted onto other nanostructures with little modification to obtain yolk-shell nanoreactors for catalysis application.

Precious metal catalysts are widely used in modern chemical industry in fields such as hydrogenation,<sup>1</sup> oxidation,<sup>2</sup> refining process<sup>3</sup> and etc. Since the pioneering work of Haruta who found that CO could be oxidized on supported Au NPs even at a sub-ambient temperature,<sup>4</sup> Au NPs have been widely employed in the oxidation of hydrocarbons,<sup>5</sup> epoxidation of olefines,<sup>6</sup> hydrogenation reactions<sup>7</sup> and so on.<sup>8</sup> The melting point of gold decrease rapidly when particle size was reduced into nanoscale, resulting in the easy aggregation of highly active species.9 In most cases, precious metal nanoparticles (NPs) were loaded onto supports with high surface area to pursue the utmost dispersion and thus to expose active sites to the most extent. However, the growth of particle-size under high temperature or during the reaction process generally results in the deterioration of the catalytic activity. This phenomena could always be observed especially in cases that the metal NPs are of ultra-small size (<10 nm) or have a low melting point, which presents one of the most common and serious problems in precious metal catalysis.

Several methods were developed to prevent the aggregation of metal NPs. Recently, it was reported that stability of metal NPs could be greatly enhanced by coating metal NPs with either oxide layer or carbon layer. For example, Xie tried to cut off the fusion of individual Au NPs by coating pre-prepared Au NPs with SnO<sub>2</sub>.<sup>10</sup> Atomic layer deposition was used by Peter and co-authors for preparing a coking-and sintering-resistance catalyst by covering Pd NPs with an Al<sub>2</sub>O<sub>3</sub>

layer.<sup>11</sup> However, extra layer coating of metal NPs may cause the mass transfer barrier during the catalytic process.

Another alternative method is the encapsulation of metal NPs in coreshell or the yolk-shell nanostructures.<sup>12</sup> For example, Shi and coauthors fabricated a magnetic core/mesoporous silica shell nanostructure to fulfill targeted drug delivery and multiphase separation;<sup>13</sup> Zhang synthesized yolk-shell microspheres containing a single Au nanoparticle core and a mesoporous silica shell and its catalytic activity was tested in the reduction of 4-nitrophenol with NaBH<sub>4</sub>.<sup>14</sup> For core-shell nanostructures, metal NPs cores are tightly surrounded by the core material,<sup>15</sup> while there is enough space for metal NPs in the yolk-shell nanostructures. Yolk-shell nanospheres is more suitable for low temperature liquid phase reactions because the hollow interiors could provide enough space for the catalytic reactions and weak interaction between metal NPs and yolk-shell nanospheres may help to keep the intrinsic properties of metal NPs. Compared with coreshell nano-spheres, the synthesis of yolk-shell nanospheres is more challenging especially for encapsulating ultra-small metal NPs, even if methods such as ship-in-bottle approach, soft templating approaches, template-free approaches, Ostwald ripening or galvanic replacement processes, and methods based on the Kirkendall effect, have been developed. Moreover, tedious multi-step synthesis is generally involved. $^{16}$ 



In this work, we reported a general one-pot method for the synthesis of yolk-shell nano-spheres encapsulated with ultra-small Au NPs using PVP protected Au (Au-PVP) as metal NPs source and TEOS (tetraethoxysilane) and BTME (1,2-bis(trimethoxysilyl)ethane) as silica

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source in base medium in the presence of CTAB (hexadecyl trimethyl ammonium bromide). It was found that Au-PVP confined in yolk-shell nanospheres is highly active in liquid-phase styrene oxidation with oxygen as oxidant. The catalyst could be facilely recycled for 8 times without obvious deterioration in activity. Compared with catalysts prepared by conventional impregnation method, Au NPs in yolk-shell nanospheres showed excellent resistance to the aggregation during the catalytic process.

The general process for the synthesis of yolk-shell nano-spheres encapsulated with Au NPs involves the hydrolysis of TEOS in basic water-ethanol solution with CTAB as surfactant, followed by the addition of Au-PVP,<sup>17</sup> then another portion of TEOS was added to the above mixture followed by the addition of BTME as illustrated in Scheme 1 (The detail of the preparation procedure could be found in supplementary information). The hydrothermal treatment of the mixture at 80 °C gives final yolk-shell nano-spheres, SiO<sub>2</sub>@Au@Organosilica (Au@O-SiO<sub>2</sub> Y-S). The TEM image of Au@O-SiO<sub>2</sub> Y-S clearly shows the yolk-shell nano-spheres with outer particle size of ~500 nm and inner core size of ~200 nm (Figure 1a). The pores on the shell were around 2 nm and Au NPs could clearly be observed in the area much larger than the core, indicating that the particles captured by SiO<sub>2</sub> were released during the formation of the shell. The uniform distribution of nano-spheres with particle size of 500 nm could be clearly observed in the SEM image of this sample (Figure 1b). The distribution of the particle size in Figure 1 shows the average diameter of Au-PVP confined in the yolk-shell nanospheres is 4.2 nm, which is similar to that of free Au-PVP (particle size in the range of 3 nm ~ 5 nm, Figure S1). The X-ray diffraction pattern of Au@O-SiO2 Y-S only affords one wide diffraction peak at 2-theta of 22 degree characteristic of the amorphous silica and no diffraction peaks from Au NPs could be observed (Figure S2). The above results indicate that Au NPs are distributed uniformly in the yolk-shell nanospheres and no aggregation of Au NPs occurs during the synthesis process. Based on nitrogen adsorption/desorption measurement (Figure S<sub>3</sub>), Au@O-SiO<sub>2</sub> Y-S has pore diameter of 2 nm, BET surface area of 689 m<sup>2</sup>/g and pore volume of 0.42 cm<sup>3</sup>/g.

For clarifying the formation mechanism, the TEM images of samples taken at different synthetic stages are summarized in Figure 1c-f. In the first stage, porous silica nanopsheres with a diameter of about 200 nm were formed. After the addition of Au-PVP, Au-PVP adheres on the surface of silica nanopsheres for decreasing the surface energy. The growth of a thin layer of SiO<sub>2</sub> on Au/SiO<sub>2</sub> nanospheres could be clearly observed with the addition of second portion of TEOS for the formation of Au@SiO<sub>2</sub> core-shell nanospheres (Au@SiO<sub>2</sub> C-S) with particle size of around 300 nm (Figure 1d). After the BTME addition and hydrothermal treatment, Au@SiO<sub>2</sub> C-S nanospheres transforms to  $Au@O-SiO_2$  Y-S nanospheres, which is mainly due to the etching effect of organosilane precursor as we reported previously.<sup>18</sup> The inner core size of Au@O-SiO<sub>2</sub> Y-S remains almost the same as the particle size of SiO<sub>2</sub> formed in the initial stage, showing silica layer formed with the addition of second portion of TEOS was removed by the addition of BTME. A control experiment shows that only organosilica hollow nanospheres (O-SiO<sub>2</sub> H-S) could be formed when no Au-PVP was added with other synthesis conditions similar to Au@O-SiO<sub>2</sub> Y-S (Figure 1f). This is probably due to the protection effect of PVP which could prevent the etching of silica core by BTME.<sup>19</sup> This further confirms the adherence of Au-PVP on the surface of silica core after its addition to the synthesis medium.



Figure 1. (a). TEM and (b). SEM image of  $Au@O-SiO_2$  yolk-shell. TEM images of (c).  $SiO_2$  core formed at the first stage, (d).  $Au@SiO_2$  core-shell after adding Au-PVP and second portion of TEOS, (e).  $SiO_2@SiO_2$  core-shell formed without adding Au-PVP, and (f). O-SiO\_2 hollow sphere formed without adding Au-PVP.

Styrene oxide is an industrially important organic intermediate used in the synthesis of fine chemicals and pharmaceuticals. The traditional preparation method involves stoichiometric oxidation using organic peracides as oxidants, which is not only expensive but also inefficient and environmentally unfriendly. The direct oxidation of styrene for the formation of styrene oxide using  $O_2$  as oxidant is highly desirable. Vladimir showed that gold clusters with 55 atoms could catalyze the oxidation of styrene using oxygen gas with styrene oxide as the main product, but the reactivity was moderate (conversions<30% on different supports).<sup>20</sup> Yu prepared Gold NPs stabilized by task-specific ionic complexes.<sup>21</sup> The optimized catalytic systems achieved 32.9% styrene conversion with 72.0% selectivity to the epoxide and could be reused four times without significant loss of activity. The catalytic performance of Au@O-SiO<sub>2</sub> Y-S was tested for styrene epoxidation using oxygen as oxidant and was compared with Au-PVP, Au/O-SiO<sub>2</sub> prepared by impregnation method and Au-PVP/O-SiO<sub>2</sub> prepared by directly loading of Au-PVP on O-SiO<sub>2</sub> hollow spheres (Table 1). Since Au-PVP NPs could not be distributed in dioxane, the control reaction using Au-PVP as catalyst was carried on in water. Only 9.1% conv. was observed on Au-PVP and the color of reaction solution turned from light brown into clear after the reaction, indicating the aggregation of Au NPs.<sup>17</sup> Au@O-SiO<sub>2</sub> Y-S could smoothly catalyze the reaction to afford 49.4% conv. with selectivity to styrene epoxide of 66.1%,

| catalyst                   | Particle size (nm) | Au loading<br>(wt %) | Conv.<br>(%)   | Sel. (%)       |               |                |
|----------------------------|--------------------|----------------------|----------------|----------------|---------------|----------------|
|                            |                    |                      |                | 1              | 2             | 3              |
| Au-PVP <sup>b</sup>        | 3 nm               | -                    | 9.1 ±0.7       | $87.6 \pm 4.0$ | $6.0 \pm 1.0$ | $6.4 \pm 0.4$  |
| Au@O-SiO <sub>2</sub> Y-S  | 4 nm               | $0.53 \pm 0.02$      | $49.4 \pm 3.2$ | $27.2 \pm 2.5$ | $6.6 \pm 0.6$ | $66.1 \pm 2.6$ |
| Au/O-SiO <sub>2</sub>      | 8 nm               | $0.42 \pm 0.01$      | $50.5 \pm 5.3$ | $32.7 \pm 3.2$ | $6.8 \pm 0.4$ | $60.5 \pm 2.9$ |
| Au-PVP/O-SiO2 <sup>d</sup> | 3 nm               | $0.54 \pm 0.01$      | $10.4 \pm 0.7$ | $64.5 \pm 3.5$ | $3.3 \pm 1.3$ | $32.1 \pm 3.2$ |

<sup>a</sup> Reaction conditions: 5.5 mmol of styrene, 0.00127 mmol of Au for each catalyst, 3 ml of dioxane, 100 °C, 15 h, 1 atm O<sub>2</sub>; <sup>b</sup> 3 ml water was used as solvent instead of dioxane; <sup>c</sup> prepared by impregnation method with O-SiO<sub>2</sub> hollow spheres as support and HAuCl<sub>4</sub> as metal source with reduction by hydrogen at 120 °C; <sup>d</sup> prepared by directly loading of Au-PVP on O-SiO<sub>2</sub> hollow spheres. **1**.benzaldehyde; **2**.acetophenone; **3**.styrene oxide

showing that Au-PVP confined in yolk-shell nanospheres is efficient to catalyze the oxidation of styrene. Au NPs loaded on silica hollow nanospheres by traditional impregnation method resulted in Au/O-SiO<sub>2</sub> with Au particle size of 8 nm (TEM see Figure S4a-b). Under similar reaction conditions the catalyst showed a similar initial activity and selectivity towards styrene oxidation with Au@O-SiO<sub>2</sub> Y-S with a conversion of 50.5% and selectivity of 60.5% towards styrene oxide. For Au-PVP /O-SiO<sub>2</sub> as mentioned before the size of PVP protected gold nano-particles is larger than the pore size in the shell of hollow nanospheres, so it is not surprising that O-SiO<sub>2</sub> H-S could not provide substantial shelter for the pre-synthesized catalysts. The activity was as low as its semi-homogeneous counterpart and the main product was benzaldehyde (10.4% conv. with 32.1% sel. to styrene oxide).

To reveal the production of styrene oxide on Au@O-SiO<sub>2</sub> Y-S, the reaction process was monitored via sampling on time stream (Figure 2a). From the time course plots, we can see that the reaction was carried on in a rather slow manner in the first 1 h. A conversion of 50.9% was achieved after 12 hours and acetophenone, benzaldehyde and styrene oxide were the main products. The selectivity changed a lot during the process and styrene oxide was the main product in the end, with a selectivity of 62.2%. It is worth noting that the inducing period could also be observed in the oxidation of cyclohexene catalyzed by Au NPs supported by mesoporous silica due to the growth in particle size during the catalytic process for the formation of active species.<sup>22</sup> In our case no obvious growth in particle size was observed as evidenced by the TEM image of the reused catalyst (Figure S5). The previous studies show that a free radical intermediate

would form when using solvent which could firstly react with activeoxygen.<sup>6</sup> The intermediate could convert into peroxide and serve as oxidant for the epoxidation reaction. From the time course, we can see that the benzaldehyde was the primary product at the beginning of the reaction but the selectivity to styrene oxide increased with the conversion of styrene and finally became the main product. Thus, the induction time may be related with the conversion of a free radical intermediate into peroxide. The low selectivity to styrene epoxide on Au-PVP and Au-PVP/SiO<sub>2</sub> may be due to either the solvent effect (when water was applied to ensure the distribution of the Au-PVP) or the aggregation of Au NPs during the catalytic process which led the reaction stop at its early stage.

To further clarify the reusability of  $Au@O-SiO_2 Y-S$  and  $Au/O-SiO_2$ both catalysts were tested by performing the reaction with the same condition for more cycles. After each cycle the catalyst was separated via centrifugation, washed several times with ethanol and then dried. No obvious deterioration of activity and selectivity was observed for  $Au@O-SiO_2 Y-S$  after even 8 cycles (Figure 2b). The conversion showed a little bit increase after first four to five cycles. On TEM images of the recovered catalyst (after 8th run, Figure S5) we can find the fragments of broken nano-reactors, which may explain the improvements of activity for the fragments may facilitate the mass transfer of both substrates and products. The size distribution of Au NPs changed only slightly (averagely from ~4.2 nm to ~4.5 nm, Figure S5). High resolution Scanning Electronic Microscope was performed to further confirmed the distribution of Au NPs on the reused catalyst (Figure S6). Nearly no Au NPs could be observed under scanning



Figure 2. (a) Time course plots of styrene oxidation on  $Au@O-SiO_2$  Y-S catalyst and (b) Reusability of  $Au@O-SiO_2$  Y-S (Filled) and  $Au/O-SiO_2$  (patterned) (the upper, middle and bottom of the column are the yield for **1 styrene oxide**, **2 acetophenone** and **3 benzaldehyde**, respectively) in the oxidation of styrene.

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mode but small bright spots could be seen in the same area when scanning-transmitting mode was applied. The same phenomenon was observed even when we point the camera to the fragment which exposure their inside wall, suggesting that most Au NPs were inside the shell. The result supported our description of the formation mechanism- the Au NPs were released from the sacrifice layer during the etching process. Large particles with a diameter over 10~20 nm could be also observed under scanning mode, indicating that Au NPs would aggregate due to losing the protection when they escaped from the nano-reactor. ICP-AES was performed to determine the leaching of metal contents and the result indicates that 90.3% of the gold was remained on the catalyst after 8 cycles. On the other hand, the activity of Au/O-SiO<sub>2</sub> deteriorated significantly after the second cycle, together with a decline on the selectivity. TEM images show that most of Au NPs on the hollow sphere disappeared and large metal aggregates emerged instead (Figure S4c-d). The results show that Au@O-SiO<sub>2</sub> Y-S is superior to the catalyst prepared by traditional impregnation-reduction method in stabilizing Au NPs during the catalytic process.

As a supplement to this work, we extended the one-pot strategy for the synthesis of nanoreactors confined with Pd NPs (the sample was denoted as  $Pd@O-SiO_2 Y-S$ ) and Ru nano-wires (the sample was denoted as  $Ru@O-SiO_2 Y-S$ ) using Pd-PVP and Ru-PVP as metal source. The TEM images clearly show that  $Pd@O-SiO_2 Y-S$  and  $Ru@O-SiO_2 Y-S$  with Pd NPs or Ru nano-wires uniformly distributed inside the nano-reactors have similar yolk-shell nanostructures to  $Pd@O-SiO_2 Y-S$  (Figure S7). The results above suggest that one-pot strategy is highly adaptable and could easily be extended to the synthesis of nano-rectors with different types of metal NPs.

In summary, an efficient one-pot method was developed for the synthesis of yolk-shell nanospheres confined with ultra-small metal NPs using predefined metal NPs as metal source, TEOS and BTME as silica source and CTAB as structural directing reagent. With Au NPs as a model, it was found that the nano-reactor confined with Au NPs could efficiently catalyze the styrene oxidation under 1 atm oxygen gas to afford a yield of styrene oxide over 30%. No obvious aggregation of Au NPs in the nano-reactor could be found during the catalysis process, which is mainly attributed to the protection effect of the shell and core of the yolk-shell nanoreactor for metal NPs. As a result, the nanoreactor could be stably recycled without degradation in both activity and selectivity.

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### Notes and references

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