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ARTICLE TYPE

# Facile and efficient synthesis of polystyrene/gold-platinum composite particles and their application for aerobic oxidation of alcohols in water

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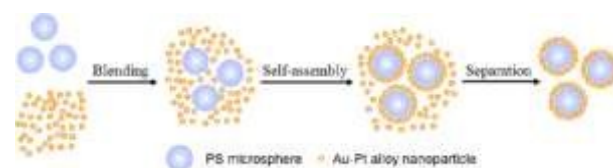
Herein we develop a facile and effective method for the synthesis of composite particles composed of polystyrene microspheres decorated with gold-platinum alloy nanoparticles, which exhibited excellent catalytic activity and recyclability for 1-phenylethanol oxidation under a mild condition (without a base, air as oxidant, in water, at 40 °C).

Aldehydes and ketones are important intermediates in the synthesis of fine chemicals and they are often synthesized by aerobic oxidation of alcohols.<sup>1-4</sup> Traditionally, the alcohol oxidations are performed by using stoichiometric amounts of expensive and toxic inorganic oxidants, such as chromate or permanganate, which usually cause environmental problems due to the large amounts of by-products.<sup>5-8</sup> In order to overcome this shortcoming, a lot of developments have been made towards the design and preparation of new catalysts in the past few decades. Among them, metal nanoparticles have shown high catalytic activity and good selectivity for aerobic oxidation of alcohols. In this respect, the pioneering work has been accomplished by Rossi et al. and Hutchings et al., but their catalysts were usually used under solvent-free condition or at high temperature.<sup>9, 10</sup> It is evident that this cannot be suitable for the aerobic oxidation of alcohols with high melting point or low stability at high temperature.<sup>11</sup> There is thus still a substantial necessity for developing catalysts that can operate in water under mild pressure.

Recently, bimetallic nanoparticles have been found to be more advantageous in terms of activity and selectivity, compared to their monometallic counterpart.<sup>12-14</sup> The improved catalytic performance of bimetallic nanoparticles can be ascribed to synergistic effects, deriving from electronic or geometrical interactions between the two metals.<sup>14</sup> Nevertheless, in order to prevent the aggregation of them owing to van der Waals attractions and simultaneously to effectively recover them for reuse in a simple manner, the formation of such bimetallic nanoparticles inevitably requires a certain support.<sup>15</sup> However, as far as we know, few papers have been reported on the preparation of polymer supported bimetallic nanoparticles, although a number of efforts have been focused on the inorganic supports. For example, Akashi et al. reported the *in situ* formation of polystyrene (PS) supported gold-platinum (Au-Pt) bimetallic nanoparticles by dispersion copolymerization of styrene and poly(*N*-isopropylacrylamide) (PNIPAAm) macromonomer in the

presence of H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>PtCl<sub>6</sub>. The coordination of metal ions to PNIPAAm played an important role in the successful synthesis of these composite particles.<sup>16</sup> Ballauff and co-workers used spherical polyelectrolyte brushes consisting of a PS core and cationic long chains to adsorb metal salt precursors by electrostatic interaction for the generation of stable Au-Pt alloy nanoparticles on the surface of PS particles.<sup>15</sup> Here it is worth noting that the preparation methods mentioned above generally include the surface pretreatments of polymer support in order to promote the deposition of bimetallic nanoparticles on them.

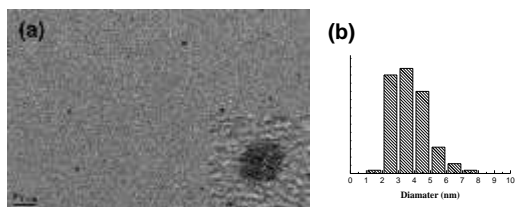
In this communication, we report a facile and effective route to coat the PS microspheres with Au-Pt alloy nanoparticles based on a thermodynamic effect.<sup>17-21</sup> The advantage of our approach relies on the fact that surface pretreatment is not required for the deposition of alloy nanoparticles on support microspheres. More importantly, the resultant PS/Au-Pt composite particles can be used as highly active and recyclable catalyst for aerobic oxidation of alcohols under an ideal green process.



**Scheme 1** Schematic representation of the proposed method for fabricating the PS/Au-Pt composite particles

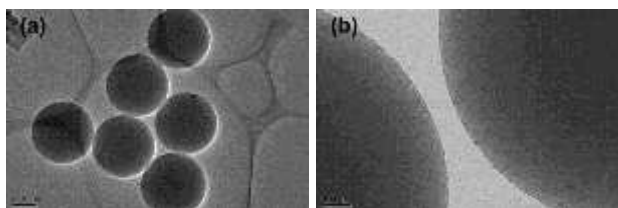
Scheme 1 illustrates the synthetic method employed to produce the PS/Au-Pt composite particles. We chose PS microspheres, which were synthesized by dispersion polymerization, as support microspheres. They were not gone through any surface pretreatments and just were transferred from isopropanol into water by centrifugation and redispersion. Note that during this transfer process, the amount of PVP adsorbed on the surface of PS microspheres might be decreased, and as a result, the hydrophobic PS microspheres shifted into metastable in water owing to the insufficient protection of stabilizers. On the other hand, the hydrophilic Au-Pt alloy nanoparticles were prepared by the co-reduction of H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>PtCl<sub>6</sub> with NaBH<sub>4</sub> in the presence of trisodium citrate.<sup>15</sup> The carboxyl groups derived from trisodium citrate made the as-prepared alloy nanoparticles hydrophilic, which was confirmed by the formation of stable aqueous dispersion of them. After mixing the PS microspheres

with the Au-Pt alloy nanoparticles in water, the alloy nanoparticles can be adsorbed and assembled spontaneously on the surface of PS microspheres, as this was more energetically favourable based on colloid thermodynamics. In other words, the formation of PS/Au-Pt composite particles was to reduce the Gibbs free energy of the colloidal system.



**Fig. 1** TEM image of Au<sub>1.25</sub>Pt<sub>1</sub> alloy nanoparticles (a) and the corresponding histogram of particle size distribution (b). The insert in panel (a) shows a HR-TEM image of an Au<sub>1.25</sub>Pt<sub>1</sub> alloy nanoparticle

Herein the Au-Pt alloy nanoparticles were first prepared by reducing equimolar amount of HAuCl<sub>4</sub> and H<sub>2</sub>PtCl<sub>6</sub> together by NaBH<sub>4</sub>.<sup>15</sup> In Table S1, the precise composition of above nanoparticles (Au<sub>m</sub>Pt<sub>n</sub>, where m/n represents the molar ratio of Au and Pt in the alloy nanoparticles) was determined by ICP-OES. Evidently, the measured composition (Au<sub>1.25</sub>Pt<sub>1</sub>) is close to the initial feed ratio of HAuCl<sub>4</sub> and H<sub>2</sub>PtCl<sub>6</sub>. In addition, it can be seen from Fig. 1 that these nanoparticles have well-defined morphology and the average size of them is about 3.6 nm with a narrow size distribution. Noticeably, such nanoparticles indeed possess of alloyed structure, which can be seen from the high-resolution TEM image (insert), exhibiting uniform lattice spacing of 0.229 nm between the values of 0.235 and 0.223 nm for pure Au (111) and Pt (111) lattice planes, throughout the entire nanoparticle.<sup>15</sup> In Fig. S1, analogous to monometallic AuNPs, the UV-vis adsorption spectrum of the physical mixture of AuNPs and PtNPs exhibits an absorption peak at about 522 nm, which is attributable to surface plasma absorption owing to AuNPs. With respect to the Au<sub>1.25</sub>Pt<sub>1</sub> alloy nanoparticles, however, no significant surface plasma absorption can be observed, suggesting that the Au<sub>1.25</sub>Pt<sub>1</sub> nanoparticles are in an alloyed structure, rather than the physical mixture of monometallic nanoparticles.<sup>22, 23</sup>



**Fig. 2** TEM images of PS/Au<sub>1.25</sub>Pt<sub>1</sub> composite particles with low (a) and high (b) magnification

TEM images of the Au<sub>1.25</sub>Pt<sub>1</sub> alloy nanoparticles coated on the PS microspheres are presented in Fig. 2. Obviously, dense dark spots can be observed, indicating the Au<sub>1.25</sub>Pt<sub>1</sub> alloy nanoparticles are immobilized successfully on the surface of PS microspheres by our proposed method. In addition, the composition of these composite particles was acquired as the electron beam was converged to them based on energy-dispersive X-ray (EDX) analysis. Both Au element and Pt element signals are visible clearly in Fig. S2, which indicate the presence of alloy nanoparticles. To further examine the formation of PS/Au<sub>1.25</sub>Pt<sub>1</sub>

composite particles and the alloyed structure of Au<sub>1.25</sub>Pt<sub>1</sub> nanoparticles, the X-ray diffraction analyses were performed. In Fig. S3, the PS/Au composite particles clearly have four diffraction peaks at about 38.1°, 44.2°, 64.8° and 77.6°, corresponding to the (111), (200), (220) and (311) planes of Au crystal. As to PS/Pt composite particles, four peaks around 39.9°, 46.6°, 68.1° and 81.4° can be assigned to (111), (200), (220) and (311) plane of Pt crystal. Remarkably, XRD pattern for the PS/Au<sub>1.25</sub>Pt<sub>1</sub> composite particles exhibits four well-defined diffraction peaks locating in the expected alloy position between those of Au crystal and Pt crystal, as reported previously.<sup>24</sup> This phenomenon not only indicates the formation of PS/Au<sub>1.25</sub>Pt<sub>1</sub> composite particles but also demonstrates the alloy structure of Au<sub>1.25</sub>Pt<sub>1</sub> nanoparticles.

Next, we turned to the catalytic performance of them for aerobic oxidation of alcohols. The catalytic activity of Au-Pt alloy nanoparticles with different composition supported on PS microspheres for aerobic oxidation of 1-phenylethanol was first examined. In Fig. S4, these different Au-Pt alloy nanoparticles were prepared by varying the molar ratio of HAuCl<sub>4</sub> and H<sub>2</sub>PtCl<sub>6</sub> and then attached onto the surface of PS microspheres by the aforementioned method. The precise compositions of these alloy nanoparticles and the corresponding amounts of them loading on PS microspheres were measured by ICP-OES, as shown in Table S1. Subsequently, a mixture of PS/Au-Pt composite particles, 1-phenylethanol, and water was shaken for 24 h without addition of base at 40 °C under air. After being cooled, the aqueous phase was separated out by centrifugation, acidified with hydrochloric acid, and extracted thrice by a small portion of ethyl acetate. Finally, the concentrated extract layer was analysed by GC. In Table 1, it is clearly found that the PS/Au<sub>1.25</sub>Pt<sub>1</sub> composite particles show the highest catalytic activity and the conversion of acetophenone can reach as high as 99%. This is a significant result because the use of air and water rather than oxygen and organic solvents under atmospheric pressure is an ideal green process. In contrast, the PS/Au or PS/Pt composite particles prepared by the same method had low activity in the absence of base (Table S2, entry 1 and 2), which was similar to previously reported works.<sup>25-27</sup> Moreover, the physical mixture of PS/Au and PS/Pt composite particles also gave a low conversion than the PS/Au<sub>1.25</sub>Pt<sub>1</sub> composite particles (Table S2, entry 3). These results were consistent with recent report that the Au-Pt alloy nanoparticles promoted the oxidation of 2-octanol more effectively under the same condition, as compared to their monometallic counterparts.<sup>28</sup> Furthermore, it is interesting to see that the non-activated cyclohexanol and 1-octanol can also be effectively converted into the corresponding carbonyl compounds in 80% and 84% yields, respectively. This is comparable to the results obtained from the aerobic oxidation of non-activated alcohols, which has originally reported by Uozumi et al.<sup>29</sup> More significantly, cinnamyl alcohol was oxidized selectively to afford the cinnamaldehyde in a quantitative yield as high as 99%. The considerable improvement of catalytic activity of supported Au<sub>1.25</sub>Pt<sub>1</sub> alloyed nanoparticles can be ascribed to the interaction and synergetic effect between Au and Pt atoms in the individual nanoparticle, which have been found previously for many bimetallic systems.<sup>5, 6, 30</sup> The coexistence of Au and Pt in alloy nanoparticles leads to a modification of electronic and chemical

properties of their parent metals, and hence enhanced catalytic properties.<sup>31</sup> In addition, the alloyed structure can also prevent the deactivation and leaching of parent metals during the catalytic reactions.<sup>1</sup>

**Table 1** Aerobic oxidation of alcohols using PS/Au-Pt composite particles as catalyst<sup>d</sup>

Entry	Substrate	Catalyst	Size <sup>b</sup> [nm]	Product	Yield <sup>c</sup> [%]
1	1-phenylethanol	PS/Au <sub>3.78</sub> Pt <sub>1</sub>	5.6	acetophenone	22
2	1-phenylethanol	PS/Au <sub>1.94</sub> Pt <sub>1</sub>	3.8	acetophenone	32
3	1-phenylethanol	PS/Au <sub>1.25</sub> Pt <sub>1</sub>	3.6	acetophenone	99
4	1-phenylethanol	PS/Au <sub>0.74</sub> Pt <sub>1</sub>	3.2	acetophenone	57
5	1-phenylethanol	PS/Au <sub>0.32</sub> Pt <sub>1</sub>	3.0	acetophenone	32
6	Cyclohexanol	PS/Au <sub>1.25</sub> Pt <sub>1</sub>	3.6	cyclohexanone	80
7	1-octanol	PS/Au <sub>1.25</sub> Pt <sub>1</sub>	3.6	octanoic acid	84
8	Cinnamyl alcohol	PS/Au <sub>1.25</sub> Pt <sub>1</sub>	3.6	cinnamaldehyde	99

<sup>a</sup> Reaction condition: substrate [10 mM], Au-Pt alloy catalyst [0.3 mM], H<sub>2</sub>O, air, 24 h, 40 °C. <sup>b</sup> Size of supported Au-Pt alloy nanoparticles. <sup>c</sup> Estimated from GC analysis.

**Table 2** Recovery and reuse of PS/Au<sub>1.25</sub>Pt<sub>1</sub> composite particles<sup>d</sup>

Entry	1st	2nd	3rd	4th	5th	6th	7th
Yield	99	99	99	99	99	99	99

<sup>a</sup> Reaction condition: 1-phenylethanol [10 mM], Au<sub>1.25</sub>Pt<sub>1</sub> alloy catalyst [0.3 mM], H<sub>2</sub>O, air, 40 °C, 24 h.

In addition to catalytic activity, the recyclability is another important criterion for heterogeneous catalyst. In our work, the PS/Au-Pt composite particles can be recycled from the solution easily and effectively by centrifugation or filtration owing to the large size of PS microspheres. The recovered catalyst particles were then used in the next round of oxidation reaction by adding them into the aqueous solution of substrate. As displayed in Table 2, the highly catalytic activity was maintained even after seven times, in which almost the same conversion of acetophenone in each run was obtained. In addition, it is also worth pointing out that no special treatment was required to reactivate the catalyst in the successive oxidation reactions. This will simplify the operating procedure clearly compared with previous work, in which Kobayashi et al. found that the activity of the polymer incarcerated Au-Pt bimetallic clusters was maintained by the treatment of the recovered catalyst with hydrogen under heating conditions.<sup>32</sup>

## Conclusions

In summary, we have developed a facile and effective method for the synthesis of Au-Pt alloy nanoparticles immobilized on the surface of PS microspheres. The complicated surface pretreatments of PS microspheres are not necessary in our designed system and the key to the success is a thermodynamic effect. Illustrating their application, PS/Au<sub>1.25</sub>Pt<sub>1</sub> composite particles exhibit high activity and excellent recyclability as heterogeneous catalyst for aerobic oxidation of 1-Phenylethanol at 40 °C without a base in aqueous media and significantly, they show high selectivity for the oxidation of cinnamyl alcohol to the cinnamaldehyde under the same condition. In addition, these composite particles can also catalyze the aerobic oxidation of non-activated cyclohexanol and 1-octanol efficiently. Hence, in combination with facile synthesis, excellent catalytic activity and stability, and convenient recovery, the PS/Au-Pt composite particles will serve as a promising catalyst in other liquid phase

catalytic reactions.

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## Notes and references

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