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Facile synthesis of polystyrene/gold composite particles as a highly active and reusable catalyst for aerobic oxidation of benzyl alcohol in water†

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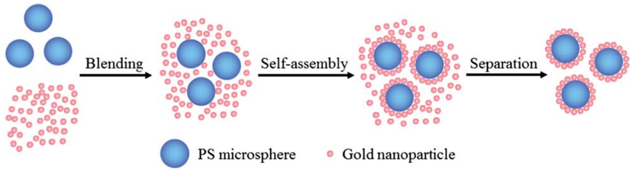
Yunxing Li,* Yan Gao, Cheng Yang, Shengsheng Sha, Jiefu Hao and Yan Wu

PS/Au composite particles have been synthesized facilely based on a thermodynamic effect. More significantly, the PS/Au composite particles can catalyze the aerobic oxidation of benzyl alcohol remarkably under mild conditions (1 atm, air as oxidant, K_2CO_3, 30 °C, in water) and be reused several times without significant loss of activity.

The selective oxidation of alcohols to the corresponding carbonyl compounds is one of the most important organic reactions in the synthesis of fine chemicals.[1–4] Traditionally, these oxidations are performed using stoichiometric amounts of inorganic oxidants, such as chromate or permanganate, but these reagents are expensive and toxic, and produce a large amount of waste.[5] Recently, noble metal nanoparticles have been found to be extremely catalytically active for aerobic oxidation of alcohols.[6–13] Unfortunately, it is often difficult to use these nanoparticles directly owing to their strong tendency to aggregate in the course of the catalytic reaction.[9,14] In addition, one problem to solve in using noble metal nanoparticles as catalysts is the difficulty in their simple and effective recovery for reuse. For these reasons, noble metal nanoparticles are often stabilized by a solid support and used as supported heterogeneous catalyst.[12–22] However, conventional preparation methods of these catalysts are usually time-consuming and cumbersome owing to surface pretreatments of supports or noble metal nanoparticles, which are used to promote the deposition of noble metal nanoparticles on the supports. For example, Rossi's group synthesized $Fe_3O_4@SiO_2$ supported gold nanoparticles (AuNPs) based on the adsorption of $AuCl^-$ ions by silica-coated magnetic nanoparticles, previously functionalized with $-NH_2$ groups, followed by metal reduction.[21] Pan and co-workers presented a synthetic strategy, in which reductants were attached onto the surface of PS microspheres by a series of reactions and subsequently metal ions were reduced *in situ* to form polymer-supported AuNPs.[19] On the other hand, there has been tremendous interest in the development of liquid-phase aerobic oxidation of alcohols with supported heterogeneous catalyst, and significant progress has been achieved. Nevertheless, environmentally undesirable solvents, high temperature, or high atmospheric pressure are used in many cases.[17,19–21,23,24] Therefore, in order to meet the requirement of green chemistry and sustainable development, there is still substantially necessary for exploring the supported heterogeneous catalyst that can be synthesized facilely, recovered effectively, and used directly under mild condition.

Recently, we reported a facile and controllable method to coat the polystyrene (PS) microspheres with AuNPs based on a thermodynamic effect.[25–27] Scheme 1 shows the synthetic method employed there. The PS microspheres synthesized by conventional dispersion polymerization were collected and dispersed in water by centrifugation. During this process, the PVP adsorbed on the surface of PS microspheres was reduced, although the PVP could not be removed completely. Then, the hydrophobic PS microspheres became metastable in water owing to the lack of protection of enough PVP. After mixing them with the hydrophilic AuNPs in water, the latter played the role of solid stabilizer spontaneously for the PS microspheres and distributed uniformly on the surface of PS microspheres to reduce the total interfacial energy of the colloidal system.



Scheme 1 Schematic representation of our method for synthesizing the PS/Au composite particles.

The Key Laboratory of Food Colloids and Biotechnology, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122, China. E-mail: yunxingli@jiangnan.edu.cn; Fax: +86-510-8591-7763; Tel: +86-510-8591-7090

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The advantages of this unique synthesis are obvious. The complicated surface pretreatments of particulate substrates were not necessary at all. Moreover, the resultant PS/Au composite particles had stable structure during the repeated centrifugations and ultrasonic treatments in water. Another convincing phenomenon about the good stability was the fact that the coverage density of AuNPs on the PS microspheres did not decrease, when adding some naked PS microspheres into the dispersion of PS/Au composite particles.[28,29] This is a noticeable advantage when these composite particles are used as supported heterogeneous catalyst, because the good structural stability allows them to retain high activity for reuse.

In this work, the size of AuNPs supported on the PS microspheres was decreased to less than 10 nm, which is a critical size for a dramatic change in their catalytic activity,[21,30,31] and then the synthesized PS/Au composite particles as supported heterogeneous catalysts were applied to the aerobic oxidation of benzyl alcohol in water under different reaction conditions.

Fig. 1a displays the high-resolution transmission electron microscopy (HR-TEM) image of the as-prepared AuNPs. Inspection of this image reveals the AuNPs have well-defined morphology and a narrow size distribution. Statistical diameter measurement indicates that the average size of the AuNPs is about 3.5 nm (insert in Fig. 1). In Fig. 1b, the dense dark spots can be observed clearly, indicating that the PS microspheres are decorated with the AuNPs successfully. In addition, by selecting different molar ratio of $HAuCl_4$ and $NaBH_4$, two different-sized AuNPs (*i.e.*, 9.5 nm and 6.7 nm) were obtained and subsequently deposited on the surface of PS microspheres, as shown in Fig. 1c and d. In fact, the formation of PS/Au composite particles can be further confirmed by the energy-disperse X-ray (EDX) spectroscopy and X-ray diffraction (XRD). As displayed in EDX spectrum of the composite particles (Fig. 2, left), the signal of Au element is present evidently. Moreover, it can be seen from the XRD pattern that there are four peaks, which correspond to (111), (200), (220), and (311) lattice planes for the Bragg reflection of Au, indicating the existence of AuNPs in the composite particles (Fig. 2, right).

Having demonstrated the successful synthesis of PS/Au composite particles, we turned to the examination of catalytic activity of these particles toward the aerobic oxidation of benzyl alcohol, which is often used as a model alcohol to test the activity of catalyst.[1,2] Inductively coupled plasma (ICP) analyses showed that 1.16, 0.65, and 0.51 wt% Au had been incorporated into the composite particles, respectively, as the size of AuNPs is about 9.5, 6.7, and 3.5 nm. A series of reaction conditions was investigated by varying the size of supported AuNPs, atmosphere, reaction time and temperature, and nature of base. The corresponding yields of benzoic acid formed under these conditions are listed in Table 1. It is evident that the supported AuNPs with lower size exhibited higher catalytic activity. However, the yield of benzoic acid exceeded 90% in all cases,

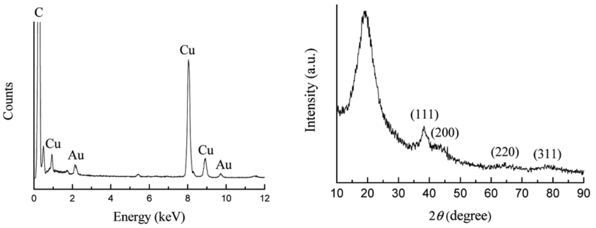

Fig. 2 EDX spectrum (left) and XRD pattern (right) of PS/Au composite particles (supported AuNPs, 3.5 nm).

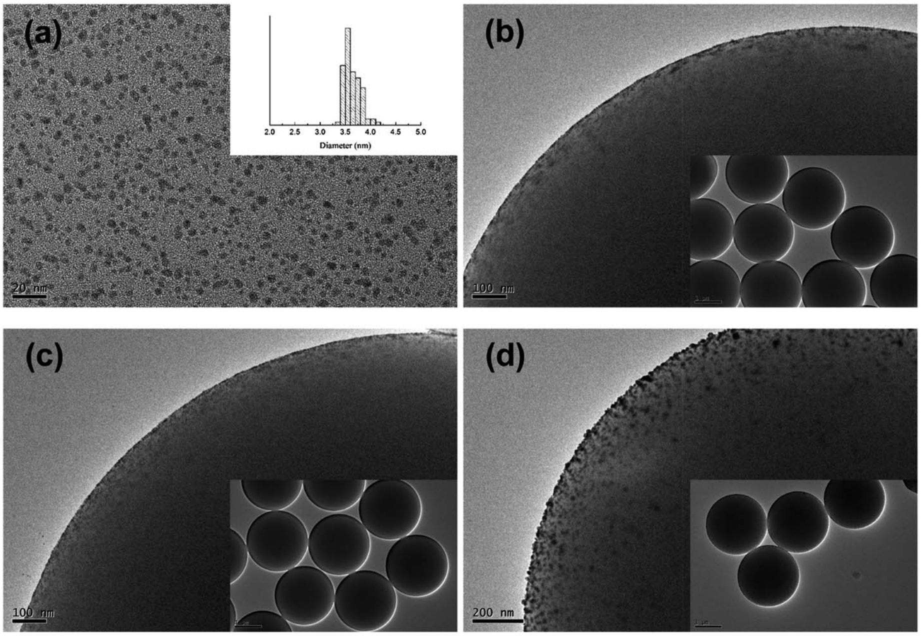

Fig. 1 HR-TEM images of AuNPs with a size of 3.5 nm (a) and PS/Au composite particles with different size of supported AuNPs: 3.5 nm (b), 6.7 nm (c), 9.5 nm (d). The insert in part (a) shows the corresponding histogram of the size distribution of AuNPs.

Table 1 Aerobic oxidation of benzyl alcohol using PS/Au composite particles as catalyst under different reaction conditions[a]

Entry	Size[b] [nm]	Time [h]	Base	Yield[c] [%]
1	9.5	12	K_2CO_3	94
2	6.7	12	K_2CO_3	97
3	3.5	12	K_2CO_3	99
4	3.5	6	K_2CO_3	97
5	3.5	3	K_2CO_3	90
6	3.5	2	K_2CO_3	72
7	3.5	1	K_2CO_3	58
8[d]	3.5	3	K_2CO_3	99
9[e]	3.5	3	K_2CO_3	99
10	3.5	3	KOH	99
11[f]	3.5	24	None	5

[a] Reaction condition: benzyl alcohol (0.1 mmol), Au catalyst (3×10^{-3} mmol), base (0.3 mmol), water (10 mL), air as oxidant, 1 atm, 30 °C. [b] Size of supported AuNPs. [c] Estimated from GC analysis. [d] Temperature is 50 °C. [e] Oxygen as oxidant. [f] Production is only benzaldehyde.

when the supported AuNPs with different size were used. At the given condition, the yield of benzoic acid increased with increasing the reaction time. As the supported AuNPs with the lowest size were used, the yield of benzoic acid was higher than 90% in 3 hours under air at 30 °C. If under otherwise identical conditions air was replaced by oxygen, the yield of benzoic acid reached 99%. Alternatively, when the reaction time was extended to 12 hours under air at 30 °C, we were pleased to find that the oxidation of benzyl alcohol also gave benzoic acid in almost quantitative yield (99%). This is a significant result because the use of air and water rather than oxygen and organic solvents under 1 atm is an ideal green process for practical application.[17,20] In addition, it is apparent that the addition of base could improve the catalytic activity of PS/Au composite particles dramatically, and oppositely, the oxidation reaction almost did not proceed at all in the absence of base. The yield of benzoic acid increased to 99% at 30 °C after 3 h as the KOH was added, which is comparable to other known catalysts.[9,13]

On the other hand, the reusability is also an important feature for the supported catalyst. Herein, the reusability of PS/Au composite particles was evaluated by performing five consecutive oxidation reactions using the same composite particles. In detail, the catalyst particles were collected simply and effectively by centrifugation and then the recovered catalyst particles were reused in the next round of oxidation reaction by mixing them with new substrate, base, and solvent. It is noteworthy that the catalytic activity was maintained at least until the fifth use, with almost the same yield of benzoic acid in each run (Table 2). In contrast, AuNPs stabilized by linear polymer PVP could not be reused owing to their negative aggregation during the course of catalytic reaction.[8,9,32] Therefore, taking practical application into account, the PS/Au composite particles reported in this work is hopeful to offer one kind of reusable catalyst for aerobic oxidation of alcohols.

Table 2 Recovery and reuse of PS/Au composite particles[a]

Entry	1st	2nd	3rd	4th	5th
Yield[b]	99	99	99	99	98

[a] Reaction condition: benzyl alcohol (0.1 mmol), Au catalyst (3×10^{-3} mmol), base (0.3 mmol), water (10 mL), air as oxidant, 1 atm, 3 h, 50 °C. [b] Estimated from GC analysis.

Conclusions

In summary, ultrafine AuNPs (<10 nm) were attached onto the surface of PS microspheres facilely based on a thermodynamic effect. The synthesized PS/Au composite particles exhibited high catalytic activity for the aerobic oxidation of benzyl alcohol under mild condition (1 atm, air as oxidant, K_2CO_3, 30 °C, in water). Moreover, the PS/Au composite particles can be recovered simply and effectively because of large size of support and reused several times without significant loss of catalytic activity. Hence, combining with facile synthesis and convenient recovery, it can be expected that the PS/Au composite particles show great potential for practical application in catalytic oxidation of alcohols.

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