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Short communication

A surfactant-free method to prepare Pd_xAu_y bimetallic nanospheres and their application in catalysis

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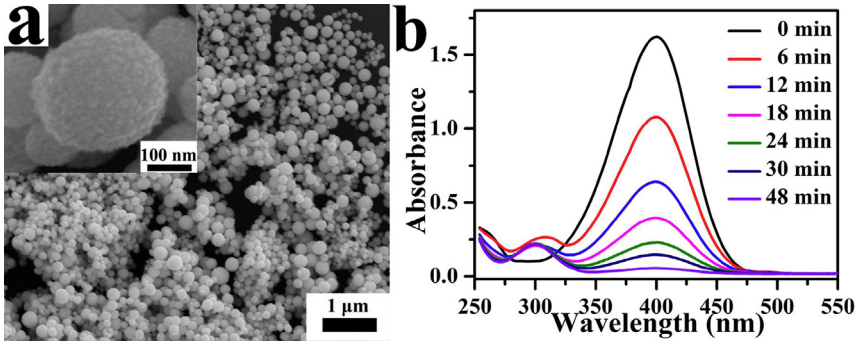
GRAPHICAL ABSTRACT

We have introduced a simple and versatile method to prepare Pd_xAu_y bimetallic nanospheres by using ascorbic acid as reducing agent in absence of surfactants. They displayed superior catalytic activity towards monometallic nanoparticles.



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ABSTRACT

Recently, bimetallic alloys have drawn more and more attentions owing to their superior catalytic performance towards the monometallic ones. However, in the most of established synthetic approaches, surfactants as structure directing agents were necessary, which resulting in the impurity of alloys and structural sensitivity to their kinds or concentrations. To overcome this drawback, herein, we have introduced a surfactant-free method to prepare Pd_xAu_y nanospheres by using ascorbic acid as reducing agent. The as-obtained Pd_xAu_y alloys with atomic ratio of Pd/Au ranging from 1:2 to 2:1 displayed a sphere-like structure. Controlled experiments indicated that an appropriate reducing potential was important for shaping final morphology. The method presented here could be used to prepare Pd_xAu_y nanospheres on the various support surface, such as reduced graphene oxide nanosheets and graphitic carbon nitride. Additionally, this versatile method could even be extended to prepare Pt-based bimetallic nanospheres. In catalytic reduction of 4-nitrophenol, bimetallic Pd_xAu_y catalysts displayed better catalytic activity towards monometallic catalysts, and Pd_1Au_2 nanospheres exhibited the best catalytic property.

In recent years, the research enthusiasm on bimetallic catalysts has grown, not only due to their controllable catalytic performance, but also owing to superiority in comparison with monometallic catalysts [1,2]. In established methods for synthesis of metallic nanostructures, surfactants were usually involved [3–10]. They not only acted as dispersants to inhabit the aggregation, but also guided the growth of

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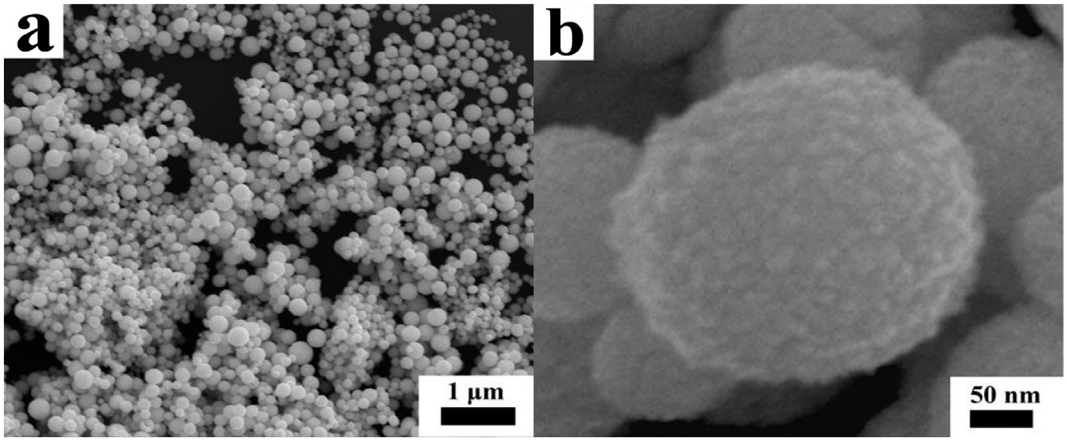

Fig. 1. SEM images of Pd_1Au_1 nanospheres at different magnifications.

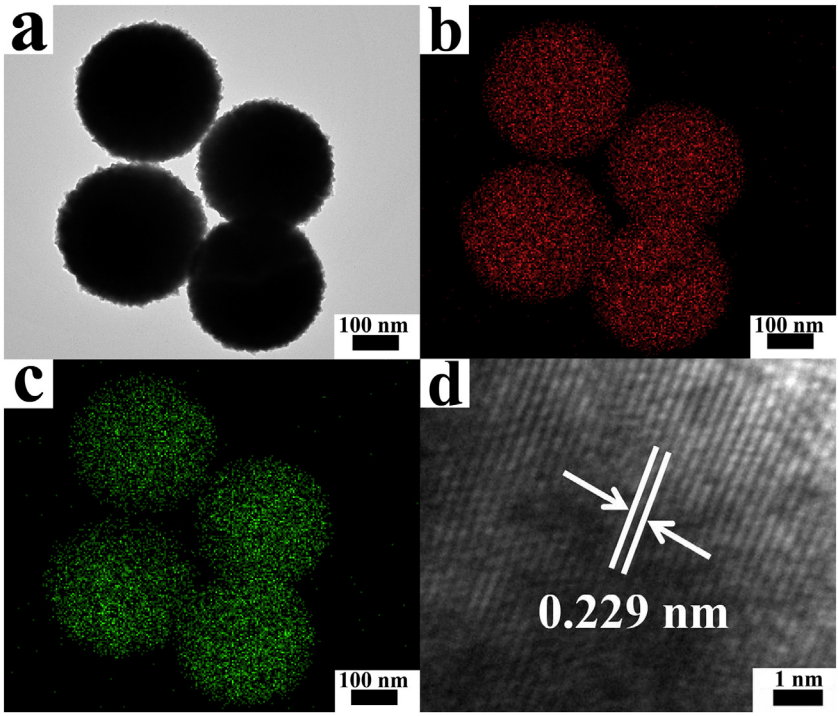

Fig. 2. (a) HAADF-STEM image of Pd_1Au_1 nanospheres. Elemental maps of (b) Pd; (c) Au. (d) HRTEM image of Pd_1Au_1 nanospheres.

metallic nanostructure. For example, to prepare Fe@Pt nanoparticles (NPs) [6], surfactant polyoxyethylene cholesteryl ether was used as directing agent. Nevertheless, surfactants often reserved on the catalyst surface to occupy reactive sites, and were hardly to be completely removed, resulting in negative influences on catalytic performance. Additionally, the morphologies of metallic nanostructures were sensitive to kinds or concentrations of surfactants, resulting in an unsatisfied reproducibility [7–10].

Herein, we have introduced a surfactant-free method to prepare Pd_xAu_y nanospheres by using ascorbic acid (AA) as reducing agent [9,10]. The influences of Pd_xAu_y compositions on morphologies were investigated. Controlled experiments revealed the important role of AA in determining sphere-like morphology. Catalytic reduction of 4-nitrophenol (4-NP) was selected as a model reaction to demonstrate superior catalytic performance and good reusability of Pd_xAu_y bimetallic nanospheres.

In scanning electron microscope (SEM) image (Fig. 1a), Pd_1Au_1 alloys exhibit a uniform spherical shape. The high-resolution image reveals numerous of tiny grains appear on their surface, leading to a rough morphology (Fig. 1b). Their sizes are determined by a number-averaged diameter (D_n), which is acquired by counting 100 nanospheres. In histogram (Fig. S1), their diameters mainly fall in the range of 200 to 350 nm, and an average value is 230 nm. The size distribution is characterized by polydispersity index (PDI) [11], which is calculated by the weight-averaged diameter D_w divided by D_n, and the value is 1.06, indicating a narrow size distribution.

Transmission electron microscope (TEM) image and corresponding elemental maps are shown in Fig. 2a–c. Both element Au and Pd homogeneously disperse in entire nanospheres, and their distributions overlap with each other, evidencing formation of bimetallic alloys instead of individual nanospheres. High-resolution TEM (HRTEM) image shows their lattice spacing is about 0.229 nm (Fig. 1d), which is larger than the lattice distance of (111) plane of Pd NPs (0.225 nm), but smaller than that of Au NPs (0.236 nm).

Fig. 3 displays the X-ray diffraction (XRD) patterns of Au NPs, Pd NPs and Pd_1Au_1 nanospheres. In curve a, four diffraction peaks located at 38.2, 44.4, 64.6 and 77.6° are assigned to (111), (200), (220) and (311) planes of Au (JCPDS No. 04-0784) [12]. In curve c, three