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ARTICLE TYPE

Highly Facile and Efficient Assembly of Palladium Nanoparticles on Polystyrene Microsphere and Their Application in Catalysis

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Catalytic applications of supported palladium nanoparticles (PdNPs) in the liquid phase reactions are of considerable importance. Herein the polystyrene/palladium (PS/Pd) composite particles composed of PS microspheres decorated with PdNPs with different sizes are prepared facilely and effectively based on a thermodynamic effect. Compared with the reported synthetic methods, surface functionalizations or modifications of PS microsphere and PdNPs are not necessary at all. The formation of PS/Pd composite particles has been demonstrated by transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and inductively coupled plasma-optical emission spectroscopy (ICP-OES). Finally, the catalytic performance of as-prepared PS/Pd composite particles is investigated during the reduction of *p*-nitrophenol by sodium borohydride, and noticeably, they have shown a high catalytic activity and a good stability.

Introduction

Noble metal nanoparticles, palladium in particular, have attracted considerable attention for their high catalytic activity in a wide range of chemical reactions, including CO and alcohol oxidations, NO reduction, Suzuki coupling reaction, Heck reaction, hydrogenation of olefins, and so on.[1-13] Recently, further research has suggested that when the size of Pd nanoparticles (PdNPs) is reduced to less than 10 nm, the particulate catalysts may exhibit dramatic change in their catalytic activity.[14-17] Unfortunately, PdNPs as well as other noble metal nanoparticles are often unstable as a result of high surface energy and strong van der Waals attraction. The aggregation of PdNPs will lead to the deterioration of their activity and selectivity in catalytic applications. Therefore, PdNPs usually require a suitable support to prevent aggregation during the reaction to be catalyzed.

A number of methods have been developed so far to afford the synthesis of PdNPs on various supports, and during the course of research and development, the supports of interest have shifted from inorganics to polymers because of their merits of simplified synthesis and good dispersibility in water.[2-11, 18-27] Among known works, the preparation method of polymer-supported PdNPs is mainly so-called *in situ* method, which was to reduce the different palladium precursors in the presence of solid supports. For example, in the former case, Thompson and co-workers have demonstrated that the preformed PdNPs can be immobilized on the amino-functionalized polystyrene (PS) microspheres based on a certain affinity between them.[27] Ballauff's group used spherical polyelectrolyte brushes, consisting of a PS core and cationic long chains, to adsorb $PdCl_4^{2-}$ ions by electrostatic interactions for in-situ generating stable PdNPs on the surface of PS particles.[3] Zhang et al. reported that the poly(styrene-*co*-4-vinylpyridine) microspheres were synthesized by soap-free emulsion polymerization, and then the resultant microspheres acted as support to immobilize the PdNPs based on the coordination interaction between pyridine group and Pd^{2+} ions.[4] Obviously, time-consuming and troublesome surface pretreatments of polymer supports are indispensable in the preparation methods mentioned above, for the sake of promoting the deposition of PdNPs on the polymer supports. However, it is worth noting that there are also several *in situ* methods that the support of PdNPs on the polymer supports is achieved without any surface pretreatments of polymer supports.[28-31] For example, Mayer et al. found the improved accumulation of PdNPs on the surface of PS latex based on hydrophobic interaction.[28] Gedanken's group reported the PdNPs deposited on the surface of PS microspheres via ultrasound irradiation.[29] Nevertheless, as a common feature of all the above works, the unavoidable coexistence of heterogeneous nucleation and homogeneous nucleation results in the lack of uniformity in size distribution and shape of the resultant PdNPs to a certain degree.

To address this issue, we have developed an alternative method for the fabrication of PS/Pd composite particles. Direct immobilization of preformed PdNPs with size less than 10 nm on the PS microspheres is completed based on a thermodynamic effect.[32-37] Remarkably, this process did not involve any surface pretreatments of support microspheres. In addition, the as-prepared PS/Pd composite particles can be used as catalyst with high activity and stability for the reduction of *p*-nitrophenol (4-NP) by sodium borohydride ($NaBH_4$).

Experimental section

Materials

Styrene (St) and azodiisobutyronitrile (AIBN) were obtained from Sinopharm Chemical Reagent Co. and purified by vacuum distillation and recrystallization, respectively. Poly(vinylpyrrolidone) (PVP K-30), trisodium citrate, sodium borohydride ($NaBH_4$), palladium chloride ($PdCl_2$), absolute ethanol, and isopropanol, hydrochloric acid (HCl), *p*-nitrophenol (4-NP) were purchased from Sinopharm Chemical Reagent Co. and used as received. Ultrapure water (18.2 MΩ·cm) was used throughout the experiments.

Preparation of Palladium Nanoparticles (PdNPs)

Trisodium citrate (0.20 mmol) and $PdCl_2$ (5.9×10^{-2} mmol) were first dissolved in water (84 mL) under stirring at room temperature. To obtain different diameter of PdNPs (e.g., 6.5 nm or 3.9 nm), 1.2 mL or 5.9 mL of freshly prepared $NaBH_4$ aqueous solution (0.075 wt%) was injected into the above-mentioned mixture solution rapidly. The reaction was allowed to proceed for 30 min.

Preparation of Polystyrene (PS) Microspheres

PVP (2.8 g) was dissolved in isopropanol (160 mL) and then the obtained solution was heated up to 70 °C in a round-bottom flask, and simultaneously purged with nitrogen to eliminate the inhibiting effect of oxygen. Subsequently, styrene (20 g) and azoisobutyronitrile (0.2 g) were added to the above-mentioned solution under vigorous mechanical stirring. The polymerization was allowed to proceed for 24 h before cooling to ambient temperature. Finally, the resultant PS microspheres were collected by centrifugation, washed with ethanol and water, and redispersed in water under ultrasonication (solid content, 10 wt%).

Preparation of Polystyrene/Palladium (PS/Pd) Composite Particles

Aqueous dispersion of PS microspheres (2 mL, 10 wt%) was added to the preformed aqueous dispersion of PdNPs. The mixture was stirred using a magnetic stirrer for 3 h at room temperature. The resulting PS/Pd composite particles were separated out by centrifugation/washing/redispersion cycles to remove the free PdNPs. Finally, the PS/Pd composite particles were dispersed in water.

Catalytic Reduction of *p*-Nitrophenol (4-NP)

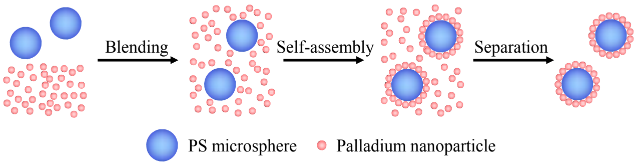
4-NP (30 μL, 0.01 M) aqueous solution and freshly prepared $NaBH_4$ aqueous solution (300 μL, 0.1 M) were added successively in a quartz cuvette at room temperature. The resultant mixture was diluted with water and injected rapidly with a given amount of the PS/Pd composite particles. The kinetic process of the reduction reaction was monitored by the variation of absorbance at 400 nm as the function of time. After each round of reaction, another 30 μL of 4-NP aqueous solution and $NaBH_4$ aqueous solution was added to the reaction solution. This step was repeated ten times to study the stability of catalyst particles.

Characterization

Transmission electron microscopy and energy-dispersive X-ray spectroscopy were performed by a JEM-2100 microscope (JEOL Co., Japan). X-ray diffraction patterns of PS microspheres and PS/Pd composite particles were recorded on a German Bruker-AXS D8 Advance. The palladium content on the PS microsphere was quantified by inductively coupled plasma-optical emission spectrometer (ICP-OES, Agilent, 700 Series). X-ray photoelectron spectroscopy was analyzed on a VG ESCALABMKII X-ray photoelectron spectrometer. UV-vis absorption spectra were recorded at room temperature on a SHIMAZDU UV-2500 spectrometer.

Results and discussion

Preparation and Characterization of PS/Pd Composite Particles.



Scheme 1 Schematic representation of the synthesis of PS/Pd composite particles

The synthetic method employed herein is represented in Scheme 1. Palladium nanoparticles (PdNPs) are synthesized by the reduction of palladium chloride ($PdCl_2$) with sodium borohydride ($NaBH_4$) in the presence of trisodium citrate. The carboxyl groups derived from trisodium citrate make the PdNPs hydrophilic, which is confirmed by the formation of a stable aqueous dispersion of PdNPs. With respect to polystyrene (PS) microspheres, it is worth noting that they are synthesized by conventional dispersion polymerization and have been used as synthesized, in the absence of any surface pretreatments. Subsequently, they are transferred from isopropanol to water by centrifugation, washing, and redispersion processes, during which the PVP adsorbed on the PS microsphere can be reduced. So the hydrophobic PS microspheres become metastable in water due to the insufficient protection of stabilizer. At last, the PdNPs assemble onto the surface of PS microspheres readily and spontaneously after a simple blending of them in water, as this is more energetically favorable based on colloid thermodynamics. In other words, the hydrophilic PdNPs play the role of solid stabilizer and distribute on the surface of hydrophobic PS microspheres to reduce the total interfacial energy of the colloidal system.

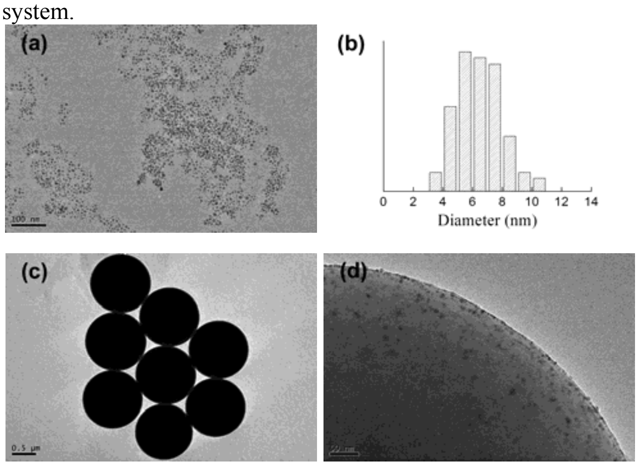


Fig. 1 TEM image of PdNPs with an average size of *ca.* 6.5 nm (a) and the size distribution histogram of them (b); TEM images of PS/Pd composite particles with low (c) and high (d) magnification

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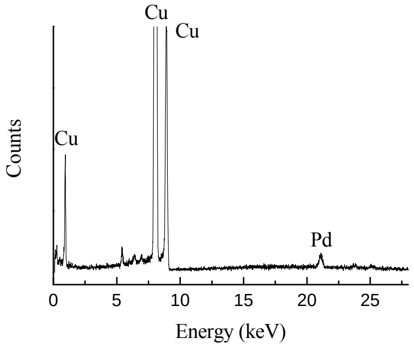

Fig. 2 EDX spectrum of PS/Pd composite particles

Figure 1a and 1b display the transmission electron microscopy (TEM) image of the as-prepared PdNPs and their size distribution histogram, respectively. The shape of PdNPs was nearly spherical and the average size of them was *ca.* 6.5 nm based on the statistical analysis. Figure 1c and 1d illustrate the typical TEM images of the resultant PS/Pd composite particles. The PS microspheres clearly retained their original spherical outline after the incorporation of PdNPs, as observed in the TEM image with low magnification. Noticeably, the TEM image with high magnification clearly displayed the numerous dark spots, suggesting that the PdNPs were immobilized on the surface of PS microspheres successfully. Furthermore, the signal of Pd element was detected in the energy-dispersive X-ray (EDX) spectrum of PS/Pd composite particles, as depicted in Figure 2. This phenomenon also indicated that the PdNPs were successfully formed via the reduction of Pd^{2+} by $NaBH_4$ and then assembled onto the surface of PS microspheres.

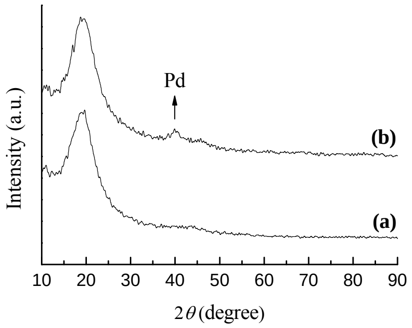

Fig. 3 XRD patterns of (a) PS microspheres and (b) PS/Pd composite particles

Figure 3a and 3b show the X-ray diffraction (XRD) patterns of the PS microspheres and PS/Pd composite particles, respectively. The PS microspheres had a broad diffraction peak centering around 19.3°, resulting from the amorphous structure of polymer. In contrast, another broad and weak diffraction peak around 39.8° corresponding to (111) lattice plane of crystalline structure of metallic Pd was observed from the XRD pattern of the PS/Pd composite particles. The peak broadening can be ascribed to the size effect of the PdNPs. These results demonstrated that the PdNPs of small size have been supported on the PS microspheres, consistent with those observed by TEM.[10, 38] To further confirm the coating of PdNPs on the PS microspheres, we performed X-ray photoelectron spectroscopy (XPS) analysis to investigate the surface composition. It can be seen from Figure 4a that, the strong doublets appear around 340 eV, which can be assigned to photoelectrons originating from Pd 3d energy level. In addition, the Pd 3d core spectrum in Figure 4b remarkably displays the characteristic Pd $3d_{5/2}$ (335.2 eV) and Pd $3d_{3/2}$ (340.5 eV) peaks, attributed to the Pd(0) species, corroborating the presence of PdNPs on the surface of PS microspheres.[10, 21]

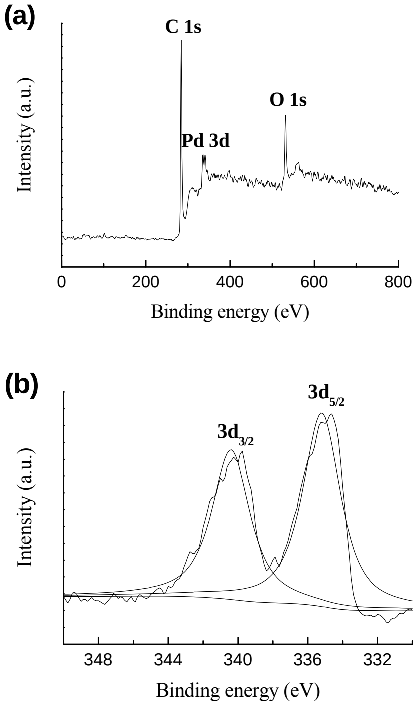

Fig. 4 XPS survey spectrum of the PS/Pd composite particles (a) and the corresponding core spectrum of Pd 3d (b)

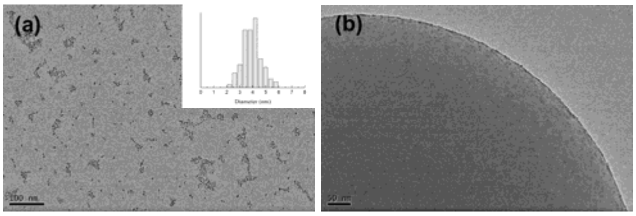

Fig. 5 TEM images of PdNPs with an average size of *ca.* 3.9 nm (a) and the corresponding PS/Pd composite particles (b). The insert in part (a) shows the histogram of size distribution of PdNPs

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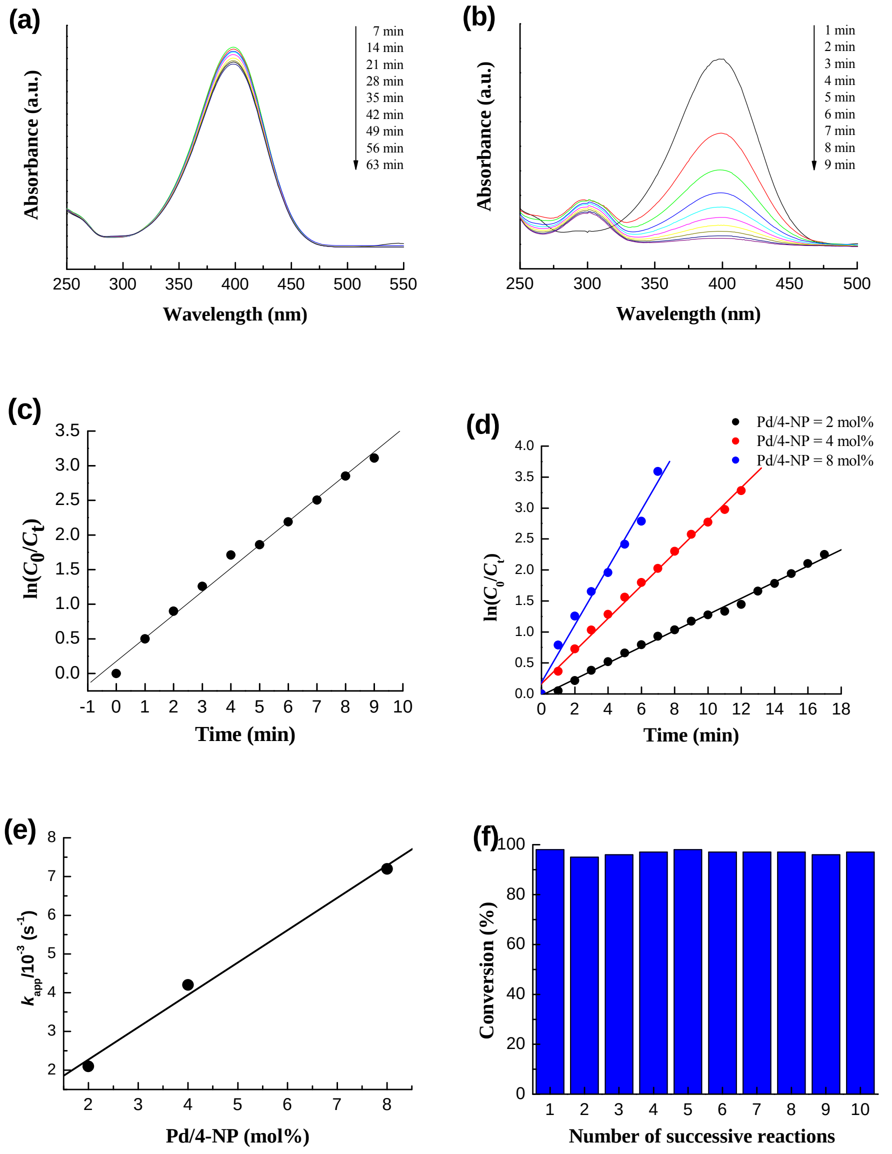

Fig. 6 (a) The reduction of 4-NP recorded at different time points without catalyst; (b) the reduction of 4-NP recorded at different time points using PS/Pd composite particles as catalyst; (c) plot of ln(C_0/C_t) versus reaction time for the aforementioned reaction; (d) plot of ln(C_0/C_t) versus reaction time for different concentrations of PS/Pd composite particles; (e) plot of k_{app} versus concentration of PS/Pd composite particles; (f) conversion against the number of successive reactions using PS/Pd composite particles as catalyst

Application of the PS/Pd Composite Particles for the Catalytic Reduction of 4-NP

Considering that a lower size of noble metal nanoparticles generally leads to a higher catalytic activity, we further prepared the PdNPs of a smaller size by adjusting the molar ratio of $PdCl_2$ and $NaBH_4$, and the statistical analysis (Insert of Figure 5a) revealed that the average size of them was *ca.* 3.9 nm. Subsequently, these PdNPs were supported on the PS microspheres by our proposed method, and the resultant PS/Pd composite particles were selected as catalyst (Figure 5b). Inductively coupled plasma-optical emission spectroscopy (ICP-OES) analysis showed that the amount of Pd was about 0.73 wt% on the surface of PS microspheres. In addition, owing to the easy preparation of the aqueous dispersion of PS/Pd composite particles, the reduction of 4-NP to *p*-aminophenol (4-AP) by $NaBH_4$ in water was chosen as a model reaction, which is conventionally used to test the catalytic activity of noble metal nanoparticles.[39]

It is known that the mixture of 4-NP and $NaBH_4$ has an absorption maximum around 400 nm, due to the formation of 4-nitrophenolate. In Figure 6a, the intensity of this peak was almost unaltered without the addition of catalyst even after one hour, although the concentration of $NaBH_4$ was in large excess compared to 4-NP (C_{NaBH4}:$C_{4\text{-}NP}$ = 100:1). This result indicated the reduction reaction proceeded insignificantly in the absence of catalyst. In contrast, the reduction was initiated immediately when a small amount of PS/Pd composite particles was added, as depicted in Figure 6b. The time-dependent absorption spectra of reaction solution represent a remarkable decrease in intensity of the absorption peak at 400 nm and a simultaneous development of new peak at 300 nm, which is due to the product of 4-AP. Since the concentration of $NaBH_4$ exceeded that of 4-NP greatly, the reduction reaction can be considered as a pseudo-first-order reaction with respect to the concentration of 4-NP. So the apparent rate constant (k_{app}) can be determined by calculating the slope of a linear plot of $\ln(C_0/C_t)$ versus reaction time, as shown in Figure 6c. Therein, the ratio of C_0 and C_t (where C_0 and C_t are the concentration of 4-NP at time 0 and t, respectively) was measured from the relative intensity of respective absorbance at time 0 (A_0) and t (A_t).

Figure 6d depicts the $\ln(C_0/C_t)$ versus reaction time for the reduction of 4-NP catalyzed by different concentrations of PS/Pd composite particles. In all runs discussed here, linear plots of $\ln(C_0/C_t)$ versus reaction time have been obtained. In Figure 6e, the values of k_{app} calculated from Figure 6d were found to increase linearly with the concentration of PS/Pd composite particles present in the system. As reported previously, the linear relationship between k_{app} and catalyst concentration indicated that the catalytic activity of PS/Pd composite particles was unrelated to their concentration used in the system.[40] Nevertheless, the catalytic efficiency was directly proportional to the concentration of catalyst particles. Therefore, it is worth noting that the value of k_{app} (2.1×10^{-3} s^{-1}) is comparable with most of those reported previously, whereas the molar ratio of PdNPs to 4-NP (Pd/4-NP = 2 mol%) is relatively low in this work. For example, reported molar ratios are 3.7, 12, and 26 mol% for PdNPs supported on TiO_2 hollow microsphere, mesoporous SiO_2, and polypyrrole capsule, where the corresponding k_{app} is about 2.7×10^{-3}, 1.6×10^{-3}, 8.87×10^{-3} s^{-1}, respectively.[41-43]

For the practical application, the stability is also an important property for catalyst, besides its catalytic activity. Since catalytic activity of PS/Pd composite particles was independent of their concentration, we can monitor the variation in catalytic activity of them by repeated addition of new 4-NP and $NaBH_4$.[40, 41, 44] Figure 6f displays the plot of conversion versus the number of successive reduction reactions that repeatedly used the PS/Pd composite particles as catalyst. Remarkably, the high conversion (> 95%) was obtained even after running for more than nine cycles. Therefore, the as-prepared PS/Pd composite particles possessed of good stability in the catalytic reaction system.

Conclusions

In summary, we report a facile and effective method for the synthesis of polystyrene/palladium (PS/Pd) composite particles based on a thermodynamic effect. The time-consuming and troublesome surface pretreatments of support microspheres and palladium nanoparticles (PdNPs) are eliminated. Moreover, the size of PdNPs supported on PS microsphere can be controlled easily by varying the molar ratio of $PdCl_2$ and $NaBH_4$ before they are mixed with PS microspheres. In addition, it is of particular importance that the as-prepared PS/Pd composite particles exhibit high catalytic activity and good stability towards the reduction of *p*-nitrophenol by $NaBH_4$. Therefore, the PS/Pd composite particles show great potential for practical applications in catalysis because of their facile synthesis, high activity, and good stability.

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Notes and references

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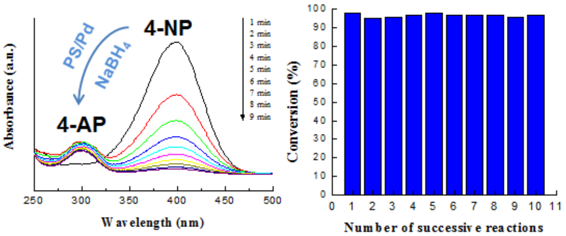

Catalytic activity **Catalytic stability**

Herein we develop a facile and effective strategy for the synthesis of composite particles composed of polystyrene microspheres decorated with palladium nanoparticles, which exhibited excellent catalytic activity and stability towards the reduction of *p*-nitrophenol by $NaBH_4$.