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ARTICLE

Water-soluble metal nanoparticles stabilized by plant polyphenols for improving the catalytic properties in oxidation of alcohols

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Plant polyphenols extracted from plants are one of the most abundant biomasses in nature, which are typical water soluble natural polymers. Herein, we reported a facile approach for the synthesis of platinum nanoparticles (PtNPs) aqueous colloid by utilizing black wattle tannin (BWT, a typical plant polyphenol) as amphiphilic stabilizer. The phenolic hydroxyls of BWT provide the PtNPs with enough hydrophilicity, and their reduction ability could protect the PtNPs from deactivation caused by oxygen atmosphere. Additionally, the hydrophilic nature of BWT could efficiently promote the oxidation of alcohols in water, meanwhile, the hydrophobic and rigid backbones of plant polyphenols are able to suppress the PtNPs from aggregating, thus ensuring the high dispersion of the PtNPs during reactions. Under mild aerobic conditions, the as-prepared BWT-Pt colloid catalyst exhibited high activity in a series of biphasic oxidation of aromatic alcohols and aliphatic alcohols. As for the cycling stability, BWT-Pt catalyst showed no obvious decrease during the 7 cycles, revealing superior cycling stability as compared with the counterparts using PVP or PEG as the stabilizer.

Introduction

Selective oxidation of alcohols to aldehydes plays a crucial role in organic synthesis due to the fact that aldehydes are valuable intermediates and as high-value components for the perfume industry.¹⁻³ Oxidation reactions carried out using various types of transition metallic nanoparticles (MNPs) have attracted much attention, especially in the reactions under mild reaction conditions.⁴⁻⁶ In general, homogeneous MNPs catalysts exhibit high activity during the reactions, but the separation of the catalysts from reaction system is quite difficult, which often leads to poor cycling stability.^{7,8} Heterogeneous MNPs catalysts are more attractive due to easy recycling compare to the homogeneous counterparts.^{9,10} Many types of heterogeneous MNPs catalysts have been designed for oxidation of alcohols with high efficiency.¹¹⁻¹⁴ Unfortunately, the oxidation reactions utilizing heterogeneous MNPs catalysts usually show the lower activity under mild reaction condition, thus often performing in organic solvents and/or under harsh reaction conditions.^{15,16} Ideally, an environmentally benign alternative is needed, which performs the catalytic reactions in water under mild reaction

condition with reusable catalysts.

In response to this, water-soluble MNPs colloid catalysts are suitable potential candidates. The reactions catalyzed by water soluble MNPs could avoid excessive use of harmful organic solvents, and the catalysts can be easily separated from reaction system by simple filtration.^{17,18,19,20} Usually, the MNPs are stabilized by water-soluble organic small molecules or amphiphilic polymers to realize their solubility.²¹⁻²³ The MNPs stabilized by hydrophilic organic small molecules generally suffer from aggregating and leaching due to the limited stability.²⁴ Conversely, amphiphilic polymers with abundant hydrophilic functional groups could stabilize the MNPs efficiently during the reactions. Previous researches have been reported about the aerobic oxidation of some aliphatic and alicyclic alcohols in water with reusable MNPs stabilized by amphiphilic polymers,²⁵⁻²⁸ while the strong interactions between amphiphilic polymers and the NPs may profoundly alter the catalytic properties of the MNPs. Additionally, the synthesis of these amphiphilic polymers required complex synthetic procedures, which also involves the use of toxic organic solvents. Hence, the green strategy to prepare the MNPs colloid catalysts with good water-solubility and reusability by using suitable stabilizer is still deserved in the selective oxidation reaction of alcohols.

Plant polyphenols, typical natural amphiphilic polymers with good water-solubility extracted from plants, are one of the most abundant biomasses in nature. There are large numbers of phenolic hydroxyls in their molecules, which has high affinity to various metal ions, including Fe³⁺, Cr³⁺ and Al³⁺.^{29,30} The reductive phenolic hydroxyls of plant polyphenols not only

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provide the MNPs with good water-solubility, but also could protect the MNPs from deactivation caused by oxygen atmosphere.^{31,32} Furthermore, the hydrophobic and rigid backbones of plant polyphenols are able to prevent the MNPs from aggregating, thus ensuring the high dispersion of the NPs during reactions.^{33,34} As a consequence, it is possible to prepare highly active and recyclable MNPs catalysts by utilizing plant polyphenols as amphiphilic stabilizer.

Herein, black wattle tannin (BWT), a typical plant polyphenol, was used as nature amphiphilic stabilizer to prepare aqueous platinum nanoparticles colloid (BWT-Pt). Compared with the traditional amphiphilic stabilizer, BWT is one kind of green stabilizer obtained from the nature plants. Meanwhile, the phenolic hydroxyls of BWT supply the good water-solubility for PtNPs and protect the PtNPs from deactivation caused by oxygen atmosphere. Notably, the prepared BWT-Pt catalysts were used for aerobic oxidation reaction of alcohols in aqueous media under mild reaction conditions, which exhibits high activity and cycling stability.

Experimental

Synthesis of BWT stabilized Pt nanoparticles

15 mg of BWT was dissolved in 5 ml of deionized water, and then 3 ml of deionized water containing 20 $\mu\text{mol Pt}^{4+}$ was added into the BWT solution. The resultant mixture was stirred constantly for 1 h to allow the sufficient chelating of BWT molecules towards Pt^{4+} via their hydroxyls. Subsequently, the BWT- Pt^{4+} solution was reduced by 2 ml of NaBH_4 (10 mg) solution to obtain the BWT-Pt catalyst. Additionally, BWT-Pt catalysts with BWT content of 2 mg, 5 mg, 10 mg, 30 mg and 60 mg were prepared by using above procedure.

Characterizations

Fourier transform infrared (FT-IR) spectra were recorded with a JASCO FT-IR 480 Plus spectrophotometer. Inductively coupled plasma (ICP) spectroscopy was conducted on a Dual-view Optima 5300 DV ICP-OEM system. Ultraviolet-visible (UV-vis) spectra were obtained with a Shimadzu UV-2501PC. Transmission electron microscope (TEM) images were taken by a JEOL JEM 2010F at an accelerating voltage of 200 kV.

Typical catalytic oxidation of alcohols

In a typical reaction, 1 mmol alcohol was added to a mixture of 5 ml of water and 0.5 mmol K_2CO_3 . Subsequently, 10 ml of the BWT-Pt catalyst solution was added into mixture. The air flow was bubbled at 20 $\text{ml}\cdot\text{min}^{-1}$, controlled by a mass flow meter, into the mixture to initiate the reaction. The mixture was stirred at 50 $^\circ\text{C}$ for 24 h. After reaction, 0.2 mmol dodecane was added as internal standard. The products were extracted twice using 3 ml of diethylether. When the extraction was completed, the biphasic system was allowed to stand, and then, the organic phase was taken out by using syringe, and dried over Na_2SO_4 . The resultant organic phase was analyzed by GC-MS and the obtained aldehyde was determined by GC. The remaining aqueous solution of BWT-Pt was recovered and directly used as catalyst in subsequent cycle of

biphasic reactions. For the analysis of aldehyde, we used GC-MS to analyze the organic phase to confirm the existing of target product of aldehyde. After that, GC was conducted to quantitatively determine the amount of obtained aldehydes by using dodecane as internal standard. To establish the standard curves, different mixtures containing varied molar ratios of aldehyde/dodecane were measured by GC, and the corresponding peak area ratios of aldehyde/dodecane were used as the function of molar ratios of aldehyde/dodecane. During the GC analysis, the peak location of aldehydes products in our samples must perfect match with that of chromatographic grade aldehydes (the standard chemicals) under the same GC conditions, and the content of target aldehyde was calculated according to the standard curves. The conversion yield of obtained aldehyde was calculated based on the use of initial mole of alcohol.

Results and discussion

PtNPs with strong oxidation ability have been demonstrated in the oxidation reaction of alcohols.³⁵ Unfortunately, their efficient reuse has always been hindered in the oxidation of alcohols due to the deactivation by oxygen and aggregation as well as leaching along cycling.³⁶ However, the BWT, a typical plant polyphenol, was employed as nature amphiphilic stabilizer to maintain activity and stability of the PtNPs. In the typical experiment, BWT-Pt was prepared by chelating Pt^{4+} with BWT in aqueous solution, followed by reduction of NaBH_4 (Fig. 1). Two adjacent hydroxyls on the B rings of BWT can act as bidentate ligands to chelate with one Pt^{4+} , giving rise to the formation of a highly stable five-membered chelating ring.³⁷ Subsequently, the chelated Pt^{4+} ions are further reduced by NaBH_4 to form the PtNPs, which is still stabilized by the hydroxyls of BWT via electron donating-accepting interactions.³⁸ Furthermore, the aromatic framework of BWT also prevents the PtNPs from aggregating by providing enough steric hindrance, leading to the formation of highly dispersed PtNPs with small particle size. In this way, the BWT molecules could provide excellent water-solubility as well as stability of the PtNPs.

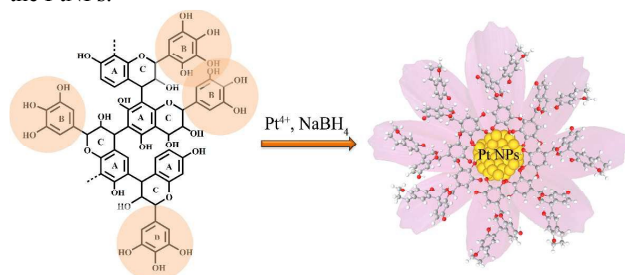


Fig. 1 Schematic illustration showing the preparation of the BWT-Pt catalyst.

In order to further investigate the preparation process of BWT-Pt, the UV-vis spectra, FTIR spectra and XPS analysis were employed to track the whole reaction process. A pure PtCl_6^{2-} solution has a strong adsorption peak at $\lambda_{\text{max}} = 258 \text{ nm}$. After the reaction with BWT, the peak at 258 nm shifts to lower energy, demonstrating the chelating of BWT molecules with Pt^{4+} ions via their phenolic hydroxyls.³⁹ After reduction of the composite, the spectrum shows higher adsorption intensity at low energy and a new adsorption peak

at 282 nm appears, which results from the formation of BWT-PtNPs (Fig. S1). The FTIR spectra of BWT and BWT-Pt (Fig. S1) show that the stretching vibration peak of the phenolic hydroxyls of BWT at 3400 cm^{-1} is narrowed after chelating with the Pt^{4+} ions, which suggests that the PtNPs are stabilized by the phenolic hydroxyls of BWT.⁴⁰ Furthermore, the interactions between Pt and BWT were studied by XPS analysis. The O 1s peak at 532.6 eV (Fig. 2b) belongs to the phenolic hydroxyls of BWT. The O 1s spectrum of BWT-Pt (Fig. 2c) show a major peak at 533.1 eV and a relatively small peak at 531.8 eV, suggesting that a part of phenolic hydroxyls of BWT bind with the Pt nanoparticles.³¹

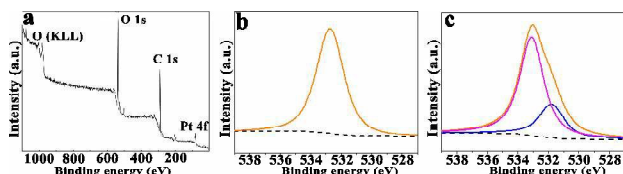


Fig. 2 XPS spectra of BWT and BWT-Pt. (a) XPS spectrum of BWT-Pt, (b) XPS O 1s spectrum of BWT, (c) XPS O 1s spectrum of BWT-Pt.

The morphology and structure identity of BWT-Pt were studied by transmission electron microscopy (TEM) and X-ray diffraction (XRD). BWT-Pt was prepared by using 2 mg, 5 mg, 10 mg and 15 mg of BWT as the stabilizer. The resultant catalysts are denoted as $\text{BWT}_{0.5}\text{-Pt}$, $\text{BWT}_{1.25}\text{-Pt}$, $\text{BWT}_{2.5}\text{-Pt}$ and $\text{BWT}_{3.75}\text{-Pt}$ respectively. As shown in Figure 3, the BWT-Pt nanoparticles prepared with 2 mg, 5 mg and 10 mg BWT suffer serious aggregating, which is alleviated with the increasing of BWT amount to 15 mg. It is a fact that the low content (less than 15 mg) of BWT is unable to effectively prevent the aggregation of PtNPs. In addition, the XRD pattern of $\text{BWT}_{3.75}\text{-Pt}$ (Fig. S2) was also measured, which shows the characteristic peaks of Pt at 40° , 46° and 67° , corresponding to (111), (200) and (220) plane of Pt, respectively. Other catalysts prepared with different content of BWT also show the existing of metallic Pt according to XRD measurements. The XPS spectrum (Fig. 2a) has also confirmed the existence of Pt. Moreover, Fig. 4 displays the TEM images of fresh $\text{BWT}_{3.75}\text{-Pt}$ catalyst and $\text{BWT}_{3.75}\text{-Pt}$ catalyst after 4 cycles of biphasic benzyl alcohol oxidation. The fresh-formed PtNPs have a mean diameter of 1.8 nm, which is highly dispersed without any obvious aggregation. After 4 cycles of biphasic benzyl alcohol oxidation, the average diameter of PtNPs increases slightly from 1.8 nm to 2.5 nm, which is still highly dispersed without any obvious aggregation. These results suggest that the content of BWT around 15 mg is enough for achieving good cycling stability, which is attributed to the steric hindrance provided by the aromatic molecular backbones of BWT. Hence, the small PtNPs with high dispersion in aqueous colloid are expected to exhibit high catalytic activity and cycling stability in the oxidations of alcohols.

To evaluate the catalytic properties of the BWT-Pt catalysts, we conducted the oxidation of a variety of alcohols, including aromatic and aliphatic alcohols. All the reactions were carried out under aerobic conditions, and representative results were summarized in Tab. 1. It should be noted that there are possibilities for catalytic oxidation of alcohols to the over oxidation products of acids. To eliminate the influence of acids on the test of aldehydes, The GC-MS

and GC together were employed to analyze catalysis products. For quantitative determination of obtained aldehyde, dodecane was used as internal standard in the biphasic catalysis. The detailed analysis procedures are showed in experimental sections. The BWT-Pt catalyst was found to be active in oxidation of these alcohols in water solvent. A strong base potassium carbonate is needed for the oxidation to proceed.⁴¹ With the existence of potassium carbonate, the conversion yield of benzyl alcohol over BWT-Pt catalyst could reach 89% while less than 10 % conversion are achieved without the base. Hence, all of the oxidation reactions were performed by the use of potassium carbonate.

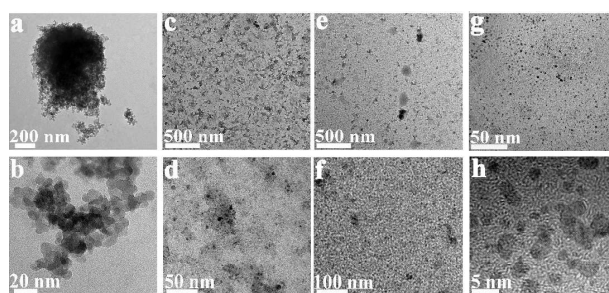


Fig. 3 TEM images of BWT-Pt catalysts with different BWT amount. $\text{BWT}_{0.5}\text{-Pt}$ (a, b), $\text{BWT}_{1.25}\text{-Pt}$ (c, d), $\text{BWT}_{2.5}\text{-Pt}$ (e, f) and $\text{BWT}_{3.75}\text{-Pt}$ (g, h).

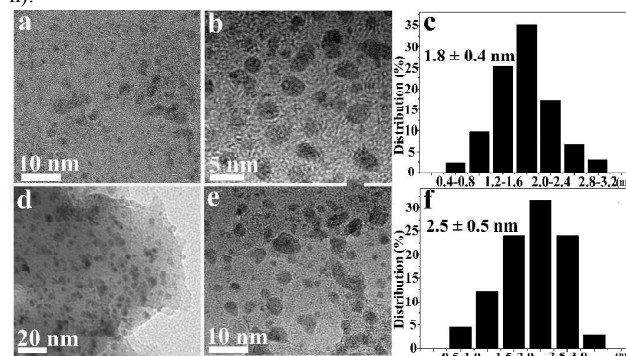
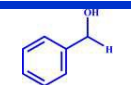
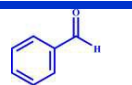
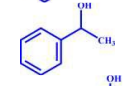
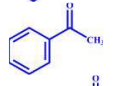
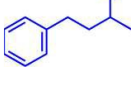
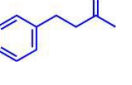
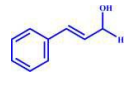
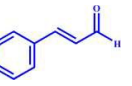
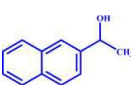
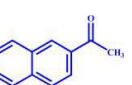
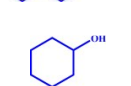
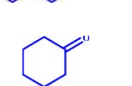

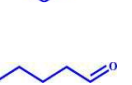




Fig. 4 TEM images, HRTEM images and size distribution(c) of $\text{BWT}_{3.75}\text{-Pt}$ (a-c) and $\text{BWT}_{3.75}\text{-Pt}$ after 4 cycles of biphasic benzyl alcohol oxidation(d-f).

Notably, the reactivity of the aliphatic alcohols is much lower than that of aromatic alcohols. Under the same reaction conditions, the conversion yields of benzyl alcohol and hexanol were 89 % and 36 %, respectively. Meanwhile, the conversion yields of aromatic alcohols with carbon chains of different length were all higher than those of aliphatic alcohols. According to the literature, one reason is probably the strong adsorption of the aromatic moieties on the metal surface.⁴² Another reason is that the benzene rings in the backbones of BWT molecular could absorb the aromatic alcohols by forming hydrophobic bond, which will promote the contacts between the reactant and the PtNPs.⁴³ In addition, the steric hindrance of BWT molecules has shown significant influence on the reactivity of BWT-Pt catalysts in the oxidation of alcohols. For instance, the aromatic alcohols with larger molecule structures have suffered lower conversion yield in the oxidation reactions catalyzed by BWT-Pt. This is because that the steric hindrance of BWT molecules leads to the reactants with large molecular structure more difficult to contact

with the PtNPs. Moreover, the conversion of benzyl alcohol decreased from 89 % to 31 % when the content of BWT within the BWT-Pt catalysts increased from 15 mg to 60 mg (Fig. S3). A higher content of BWT may enhance the steric hindrance and restrict accesses of substrates to PtNPs surface due to the increase of intermolecular interactions within BWT molecules. Thus, the dosage of BWT should be controlled in a proper range to ensure the reactivity and stability of BWT-Pt catalysts. In other words, the accessible area of noble nanoparticles is responsible for the activity of catalyst. Usually, N₂ adsorption-desorption can be used to characterize the accessibility. However, the BWT-Pt is colloid solution, which is impossible for the measurement of specific surface area because this measurement requires that the catalyst is solid. We also found that the cyclohexanol, a kind of alicyclic alcohols, could be catalyzed by BWT-Pt to produce the corresponding cyclohexanone with the yield of 47%. The corresponding activity is appreciable compared with other reported catalysts.⁴⁴ The catalytic reactivity of BWT-Pt in the oxidation of non-activated alicyclic alcohols can attributed to the amphiphilic nature of the BWT, which decrease the interfacial resistance between the aqueous catalyst and organic substrates.³⁸ As control, the oxidation of benzyl alcohol was carried out just utilizing BWT as catalyst, which exhibited no catalytic reactivity under the same experimental conditions, thus demonstrating that the catalytic activity of BWT-Pt was completely derived from the PtNPs.

Tab. 1 The catalytic activity of BWT-Pt in oxidation of alcohols in aqueous solution.

Substrates	Products	Yield (%)	Time (hour)
		89	24
		82	24
		45	24
		59	24
		38	24
		47	24
		12	24
		36	24

* Reaction conditions: 1mmol of alcohol, catalyst contains 20 μmol of Pt and 15 mg of BWT, 15 ml of water, 0.5 mmol of K₂CO₃, 50 °C.

The BWT-Pt catalysts with good cycling stability were demonstrated in the catalytic oxidation of alcohols. Three typical alcohols were utilized as substrates to study the cycling stability of

BWT-Pt, including benzyl alcohol, cyclohexanol and hexanol. As shown in Fig. 5, the conversion of the three kinds of alcohols catalyzed by BWT-Pt catalysts show no significant decrease during the 7 reaction cycles, revealing high cycling stability of the catalysts. However, the decrease in reactivity of MNPs catalysts during the cyclic reaction were a common phenomenon due to the leaching and aggregating of metal NPs.^{9,17} The leached Pt is negligible by ICP-AES analysis and PtNPs still exhibit good dispersion without obvious aggregation in TEM analysis (Fig. 4d, e, f) after 4 reaction cycles, suggesting that the leaching and aggregation of PtNPs have been effectively suppressed due to the good stabilization of BWT toward PtNPs.

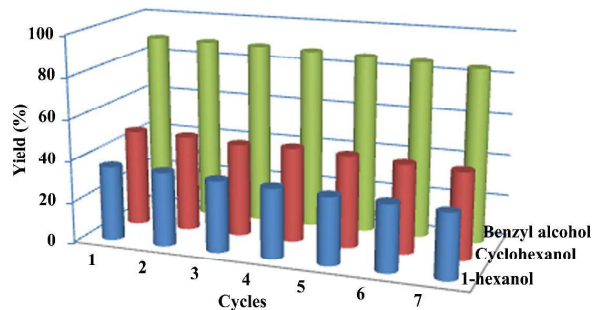


Fig. 5 Cycling stability of BWT in oxidation of alcohols. Reaction conditions: 1 mmol of alcohol, catalyst contains 20 μmol of Pt and 15 mg of BWT, 15 ml of water, 0.5 mmol of K₂CO₃, 50 °C, 24 hours.

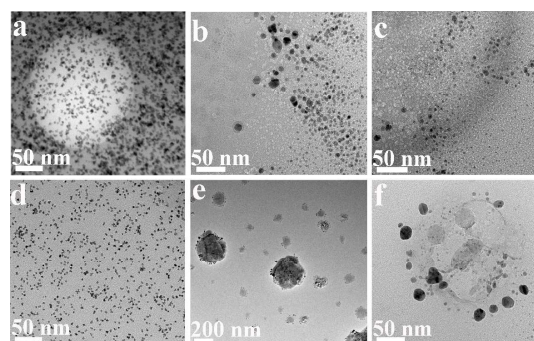
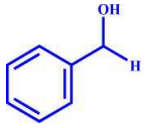


Fig. 6 TEM images of fresh PVP-Pt(a) and PEG-Pt(d) catalysts and TEM images of PVP-Pt(b, c) and PEG-Pt(e, f) catalysts after 4 cycles of biphasic benzyl alcohol oxidation.

To further demonstrate the advantages of BWT as high efficient stabilizer of PtNPs, PVP and PEG were also as stabilizers to prepare PtNPs colloid catalysts. As shown in Fig. 6, fresh PVP-PtNPs and PEG-PtNPs have average particle size of 4.0 and 3.5 nm, respectively. The PVP-PtNPs and PEG-PtNPs exhibit quite poor cycling stability. As shown in Tab. 2, the yield of benzaldehyde over PVP-PtNPs and PEG-PtNPs in oxidation of benzyl alcohol are decreased from 46.1 % (1st cycle) to 19.9 % (4th cycle) and 38.6 % (1st cycle) to 15.3 % (4th cycle), respectively. Probably, PVP and PEG just cover up the Pt surfaces, and thus, the stabilization to Pt NPs is weak, which leads to the aggregation and leaching of Pt NPs during cycling. These assumptions are confirmed by the ICP measurements and TEM observations. Based on ICP measurements, 6.3 % and 8.1 % of Pt are leached into the organic phase after 1st cycle of benzyl alcohol oxidation using PVP-PtNPs and PEG-PtNPs as the catalysts, respectively. Although the fresh PVP-PtNPs and

PEG-PtNPs have good dispersion, these particles tend to aggregate together after repeated 4 cycles of catalytic reaction. As shown in Fig. 6b-c, the size most of PVP-PtNPs is increased to 15 nm after 4 cycles, and the wide particle size distribution of PVP-PtNPs is also observed owing to the aggregation of PVP-PtNPs. For PEG-PtNPs (Fig. 6e-f), more serious aggregation of PtNPs is observed, of which the particle size can even reach 500 nm. On the contrary, the BWT-Pt catalyst exhibits much higher stability, which exhibits 30.5 % yield of benzaldehyde in 4th cycle. These results strongly verify that the BWT as stabilizer is essence for achieving high activity and stability for biphasic oxidation of alcohol. For BWT-Pt, the recovery of catalyst inevitably leads to some loss of activity, which could be responsible for the observed activity loss in Tab. 2.

Tab. 2 Cycling stability of BWT-Pt, PVP-Pt and PEG-Pt as catalysts in biphasic benzyl alcohol oxidation.

Yield (%)	cycles	1	2	3	4
	BWT-Pt	36.5	34.7	33.2	30.5
	PVP-Pt	46.1	32.9	25.6	19.9
	PEG-Pt	38.6	29.8	20.4	15.3

Reaction conditions: 1 mmol of alcohol, catalyst contains 20 μ mol of Pt and 15 mg of stabilizer, 15 ml of water, 0.5 mmol of K_2CO_3 , 50 $^{\circ}C$, 10 hours.

We can simply mix the Au^{3+} solution with BWT solution together to get the BWT-AuNPs colloid solutions. As shown in Fig. S4, the synthesized Au nanoparticles colloid solution is dark red, and the surface plasmon resonance (SPR) peak of Au NP is clearly observed at 535 nm in the UV-vis spectra of BWT-AuNPs.^{45,46}

Conclusions

In conclusion, a facile strategy was developed to synthesize PtNPs aqueous colloid by utilizing natural plant polyphenols as amphiphilic stabilizer. The as-prepared BWT-Pt catalysts feature to small particle size and well dispersity due to the stabilization effect of BWT derived from its unique molecular structure. Under mild aerobic conditions, the BWT-Pt catalysts exhibited high activity and cycling stability in the oxidation of aromatic alcohols and aliphatic alcohols. Additionally, the amphiphilic nature of BWT could efficiently promote the oxidation of alcohols in water. The experimental results suggest that the hydroxyls in the BWT play critical role in stabilizing the PtNPs, which also prevent the Pt NPs from aggregating and leaching during the reactions.

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†Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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