Supporting Information

Soluble amphiphilic tannin-stabilized Pd(0) nanoparticles: highly active and selective homogeneous catalyst used in biphasic catalytic system

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Supporting Information 1(S1). Schematic diagram of molecular sctructure of bayberry tannin (BT).

As shown in S1, BT consists of flavan-3-ols and flavan-3-ols gallate, and has a large number of adjacent phenolic hydroxyls in its B-rings, which are able to chelate with many metal ions by the formation of a five-membered chelate ring. On the other hand, BT is able to form hydrophobic bonds with hydrophobic compounds via the bend folding of its aromatic backbone.



S2. Schematic illustration showing the formation of BT-Pd(0).

S3. Preparation of BT-stabilized Pd(0) nanoparticles

10 mL of PdCl₂ solution [1.0 gPd(II)/L] was mixed with 35 mL of BT solution at different concentrations. After magnetic stirring for 20 min, 5 mL of 1.0 mmol/L NaBH₄ solution was drop-wise added into the above mixture to reduce Pd(II) ions within 3.0 h, and the reduction process was kept at room temperature for another 6.0 h. Finally, a series of BT_x- Pd(0) were prepared, where *x* is the mass ratio of BT/Pd varying from 2.5 to 150, and the concentration of Pd(II) is fixed at 200 mg/L.



S4. UV-Vis spectra of a) PdCl₂, b) BT-Pd(II), c) BT-Pd(0).





The FTIR spectrum of BT is shown in S5a. The peak at 3400 cm⁻¹ can be attributed to the stretching vibration of phenolic hydroxyls (O-H bond) in tannin, and its broad range is due to the formation of hydrogen bonds with water molecules. The peaks in the vicinity of 1620–1450cm⁻¹ (1610, 1510, and 1470 cm⁻¹) indicate the presence of aromatic rings of tannin. The absorption peak at 1380 cm⁻¹ arises from the inplane deformation of phenolic hydroxyls (O-H bond). (C.W. Oo, M.J. Kassim, A. Pizzi, Ind. Crop. Prod. 2009, 30, 152; Y. Nakano, K. Takeshita, T. Tsutsumi, Water Res. 2001, 35, 496.)

After reaction of BT and Pd(II), the stretching vibration of phenolic hydroxyls (O-H bond) shows a red shift, from 3400 cm⁻¹ to 3200 cm⁻¹, and the inplane deformation of phenolic hydroxyls (1380 cm⁻¹) nearly disappears, as shown in S5b. These changes suggest that the phenolic hydroxyls of BT have chelated with Pd(II).



S6. a) XPS Pd 3d spectra of $BT_{12.5}$ -Pd(0), b) XPS O 1s spectra of BT, c) XPS O 1s spectra of $BT_{12.5}$ -Pd(II), and d) XPS O 1s spectra of $BT_{12.5}$ -Pd(0).

In S6a, the Pd 3d spectra located at 335.5 eV and 341.1 eV indicate the complete reduction of $BT_{12.5}$ -Pd(II) to $BT_{12.5}$ -Pd(0). In S6b, the O 1s peak at 532.6 eV belongs to the phenolic hydroxyls of BT while this peak moves up to 532.9 eV (Figure 6c) due to the coordination of Pd(II) with phenolic hydroxyls of BT. After reduction, the O 1s spectra of $BT_{12.5}$ -Pd(0) show a major peak at 532.2 eV and two relatively small peaks at 533.3 eV and 536.6 eV, respectively. The major peak at 532.2 eV should belong to the phenolic hydroxyls of BT reverted from "C-O-Pd(II)", while the peak at 533.3 eV should be attributed to "C-O-Pd(0)" structure, which suggests that a part of phenolic hydroxyls of BT still bind with the Pd(0) nanoparticles. In addition, the small peak at 536.6 eV is derived from the water remained in the samples.



S7. GC spectra of organic phase (a) and aqueous phase (b)

after the hydrogenation is completed in biphasic system.



S8. TEM image of BT₁₀₀-Pd(0) (a) and the corresponding histogram of size distribution (b).



S9. TEM images of commercial catalysts 3%Pd(0)-C (a) and 1%Pd(0)-SiO₂ (b).

Recycle	Average TOF(mol/mol.min)	Conversion yield (%)
1	6.2	99.5
2	6.1	98.1
3	6.3	99.9
4	5.9	94.7
5	5.0	80.4

S10. Activity of the catalyst during its recycling.^a

^a Catalyst/substrate, 20.0 µmol/2.5 mmol; Solvent, ethyl acetate; Pressure, 2.0 MPa; Temperature,

50 $^{\rm o}C$; Reaction time, 20.0 min; Selectivity to the corresponding aniline is higher than 99.5% measured by GC-MS.