Supporting information

Highly stable and active palladium nanoparticles supported on porous carbons for practical catalytic applications†

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A. Experimental

A1. Chemicals

Phloroglucinol (99.98%, Acros), formaldehyde (37% in water, Acros), HCl (37% Acros), triblock copolymer Pluronic F-127 ($EO_{106}PO_{70}EO_{106}$, Mw = 12,600, Sigma-Aldrich), ethanol (C_2H_5OH, 99%), palladium(II) acetylacetonate ($Pd(acac)_2$, 96%, Sigma-Aldrich) and 4-nitrophenol (Sigma-Aldrich) were obtained commercially and used without further purification. A 0.05 M acetate (HAc + NaAc; pH 5.0) buffer solution was the supporting electrolyte during analysis. A conventional three-electrode cell system with modified glassy carbon electrode (GCE) as the working electrode, Ag/AgCl (in saturated KCl) as the reference electrode, and a platinum wire as the counter electrode were used. All other chemicals used were analytical grade and all solutions were prepared by using ultrapure water (Millipore).

A2. Characterization techniques

All powdered X-ray diffraction (XRD) patterns were recorded on a PANalytical (X'Pert PRO) diffractometer using CuKα radiation (λ = 0.1541 nm). Nitrogen porosimetry measurements were carried out by Quantachrome Autosorb-1 volumetric adsorption analyzer at -196 °C (77 K). Prior to the measurements, the sample was purged with flowing N_2 at 150 °C for at least 12 h. All pore size distribution profiles were derived from the adsorption branches of isotherms using the Barrett–Joyner–Halanda (BJH) method. The morphology of the sample was observed by field emission-transmission electron microscopy (FE-TEM). All TEM images were obtained at room temperature (RT, 25 °C) using an electron microscope (JEOL JEM-2100F) that has a field-emission gun at an acceleration voltage of 200 kV. The histogram for metal particle size distribution were determined by counting more than

70 NPs in the FE-TEM profile. Detailed composition characterization of the Pd/CPM composites was carried out with energy-dispersive X-ray (EDX) analysis (equipped along with the FE-TEM apparatus). Thermogravimetric analyses (TGA) were performed on a Netzsch TG-209 instrument under air atmosphere. UV-Vis absorption spectral measurements were carried out with a SPECORDS100 diode-array spectrophotometer. Room-temperature FT-IR spectra were recorded on a Bruker IFS28 FT-IR spectrometer over the region of 4000–400 cm^{-1} (spectral resolution $\pm$ 2 cm^{-1}) with a dry KBr pellet. The Raman data of the as-synthesized CPMs were recorded on a Jobin Yvon T64000 Spectrometer equipped with a charge coupled device (CCD) detector cooled with liquid nitrogen. The backscattering signal was collected with a microscope using an Ar^+ laser centered at 488 nm as the excitation source. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) studies were performed by using a CHI 900 electrochemical analyzer (CH instruments).

A3. Synthesis of the Pd/CPM catalyst

As illustrated in **Scheme 1** (see main text), carbon porous materials (CPMs) were synthesized by carbonization of nanostructured polymeric composites, which were obtained by self-assembly of triblock copolymer (Pluronic F127) and phenolic resin (phloroglucinol-formaldehyde) under acidic conditions *via* a soft-template method.[1,2] Typically, 3.3 g of phloroglucinol and 2.4 g of Pluronic F127 were dissolved in 4.5 mL of C_2H_5OH and 4.5 mL H_2O under constant stirring at 15-20 °C. Upon complete dissolution of the mixture, 4.5 mL of 3.0 M HCl was slowly added till the appearance of light pink color at the bottom of the vessel, followed by dropwise addistion of 3.39 g of formaldehyde (37% in H_2O) onto the above solution. After stirring for about 30-40 min at RT, the clear mixture turned turbid, indicating the formation of phloroglucinol-formaldehyde-F127 nanocomposite, and phase-separated

spontaneously. The light yellow polymer phase was centrifuged at 3500 rpm for ca. 10 min, while the ethanol and water discarded. Subsequently, the polymer composite was dissolved in desiable amount of Pd(acac)$_2$ (16.5 mg for 0.5 wt% loading; 33.0 mg for 1.0 wt% loading) in 5 mL tetrahydrofuran (THF) to get the clear orange color solution. The gel was then loaded on a large Petri dish, dried at RT overnight, then cured at 353 K (typically for 2 h) and then subjected to microwave irradiation (MW power: 300W, 2-3 h,), followed by curing (at 393 K overnight). Carbonization was carried out under N$_2$ atmosphere in a horizontal quartz tube furnace first at 673 K for 2 h with a heating rate of 1 K min^{-1}, then at 1123 K for 3 h with a heating rate of 5 K min^{-1}. After carbonization, a natural cooling process was performed. The obtained materials was labeled as Pd/CPM-1 and Pd/CPM-2, corresponding to a Pd loading of 0.5 and 1.0 wt%, respectively.
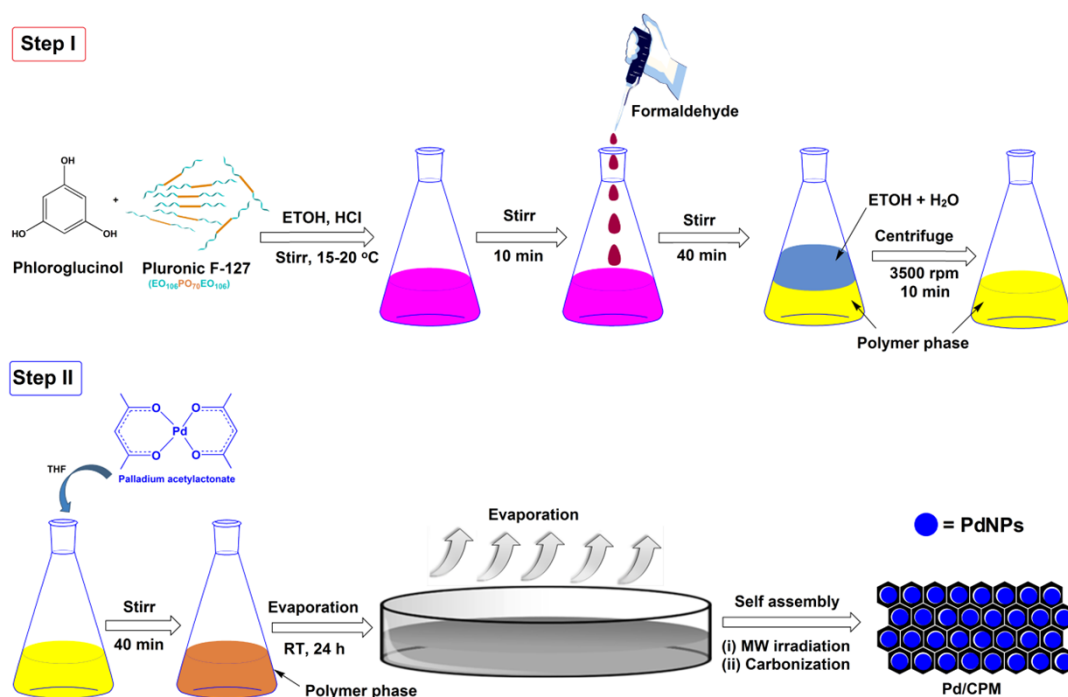

Fig. S1   Schematic illustrations of synthesis procedures of Pd/CPM catalysts by microwave-assisted method.
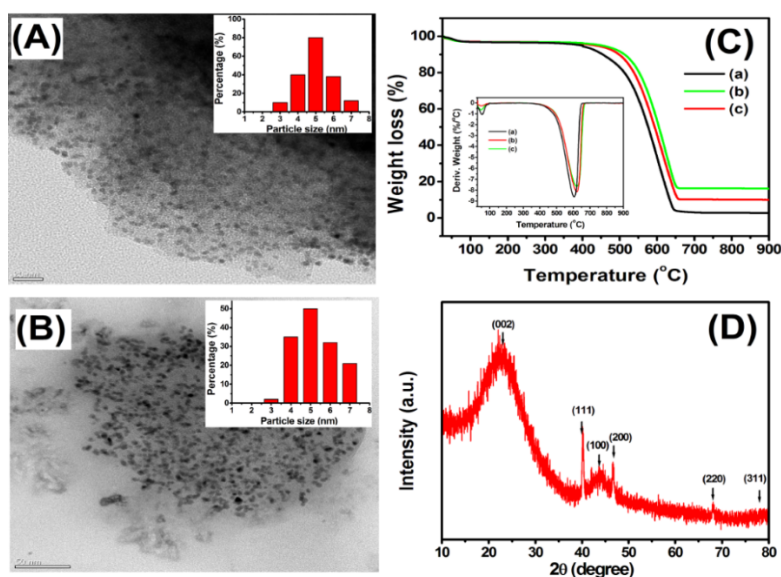
Fig. S2 FE-TEM images of (A) fresh and (B) recycled spent Pd/CPM-2 catalyst. (C) TGA curves of (a) pristine CPM (b) Pd/CPM-1, and (c) Pd/CPM-2 samples recorded under air atmosphere. (D) XRD pattern of the spent Pd/CPM-2 catalyst. Insets in (A) and (B) are histograms revealing the particle size distributions of PdNPs. Inset in (C) show the corresponding DTG curves.

B. Catalytic Reduction of 4-NP

Typically, the reduction reaction was carried out by mixing 100 mL aqueous solution of 4-NP (1×10^{-4} M) with $NaBH_4$ (1.3 M) as the reducing agent. The reacting suspension (4-NP + $NaBH_4$) was kept at a desirable temperature using a water bath (< 10 ^{o}C) under continuous stirring condition, forming the 4-nitrophenolate ion (4-Nip). To the mixture, ca. 2 mg of Pd/CPM catalyst was added and stirred at RT, which was designated as the initial induction period of the reaction (t_o). The disapearance of 4-Nip (dark yellow color) and subsequent formation of 4-aminophenol (4-NP) were monitored by using a UV-Vis spectrophotometer. This is accomplished by withdrawing 2 mL of the reaction mixture at a time interval of 2 s during the reaction process. The solid suspension was separated from the solution by centrifugation and reused. As shown in **Fig. S3**, while the light yellow 4-NP reactant exhibits a strong UV-Vis absorption peak at 318 nm , an increase in alkalinity is anticipated after the addition of $NaBH_4$, forming 4-Nip (dark yellow), which shows a new absorption band at 400 nm.[3,4] Subsequently, the 4-Nip is further catalyzed by the Pd/CPM catalyst to form 4-aminophenol (4-AP), whcich gives rise to an absorption band at 300 nm.
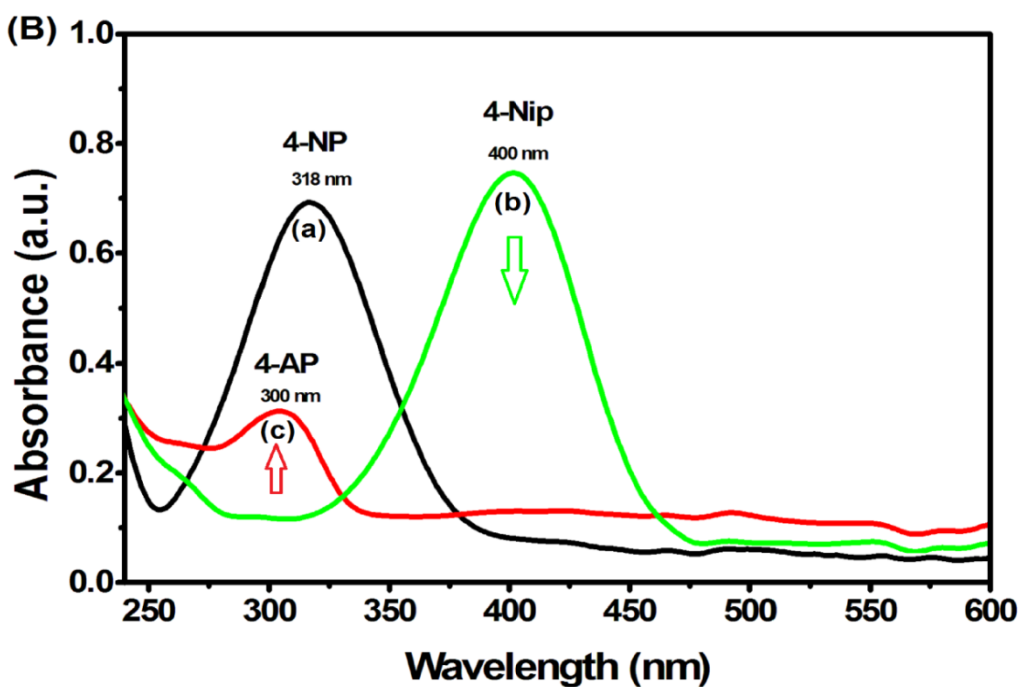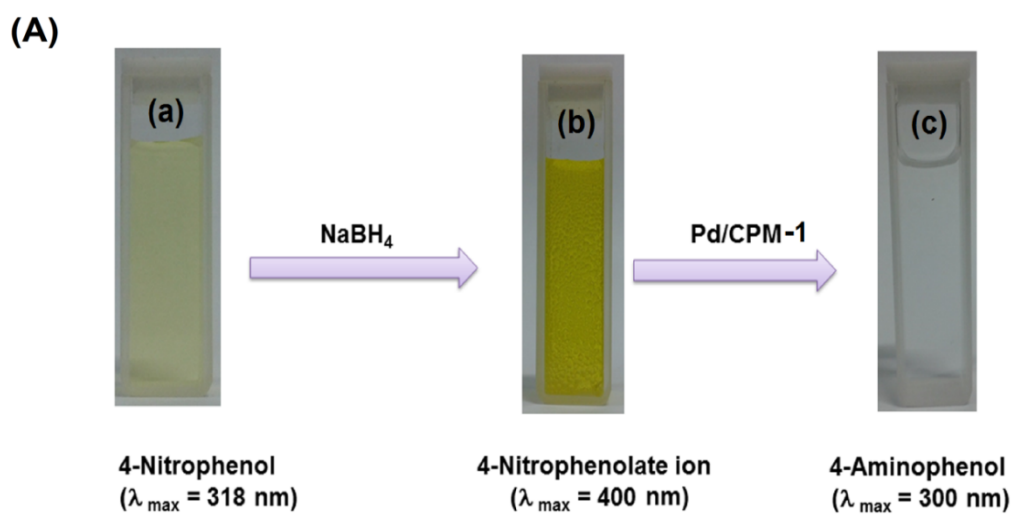
(A)

4-Nitrophenol
(λ_{max} = 318 nm)

4-Nitrophenolate ion
(λ_{max} = 400 nm)

4-Aminophenol
(λ_{max} = 300 nm)

(B)

Fig. S3 (A) Catalytic reduction of 4-NP to 4-AP. (B) UV-Vis spectra of (a) 4-NP, (b) 4-Nip, and (c) 4-AP.

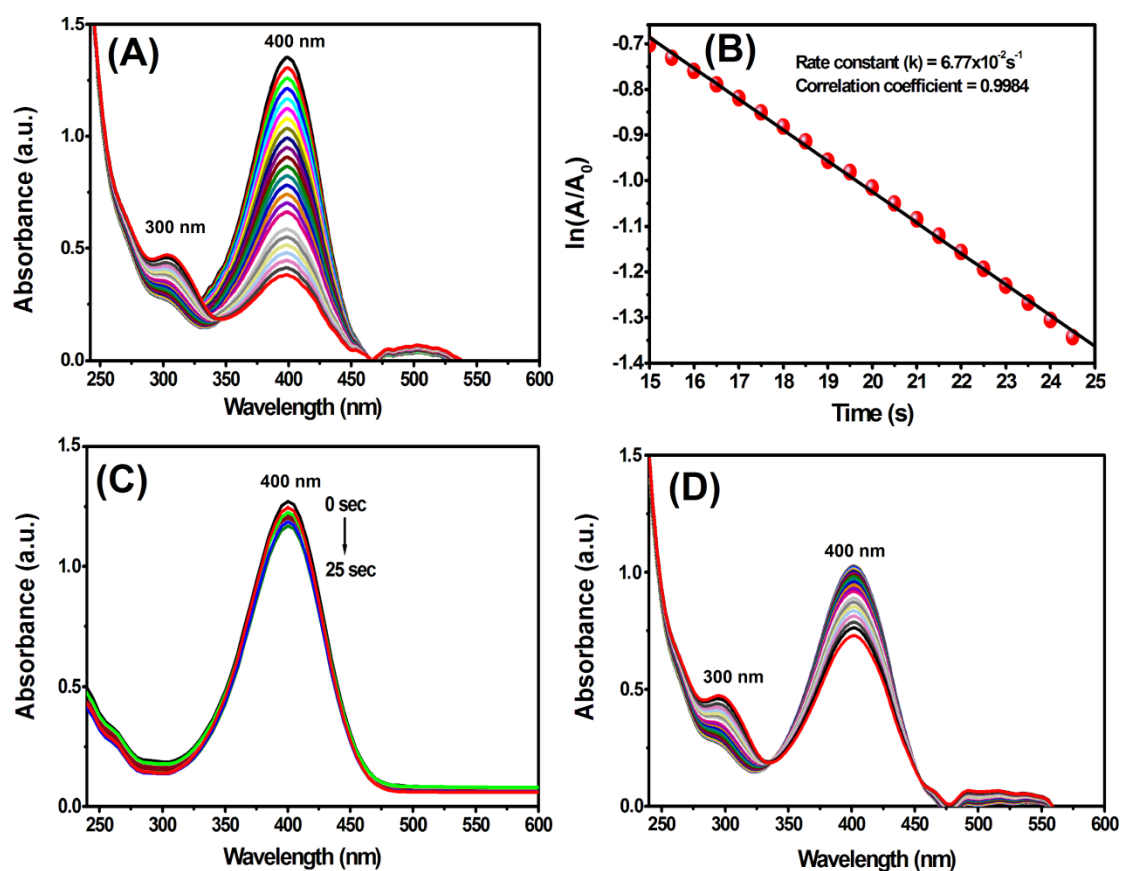## C. Catalytic Reduction of 4-NP over Pd/CPM-2

Fig. S4 (A) UV-Vis spectra obtained from successive reduction of 4-Nip (aqueous 4-NP in NaBH$_4$ solution; 25 cycles; time interval 2s) over the Pd/CPM-2 catalyst, leading to (B) a linear decrease in absorption peak intensity with increasing reaction time. UV-Vis spectra of 4-Nip (aqueous 4-NP in NaBH$_4$ solution) (C) before and D) after introduction of the Pd/CPM-2 catalyst over a reaction time of 25 s.

D. Catalytic Performances of Pd/CPM Catalysts during Suzuki-Miyaura Coupling Reactions

Aryl halide (1.0 mmol), phenyl boronic acid (1.2 mmol), K_2CO_3 (1.5 mmol), and 5 mg of Pd/CPM-2 catalyst were added to 5 mL of aqueous dimethylformamide (DMF : H_2O = 1 : 1) in a 10 mL thick-walled glass tube equipped with a pressure sensor and a magnetic stirrer. The reaction tube was then placed inside the cavity of a focused microwave (MW) synthesis system (Discover series, CEM GmbH) operating at 100 °C with a power of 300 W for 10-15 min. The catalyst wsa reused after separating the product from the reaction mixture.

Table S1 Catalytic performances of Pd/CPM catalyst during Suzuki-Miyaura reaction of aryl halides[a]

Entry	Reactant	Product	Time (min)	Product yield (%)[b]	
				Pd/CPM-1	Pd/CPM-2
1	Ph-Cl	Ph-Ph	15	82	88
2	Ph-Br	Ph-Ph	15	90	95
3	Ph-I	Ph-Ph	10	96	99

[a]Reaction conditions: catalyst (5 mg), aryl halide (1.0 mmol), phenylboronic acid (1.2 mmol), K_2CO_3 (2 mmol), and DMF : H_2O = 1 : 1 (5 mL) were stirred at 100 °C for 10–15 min under MW irradiation. [b] Product yields were determined by using GC. The Pd/CPM-1 and Pd/CPM-2 catalysts contain 0.5 and 1.0 wt% Pd, respectively.

Table S2 Effect of catalyst amount on screening of the C-C coupling reactions over the Pd/CPM-2 catalyst[a]

Entry	Catalyst (mg)	Product yield (%)[b]		
		Ph-Cl	Ph-Br	Ph-I
1	2.5	76	80	85
2	5.0	88	95	99
3	7.5	88	96	99

[a]Reaction conditions: catalyst (Pd/CPM-2), aryl halide (1.0 mmol), phenylboronic acid (1.2 mmol), K_2CO_3 (2 mmol), and DMF : H_2O = 1 : 1 (5 mL) were stirred at 100 °C for 10–15 min under MW irradiation. [b] Product yields were determined by using GC.

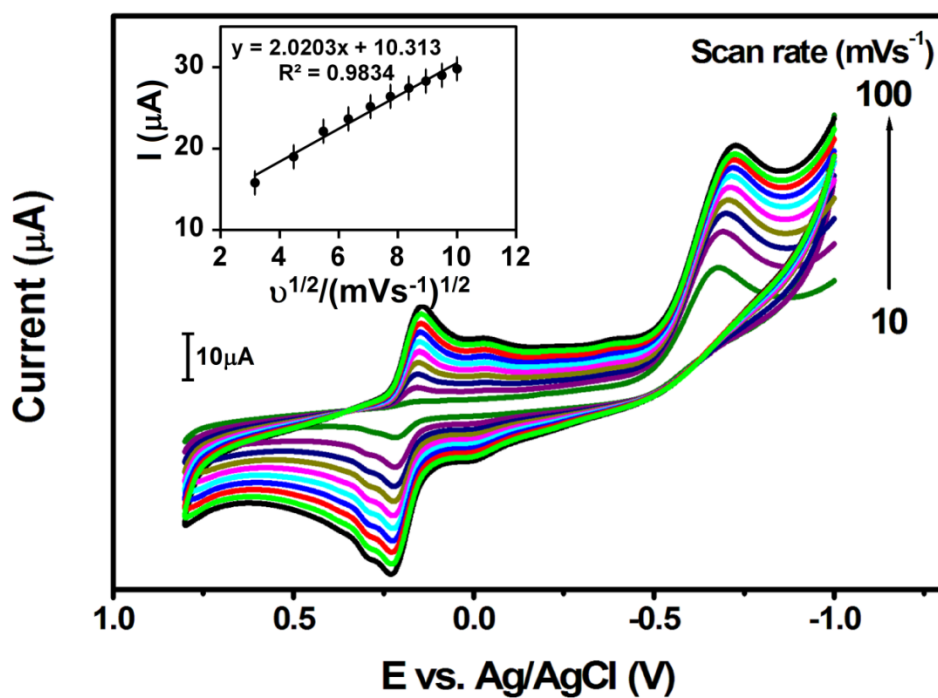# E. Detection of 4-NP over Pd/CPM-1 modified GCE

Fig. S5   CV curves of Pd/CPM-1 modified GCE in the presence of 0.3 mM 4-NP in 0.05 M acetate buffer solution (pH 5.0) recorded at different scan rates ranging from 10 to 100 mV s^{-1}. Inset: Linear correlation between peak current and square root of scan rate.

Table S3   Performance of Pd/CPM-1 modified GCE for detection of 4-NP in real samples

Sample	Analyte	Amount (μM)		Recovery (%)
		Introduced	**Detected**	
Tap water	4-NP	50	49.2	98.4
		100	102.4	102.4
Lake water	4-NP	50	48.9	97.8
		100	100.5	100.5

F. References

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