Electronic Supplementary Information (ESI)

Simple and Direct Synthesis of Oxygenous Carbon Supported Palladium Nanoparticles with High Catalytic Activity

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Experimental Section

Preparation for Pd/C: One hundred microliter of H_2PdCl_4 (56.4 mM) aqueous solution was mixed with 1 mL of ethylene glycol. This mixture solution was quickly poured onto 2.5 g P_2O_5 in 25 mL beaker. (*Carefully handle the beaker to avoid burn hurt because the reaction temperature suddenly increases up to 198 °C!*) The reaction mixture was quickly carbonized by the spontaneous heat, then naturally cooled down to room temperature. The product of Pd/C in the black mixture was dispersed in water with the aid of ultrasonication, and thoroughly washed with water to remove the soluble byproduct of phosphoric acid by filtering through 220 nm filter membrane, followed by collecting and dispersing them in water for further characterizations and catalytic tests. The synthesis procedure of Pt/C and Au/C were exactly same with that of Pd/C, except for using 100 μL of H_2PtCl_4 (19.2 mM) and $HAuCl_4$ (24.3 mM) as the metal precursor, respectively.

Catalytic Reduction of 4-Nitrophenol: For the 4-nitrophenol degradation experiment at 25 °C, 1 mL of $NaBH_4$ (1.2 M) solution, 1 mL of 4-nitrophenol (5 mM) solution and 1 mL of water were homogenously mixed and injected into a beaker. Then, 10 μL (containing one fold of Pd dosage) of as-prepare Pd/C dispersion (0.72 mM of Pd) was quickly injected into the beaker to start the reaction. For the control experiments, the commercial Pd/C catalyst was dispersed in water (containing 7.2

mM Pd). Then 1 μL (1 fold of Pd dosage) or 50 μL (50 fold of Pd dosage) were added. The intensity of the absorption peak at 400 nm was monitored by UV-vis spectroscopy by taking out a portion of 100 μL mixture solution and quickly diluted to 1 mL. This step is to minimize the affection of bubbles for the UV-vis measurement as well as avoid the exceeding measurement range of the concentrated 4-nitrophenol. The lower concentration of 4-nitrophenol will lead to very quick degradation beyond the successive UV-vis measurement. For multiple rounds of the reaction (successive reactions), the spectrophotometer cell was directly used as the reaction container. One microliter of as-prepared Pd/C (0.72 mM of Pd concentration) was first injected to 3 mL of water with stirring. For each new round 4.5 mg of $NaBH_4$ powder and 10 μL of 4-nitrophenol (5 mM) were added under the vigorous stirring when the previous round of reaction was finished. For the continuous flow degradation of the 4-nitrophenol (Figure S8), the as-prepared Pd/C that barred by the filter membrane was directly used. Crude Pd/C (containing 76.4 μg Pd) was barred and washed by the filter membrane. Then a thin layer of the silica gel was lay on the Pd/C to prevent from disturbance of the solution shaking. Finally, 100 mL of 1 mM 4-nitrophenol containing 0.2 g $NaBH_4$ was slowly adding into the filter head, followed by vacuum filtering for about 45 min.

Characterization: A drop of the Pd/C aqueous dispersion solution was carefully placed on the copper grid and dried at ambient condition for transmission electron microscopy (TEM) characterization. TEM and high-resolution TEM (HRTEM) equipped with electron dispersive X-ray spectrometry (EDX) were performed on Tecnai G_2 (FEI) instrument with an accelerating voltage of 200 kV. Scanning electron microscopy (SEM) was conducted using an XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 15 kV. X-ray powder diffraction (XRD) experiments were carried out by using a D/MAX 2500V/PC X-ray diffractometer using Cu (40 kV, 40 mA) radiatio. Infrared spectra were collected on a VERTEX Fourier transform infrared (FT-IR) spectrometer (Bruker). Surface enhanced Raman scattering (SERS) spectra were obtained by using a Renishaw 2000 (Renishaw Co., United Kingdom) equipped by Ar^+ ion laser giving the excitation line of 514.5 nm with the laser spot diameter of 1.6 μm and air cooling charge coupled device (CCD) as the detector.

Figures

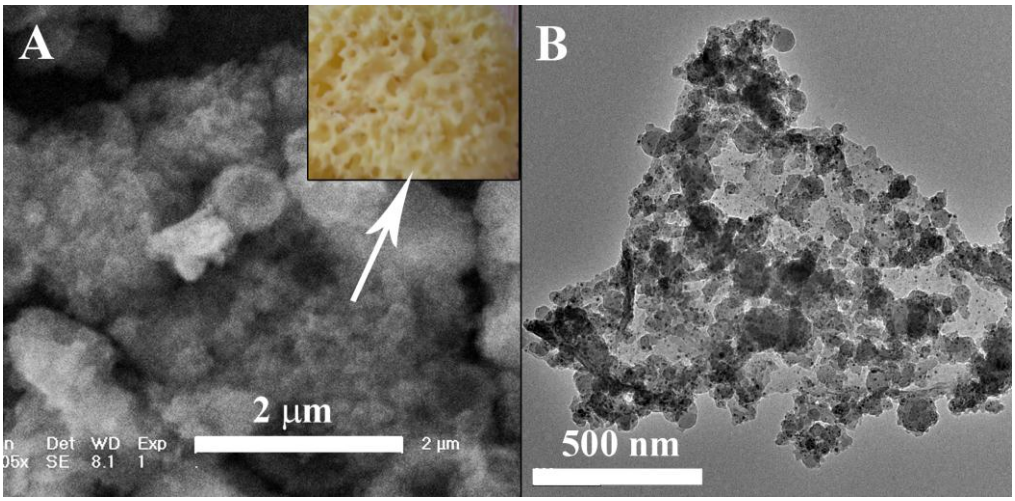

Figure S1. (A) SEM image of Pd/C. Inset: an optical picture of the household sponge. (B) TEM image of Pd/C at low magnification.

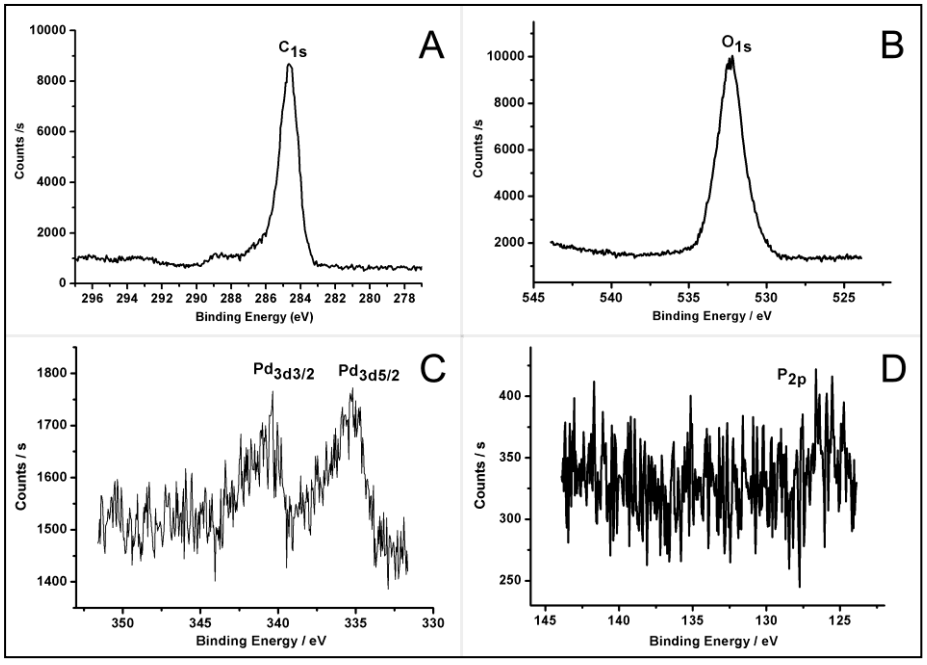

Figure S2. XPS spectra of the as-prepared Pd/C: A) C 1s, B) O 1s, C) Pd 3d, D) P 2p.

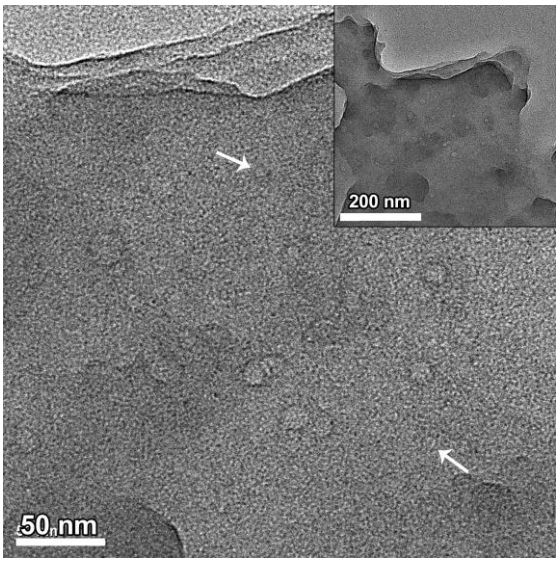

Figure S3. TEM images of the Pd/C after removing the Pd NPs at different magnifications. Some unconspicuous hollows are pointed out by arrows.

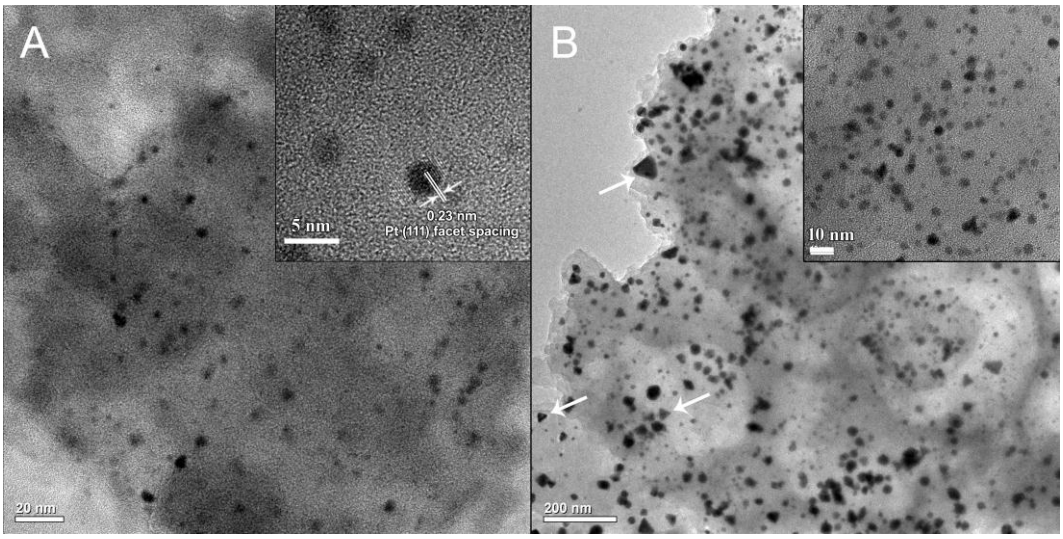

Figure S4. (A) TEM images of Pt/C at different magnifications. Note that the Pt (111) facet spacing was confirmed. (B) TEM images of Au/C at different magnifications. Some Au triangle plates were obtained (arrows).

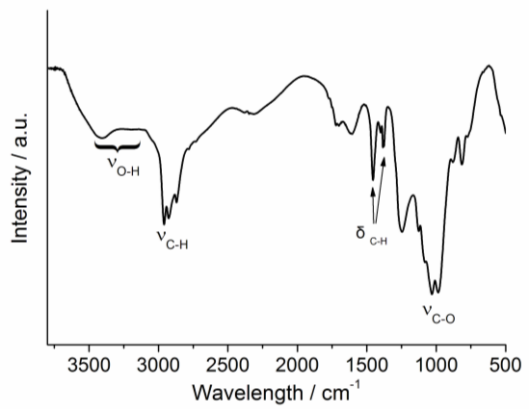

Figure S5. Fourier transform infrared spectrum of the carbonaceous supporter without the Pd NPs.

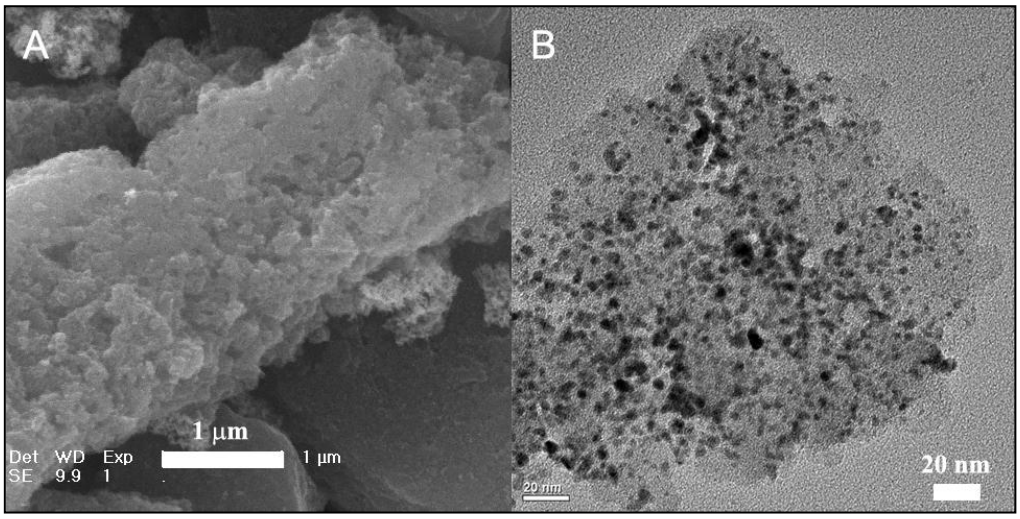

Figure S6. SEM (A) and TEM (B) image of commercial Pd/C catalyst (E-tek).

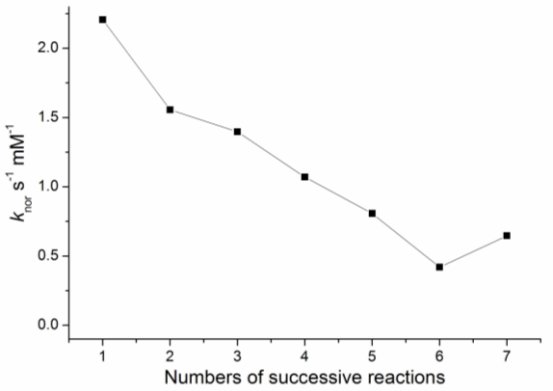

Figure S7. Plots of k_{nor} against the number of successive reduction reactions that employed the as-prepared Pd/C as the catalysts.

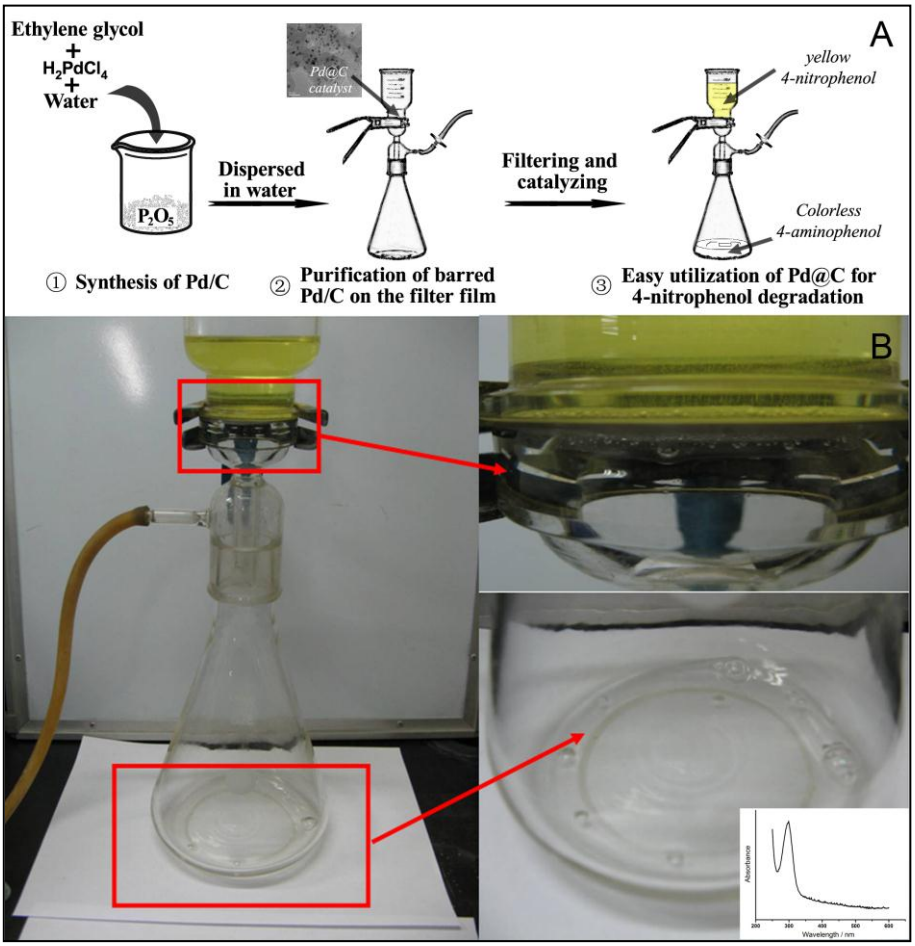

Figure S8. (A) Scheme of handing the as-prepared Pd/C for "filtering and catalyzing" for the degradation of 4-nitrophenol. (B) Digital photograph of the contrastive colors between the two sides of the filter film when 4-nitrophenol is passing through the as-prepared Pd/C catalyst.