Electronic Supplementary Information (ESI)

Performing Catalysis Reaction on a Filter Paper: Development of Metal Palladium Nanoparticle-Based Catalyst

Yili Zhao,[a,b,c] Lei Liu,[a] Daniel Shi,[a] Xiangyang Shi,*[a] Mingwu Shen*[a]

[a] Key Laboratory of Science and Technology of Eco-Textiles, Ministry of Education, College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai 201620, People's Republic of China

[b] Zhejiang Provincial Key Laboratory of Fiber Materials and Manufacturing Technology, College of Materials and Textiles, Zhejiang Sci-Tech University, Hangzhou, 310018, People's Republic of China

[c] State key laboratory of Molecular Engineering of Polymers, Fudan University, Shanghai 200433, People's Republic of China

* To whom correspondence should be addressed. Email: xshi@dhu.edu.cn (X. Shi) and mwshen@dhu.edu.cn (M. Shen).

Part of experimental section:

Materials

Potassium palladium chloride (K_2PdCl_4) was purchased from Alfa Aesar (Ward Hill, MA). Potassium dichromate ($K_2Cr_2O_7$), formic acid, $NaBH_4$ and filter paper were acquired from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). 4-NP was obtained from Aladdin Reagent Co., Ltd. (Shanghai, China). Branched PEI (Mw= 25 000) was acquired from Aldrich (St Louis, MO). Pd-activated carbon was purchased from Shanxi Rock New Materials Co., Ltd. (Baoji, China). The water used in all experiment was purified using a Milli-Q Plus 185 water purification system (Millipore, Bedford, MA) with a resistivity higher than 18.2 MΩ·cm.

Characterization techniques

The formed Pd NP-containing filter paper was characterized by transmission electron microscopy (TEM, JEM2100, JEOL Ltd., Tokyo, Japan) at an operating voltage of 200 kV. In order to confirm the distribution of the Pd NPs onto the surface of filter paper, the Pd NP-immobilized filter paper was embedded in epoxy resin and then cut into ultrathin sections with an ultramicrotome equipped with a diamond knife. The diameter of Pd NPs was measured by image analysis software ImageJ 1.40G (http://rsb.info.nih.gov/ij/download.html). More than 300 NPs in the representative TEM images of the Pd NP-containing filter paper were measured to obtain the diameter distribution histogram. The morphology of the filter paper before and after immobilization of Pd NPs was observed using scanning electron microscopy (SEM, TM-100, Hitachi, Tokyo, Japan) with an operating voltage of 10 kV, and the samples were sputter-coated with 10 nm thick carbon films before SEM measurements. Energy dispersive spectroscopy (EDS, IE300X, Oxford, UK) attached to the SEM was used to analyze the elemental composition of the samples. Thermal gravimetric analysis (TGA) was performed using a TG 209 F1 (NETZSCH Instruments Co., Ltd., Selb/Bavaria, Germany) thermogravimetric analyzer with a heating rate of 10 ^{o}C/min in an air atmosphere. The Pd content of the Pd NP-immobilized filter paper before and after catalytic reactions was confirmed with a Leeman Prodigy inductively coupled plasma-optical emission spectroscopy (ICP-OES) system (Hudson, NH). The Pd NP-immobilized filter paper

(5 mg) was treated with *aqua regia* (1 mL) for 3 h and the extract solution of Pd was diluted 4 times before analysis.

Catalysis experiments

The reduction of Cr(VI) to Cr(III) was performed to evaluate the catalytic efficiency and reusability of Pd NP-immobilized filter paper according to a procedure reported in the literature but with some modifications.[1, 2] A mixture solution of water (15 mL), $K_2Cr_2O_7$ solution (3 mM, 10 mL), and formic acid (1.5 mL) was prepared in a 100-mL glass beaker at a water bath with a temperature of 50 ^oC, and then a piece of Pd NP-containing filter paper (18 mg, 1×2 cm^2) was immersed into the above mixture solution under gentle magnetic stirring. At each predetermined time interval, 0.5 mL of the aqueous solution was withdrawn and diluted to 1.0 mL for the analysis of transformation efficiency of Cr(VI) to Cr(III) using a Lambda 25 UV-vis spectrometer (Perkin Elmer, Boston, MA). The catalytic activity of Pd-activated carbon (18 mg) towards the transformation of Cr(VI) to Cr(III) was also evaluated using a similar procedure. After one catalytic reaction cycle, the Pd NP-containing filter paper was washed with water and dried for the next cycle of catalytic reaction. The filter paper without Pd NPs was also investigated for comparison.

The catalytic efficiency and reusability of the Pd NP-immobilized filter paper were also estimated by the conversion of 4-NP to 4-AP according to our previous study.[3] In brief, a 4-NP aqueous solution (0.6 mL, 10 mM), a $NaBH_4$ aqueous solution (0.6 mL, 10 M) and water (16.8 mL) were mixed in a 50-mL flask under magnetic stirring, the Pd NP-immobilized filter paper was then immersed into the above flask at room temperature. At a given time interval, 0.5 mL of solution was withdrawn and diluted to 1.5 mL with water before UV-vis spectroscopic measurements using a Lambda-25 UV-vis spectrophotometer. To test the reusability of the Pd NP- immobilized filter paper, the paper was pulled out from the reaction mixture after one cycle of catalytic reaction and rinsed with water, and then the

paper was dried for the next cycle of catalytic reaction. For comparison, the filter paper without Pd NPs was also investigated.

To quantify the catalytic efficiency of the above two reactions, the remaining fraction of Cr(VI) or 4-NP was calculated according to the following equation:

$$\text{Remaining fraction of Cr(VI) or 4-NP} = C_t/C_0 \times 100\% \quad (1)$$

where C_0 is the initial concentration of Cr(VI) or 4-NP and C_t is the concentration of Cr(VI) or 4-NP at time *t*.

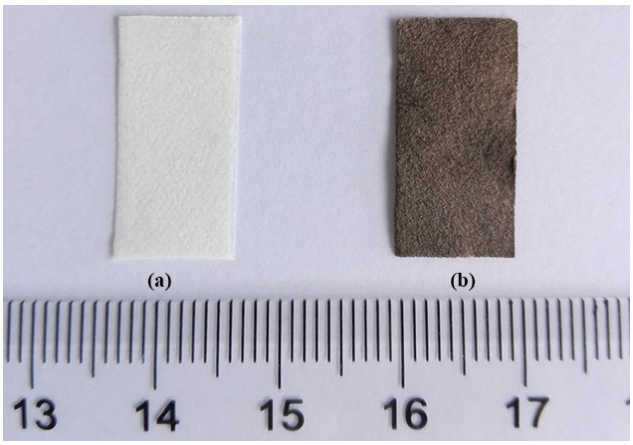

Figure S1. Photograph of the filter paper before (a) and after immobilization of Pd NPs (b).

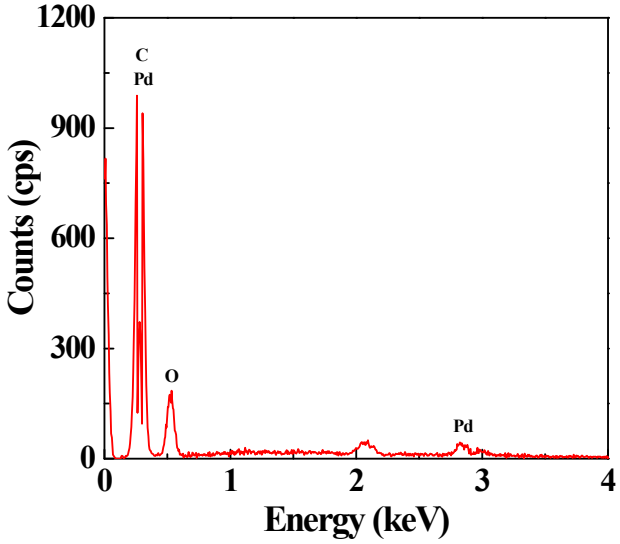

Figure S2. EDS spectrum of the Pd NP-loaded filter paper.

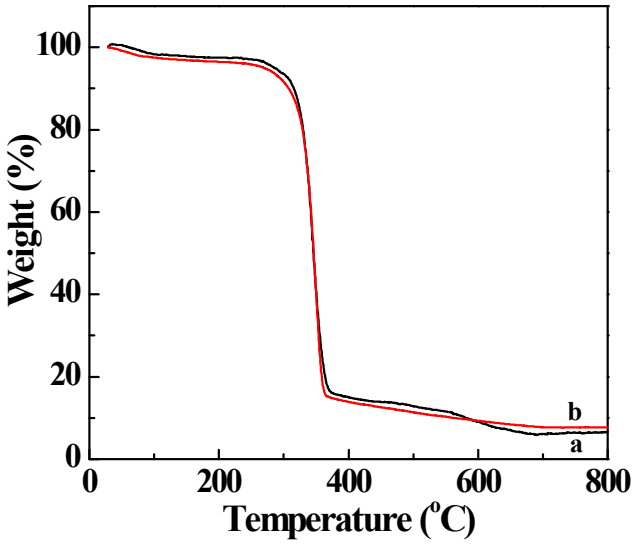

Figure S3. TGA curves of the filter paper without (a) and with (b) the immobilization of the Pd NPs.

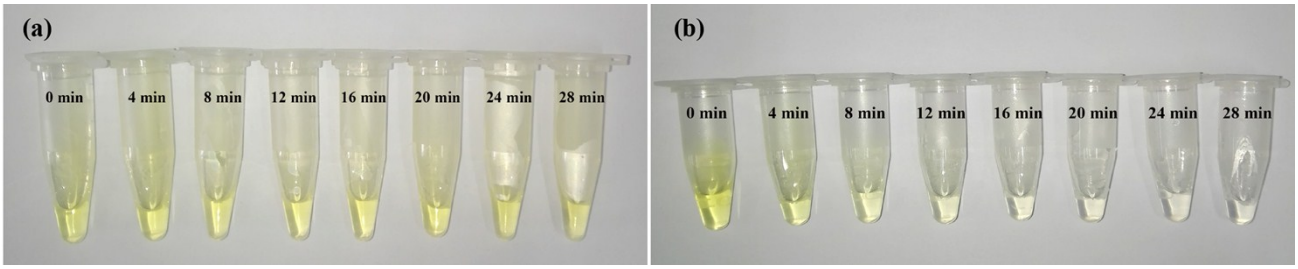

Figure S4. Photograph of the $K_2Cr_2O_7$ solution treated with the filter paper without the Pd NPs (a) and with Pd NPs (b) at different time intervals.

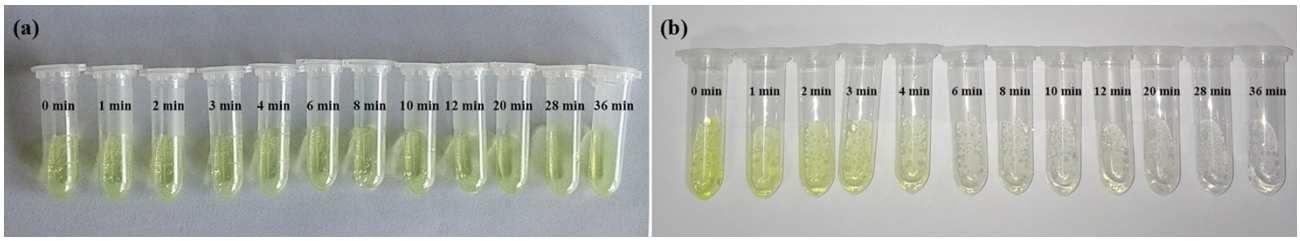

Figure S5. Photograph of the 4-NP solution treated with the filter paper without Pd NPs (a) and with Pd NPs (b) at different time intervals.

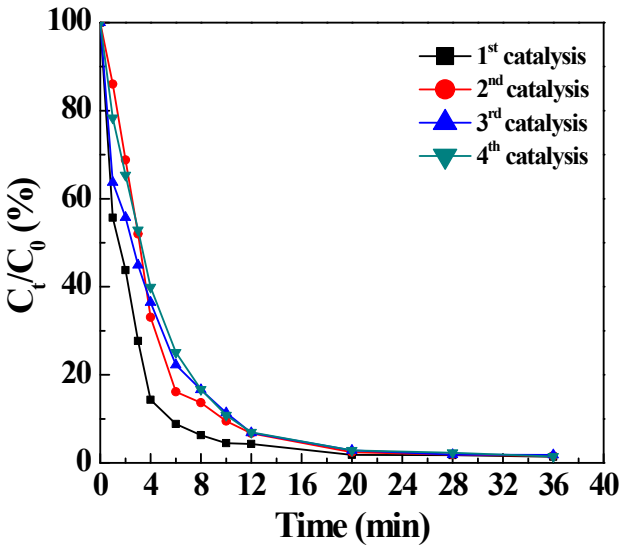

Figure S6. Remaining fraction of 4-NP as a function of time in the presence of Pd NP-loaded filter paper for the first, second, third, fourth and fifth cycle of catalytic reaction.

References

1. M. A. Omole, I. O. K'Owino and O. A. Sadik, *Appl. Catal., B*, 2007, **76**, 158-167.

2. Y. P. Huang, H. Ma, S. G. Wang, M. W. Shen, R. Guo, X. Y. Cao, M. F. Zhu and X. Y. Shi, *ACS Appl. Mater. Inter.*, 2012, **4**, 3054-3061.

3. D. M. Hu, Y. P. Huang, H. Liu, H. Wang, S. G. Wang, M. W. Shen, M. F. Zhu and X. Y. Shi, *J. Mater. Chem. A*, 2014, **2**, 2323-2332.