Supporting Information for Nanoscale

# **Electronic Supporting Information**

Mussel-inspired construction of thermo-responsive double hydrophilic diblock copolymers decorated reduced graphene oxide as effective catalyst supports for highly dispersed superfine Pd nanoparticles

## **Experimental section**

Synthesis of 2,5-dioxopyrrolidin-1-yl 2-(((dodecylthio)carbonothioyl)thio)-2-methylpropanoate (DYDCTM)

S-Dodecyl-S'-( $\alpha, \alpha'$ -dimethyl- $\alpha''$ -acetic acid) trithiocarbonate (DDMAT) (1.0 g, 2.74 mmol) and *N*hydroxysuccinimide (0.47 g, 4.11 mmol) were dissolved in tetrahydrofuran (THF) (20 mL) in a 100 mL 3-necked flask under N<sub>2</sub> atmosphere and magnetic bar. The flask was kept in an ice-water bath, and *N*,*N'*-diisopropylcarbodiimide (DIC, 0.52 g, 4.11 mmol) was added gradually over 30 min. The reaction mixture was carried out overnight at room temperature. The solvent was removed under vacuum and the crude product was dissolved in ethyl acetate. The organic layer was washed with saturated sodium bicarbonate solution, water and salt water, respectively, and then dried with anhydrous magnesium sulfate. The solvent was removed under vacuum and the yellow solid was recrystallized from ethyl acetate/hexane and washed with water to yield yellow crystals. <sup>1</sup>H NMR (600 MHz, CDCl3,  $\delta$  ppm): 3.31 (c, 2H,-CH<sub>2</sub>-); 2.81 (e, 4H, -CH<sub>2</sub>-CH<sub>2</sub>-); 1.88 (d, 6H, s, -CH<sub>3</sub>-); 1.20 - 1.45 (b, 20H,  $-C_{10}H_{20}$ -); 0.89 (a, 3H, CH<sub>3</sub>- $C_{10}H_{20}$ -).

# Synthesis of 1-((3,4-dihydroxyphenethyl)amino)-2-methyl-1-oxopropan-dodecyl carbonotrithioate (DAMODC)

DAMODC (0.9 g, 1.95 mmol) and dopamine hydrochloride (0.41 g, 2.14 mmol) were dissolved in anhydrous methanol (40 mL) at N<sub>2</sub> atmosphere. Triethylamine (0.24 g, 2.34 mmol) was added and the yellow solution was stirred at room temperature for 2 days. Subsequently, the solvent was removed in vacuum and the yellow residue was re-dissolved in diethyl ether and washed three times with 1.0 M HCl, twice with water, once with brine and dried over magnesium sulfate. The solvent was removed to give an orange oil (0.9 g), and the hexane (100 mL) was added and the mixture was stirred for 30 min. Finally, a yellow precipitate was collected by filtration (0.65 g, 67.0 %). **<sup>1</sup>H NMR** (600 MHz, CDCl3,  $\delta$  ppm): 6.2-7.0 (m, 1H, -CH=CH-OH; n, 1H, -CH=CH-OH; e, 1H, -NH-; h, 1H - CH=CH-); 3.44 (f, 2H, -CH<sub>2</sub>-NH-); 3.26 (c, 2H, -CH<sub>2</sub>-C<sub>10</sub>H<sub>20</sub>-); 2.66 (g, 2H, -CH<sub>2</sub>-Ph(OH)<sub>2</sub>); 1.63-1.69 (d, 3H, -CH<sub>3</sub>); 1.20-1.37 (b, 20H, -C<sub>10</sub>H<sub>20</sub>-); 0.88 (a, 3H, CH<sub>3</sub>-C<sub>10</sub>H<sub>20</sub>-).

#### Synthesis of P(PEGMA-co-ETMA)-CTA modified reduced graphene oxide (PrGO)

0.1 g of GO was dispersed in 100 mL Tris-Cl buffer (pH = 8.5, 10 mM) using an ultrasonic bath for 30 min to obtain an uniform dispersion. Then 0.5 g of P(PEGMA-co-ETMA)-CTA was added and the mixture was stirred by a magnetic for 24 h. The crude product was collected by centrifugation, washed with water and alcohol several times and dried at 25 °C.

#### Synthesis of PrGO-supported PdNPs (PdNPs@ PrGO)

30.0 mg PrGO was dispersed in 150 mL distilled water under ultrasonic treatment, and then PdCl<sub>2</sub> (6.0 mL, 0.885 mg mL<sup>-1</sup>) was added into the PrGO dispersion solution. After stirring for 2.0 h, 6.0 mL fresh prepared NaBH<sub>4</sub> solution (0.2 M) was added, and the stirring was maintained for 24 h. The

above mixture was centrifuged and washed with water and ethanol three times, separately. About 4.48 wt % of Pd content in PdNPs@PrGO catalyst was determined via ICP-AES. The final precipitated product was re-dispersed in water for further use in catalytic studies (67 µg mL<sup>-1</sup>).

#### Synthesis of GO-supported PdNPs (PdNPs@GO)

GO (30.0 mg) were dispersed in 100 mL ultrapure water and the suspension was treated with ultrasound for 30 min, and then  $PdCl_2$  (6.0 mL, 0.885 mg mL<sup>-1</sup>) was added into the above solution. After stirring for 2.0 h, 6.0 mL fresh prepared NaBH<sub>4</sub> solution (0.2 M) was added, and the stirring was maintained for 24 h. Then, PdNPs@GO was obtained via repeatedly washing and centrifuging with D.I. water. About 6.85 wt % of Pd content in PdNPs@GO catalyst was determined via ICP-AES. The final precipitated product was re-dispersed in water for further use in catalytic studies (67  $\mu$ g mL<sup>-1</sup>).



Scheme S1 Synthetic route of catechol-terminated chain transfer agent: (i) NHS/DIC, THF, 0 °C  $\rightarrow$  r.t, 24 h; (ii) HCl/TEA, MeOH, r.t, 48 h.



Fig. S1 <sup>1</sup>H NMR spectra of DYDCTM and DAMODC in CDCl<sub>3</sub>.



Fig. S2 FTIR spectra of P(PEGMA-co-ETMA)-CTA (a), GO (b), PrGO (c) and PdNPs@PrGO (d).



Fig. S3 TEM images of (a) PdNPs@BPrGO (10 mM), (b) PrGO, (c) PdNPs@PrGO (5 mM), and (d) PdNPs@GO (5 mM).



**Fig. S4** Optical photographs of (a) PdNPs@BPrGO, (b) PdNPs@PrGO, and (c) PdNPs@GO dispersed in aqueous solution after two weeks, all of their concentration are 1.0 mg mL<sup>-1</sup>.



Fig. S5 Successive reduction of MB using (a) PdNPs@PrGO (20  $\mu$ L) and (b) PdNPs@PrGO (10  $\mu$ L) as the catalysts (67  $\mu$ g mL<sup>-1</sup> catalyst, 2.0 mL of 0.013 mM MB and 1.0 mL of 0.5 M NaBH<sub>4</sub> were used for the reduction of MB).



**Fig. S6** Successive reduction of MB using (a) PdNPs@BPrGO (20  $\mu$ L), (b) BPrGO (20  $\mu$ L), (c) GO (20  $\mu$ L) and (d) ln( $C_t/C_0$ ) vs. reaction time (*t*) plots for PdNPs@BPrGO (20  $\mu$ L), BPrGO (20  $\mu$ L) and GO (20  $\mu$ L) catalysts (67  $\mu$ g mL<sup>-1</sup> catalyst, 2.0 mL of 0.013 mM MB and 1.0 mL of 0.5 M NaBH<sub>4</sub> were used for the reduction of MB).



**Fig. S7** Successive reduction of RZ using (a) PdNPs@BPrGO (5  $\mu$ L), (b) BPrGO (5  $\mu$ L) and (c) GO (5  $\mu$ L) as the catalysts (4.5  $\mu$ g mL<sup>-1</sup> catalyst, 2.0 mL of 0.013 mM RZ and 1.0 mL of 0.5 M NaBH<sub>4</sub> were used for the reduction of RZ). Inset: Optical photograph of RZ-NaBH<sub>4</sub> solution before and after addition catalyst shows the color change from blue into pink during the reduction of RZ into RF.



Fig. S8 UV-vis absorption spectra of *p*-NP solution before and after adding NaBH<sub>4</sub>.



**Fig. S9** Successive reduction of *p*-NP using (a) PdNPs@BPrGO (30  $\mu$ L), (b) BPrGO (30  $\mu$ L), and (c) GO (30  $\mu$ L) as catalysts (67  $\mu$ g mL<sup>-1</sup> catalyst, 2.0 mL of 0.325 mM *p*-NP and 1.0 mL of 0.2 M NaBH<sub>4</sub> were used for the reduction of *p*-NP).



**Fig. S10** Successive reduction of *p*-NP using (a) PdNPs@BPrGO (30  $\mu$ L), (b) PdNPs@PrGO (30  $\mu$ L), (c) PdNPs@GO (30  $\mu$ L), and (d) ln ( $C_t/C_0$ ) vs. reaction time (*t*) plots for PdNPs@BPrGO (30  $\mu$ L), PdNPs@PrGO (30  $\mu$ L) and PdNPs@GO (30  $\mu$ L) catalysts (67  $\mu$ g mL<sup>-1</sup> catalyst, 2.0 mL of 0.325 mM *p*-NP and 1.0 mL of 0.2 M NaBH<sub>4</sub> were used for the reduction of *p*-NP).



**Fig.S11** Temperature dependence of optical transmittance at 600 nm for the diblock copolymer of P(PEGMA-co-ETMA)-b-PNIPAM in water.

Table S1 Comparison of the ability of various catalysts for catalyzing the reduction of MB.

Samples	Time (s) <sup>[a]</sup>	k (min <sup>-1</sup> ) <sup>[b]</sup>	TOF (min <sup>-1</sup> ) <sup>[c]</sup>	References
CN-supported PdNP nanohybrids	43200	1.8	1.91	1
Pd-TNPs/RGO	420	0.4	1.226	2
Ag/MFC	600	0.34	-	3
graphene-PDA-Pd	300	0.1224	-	4
Pd NPs (pc-7)	420	1.006	108.27	5
Pd-PIBrGO	30	9.563	2198.4	6
Mesoporous 3D wood@Pd membrane	Rapidly	-	2.02	7
MpSi-Pd	4	0.655	1.78	8
Pd NPs@GO	450	0.29	9.10	This work
Pd NPs@PrGO	30	7.45	2113	This work
Pd NPs@BPrGO	20	10.83	2823	This work

[a] The reduction time of MB in the presence of catalyst. [b] Apparent rate constant. [c] Turnover frequency.

Samples	Detection limit (mM)	<i>k</i> (min <sup>-1</sup> )	TOF( min <sup>-1</sup> )	References
Graphene-PDA-Pd	1	0.283	-	4
MpSi-Pd	1	0.159	1.4	8
Au@DHBC NP	0.75	0.333	13.3	9
Ag-Au-rGO	5	0.2082	2.5	10
Au NPs@GFDP	50	0.665	7.3	11
PS@RGO@Pd	10	0.286	-	12
Pd/CNs	0.12	0.342	14.7	13
CMF@PDA/Pd	0.05	-	0.03	14
Pd@RGO	1	-	5.7	15
PdNPs@GO	50	0.01	7.9	This work
PdNPs@PrGO	50	0.26	43.4	This work
PdNPs@BPrGO	50	0.62	65	This work

**Table S2**Comparison of the ability of various catalysts for catalyzing the reduction of *p*-NP.

### The grafting density is calculated by the following formula:<sup>16</sup>

Chain per carbon:  $Apg = Mc \times Wp/Mp \times Wc$ 

where *M*c is the relative molar mass of carbon ( $Mc=12 \text{ g mol}^{-1}$ ), *M*p is the average-number molar mass (*M*n) of grafted polymer ( $Mn=32700 \text{ g mol}^{-1}$ ), The values of *W*c, and *W*p were obtained from the TGA curves of GO and block copolymer–GO hybrid. In this paper, *W*c, and *W*p can be calculated and determined as 28% and 72%, respectively. So the grafting density of block copolymer chains on GO was calculated to be 0.11 chains per 100 carbons.

The turnover frequency (TOF) values of the catalytic reactions were calculated according to following equation:<sup>17</sup>

$$TOF = \frac{[MB] \times conversion}{[Pd] \times t}$$

were the molar concentration of methylene blue [MB] was fixed to be  $1.04 \times 10^{-5}$  M, and [Pd] was determined by ICP-AES. The conversion at time *t* can be obtained from Fig. 8d. The TOF values for all the runs was calculated with the conversion of MB at 30%. The calculation for TOF values of the catalytic reduction of nitrophenols with the conversion of NPs at 100%..

#### References

- 1. J. Hu, Y. L. Dong, Z. U. Rahman, Y. H. Ma, C. L. Ren and X. G. Chen, Chem. Eng. J., 2014, 254, 514–523.
- 2. G. Fu, L. Tao, M. Zhang, Y. Chen, Y. Tang, J. Lin and T. Lu, Nanoscale, 2013, 5, 8007–8014.
- 3. M. Zhu, C. Wang, D. Meng and G. Diao, J. Mater. Chem. A, 2013, 1, 2118–2125.
- 4. J. X. Ma, H. Yang, S. Li, R. Ren, J. Li, X. Zhang and J. Ma, RSC Adv., 2015, 5, 97520–97527.
- 5. V. Vilas, D. Philip and J. Mathew, Mater. Chem. Phys., 2016, 170, 1–11.
- K. Y. Cho, Y. S. Yeom, H. Y. Seo, P. Kumar, A. S. Lee, K.Y. Baek and H. G. Yoon, *J. Mater. Chem. A*, 2015, 3, 20471–20476.
- 7. F. Chen, A. S. Gong, M. Zhu, G. Chen, S. D. Lacey, F. Jiang, Y. Li, Y. Wang, J. Dai, Y. Yao, J. Song, B. Liu, K. Fu, S. Das and L. Hu, ACS Nano, 2017, 11, 4275–4282.
- 8. T. Kim, X. Fu, D. Warther and M. J. Sailor, ACS Nano, 2017, 11, 2773-2784.
- 9. E. Seo, J. Kim, Y. Hong, Y. S. Kim, D. Lee and B. S. Kim, J. Phys. Chem. C, 2013, 117, 11686–11693.
- K. Hareesh, R. P. Joshi, D. V. Sunitha, V. N. Bhoraskar and S. D. Dhole, *Appl. Surf. Sci.*, 2016, 389, 1050–1055.
- 11. D. Wang, H. Duan, J. Lu and C. Lu, J. Mater. Chem. A, 2017, 5, 5088–5097.
- 12. X. Ni, Z. Wu, X. Gu, D. Wang, C. Yang, P. Sun and Y. Li, Langmuir, 2017, 33, 8157-8164.
- 13. X. Wu, C. Lu, W. Zhang, G. Yuan, R. Xiong and X. Zhang, J. Mater. Chem. A, 2013, 1, 8645–8652.
- 14. J. Xi, J. Xiao, F. Xiao, Y. Jin, Y. Dong, F. Jing and S. Wang, Sci. Rep., 2016, 6, 2045–2322.
- 15. W. Dong, S. Cheng, C. Feng, N. Shang, S. Gao and C. Wang, Catal. Commun., 2017, 90, 70-74.
- 16. B. Hu, L. Liu, Y. Zhao and C. Lü, RSC Adv., 2016, 6, 51057-51067.
- 17. X. Liu, F. Cheng, Y. Liu, H. Ji and Y. Chen, J. Mater. Chem., 2010, 20, 360-368.