Supporting Information for ***New Journal of Chemistry***

Electronic Supporting Information

Quaternized POSS modified rGO-supported Pd nanoparticles as high efficient catalyst for reduction and Suzuki coupling reactions

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Experimental section

Synthesis of graphite oxide

GO was prepared according to the modified Hummer's method. Firstly, 1.0 g of graphite powders, 1.25 g of $K_2S_2O_8$, 1.25 g of P_2O_5 and 4.0 mL of H_2SO_4 (98%, 4 mL) were added into a three round-bottom flask, at same time was stirred them at 80 ^{o}C for 4.5 h. After the solution was cooled to room temperature, 170 mL of distilled water was added. The black mixture was filtered using a water pump and washed several times with distilled water, then dried under vacuum at 120 ^{o}C for 12 h to obtain the pre-oxidized graphite. Secondly, 1 g of pre-oxidized graphite was added to the three round bottom flask, 50 mL of H_2SO_4 (98%) and 5.0 g of $KMnO_4$ was slowly added under an ice bath to keep the mixture cooled down around 20 ^{o}C, the color of the solution was dark green. Then, the solution was stirred for 3.5 h at 35 ^{o}C and 30 mL of water was slowly added to the above solution. Next the mixture was further stirred for 15 min at 98 ^{o}C and the color of the solution was observed to be turn bright yellow, 240 mL of water and 6 mL of 30 wt% H_2O_2 were separately added to the above mixture.The resulting mixture was obtained by centrifugation and washed several times with 10 wt% HCl solution and distilled water to remove residual acid. Finally, the graphite oxide was subjected to ultrasonication for 1 h under a water bath. The GO dispersion was collected by centrifugation centrifuged and dried by freeze-drying.

Synthesis of GO-supported PdNPs (PdNPs@rGO)

GO (30 mg) was dispersed into distilled water (150 mL) using ultrasonication for 30 min. $PdCl_2$ (6.0 mL, 0.885 mg mL^{-1}) was added into the above solution for ultrasound 2.0 h $PdCl_2$. 6.0 mL of freshly prepared $NaBH_4$ solution (0.2 M) was added and the reaction solution was continuously stirred at room temperature for 24 h. The product PdNPs@rGO was collected by centrifugation and washed several times with water and ethanol to remove unsupported palladium nanoparticles and $PdCl_2$, then dried at room temperature in a vacuum. The amount of Pd in the PdNPs@rGO catalyst was determined by ICPAES to be about 6.94 wt%

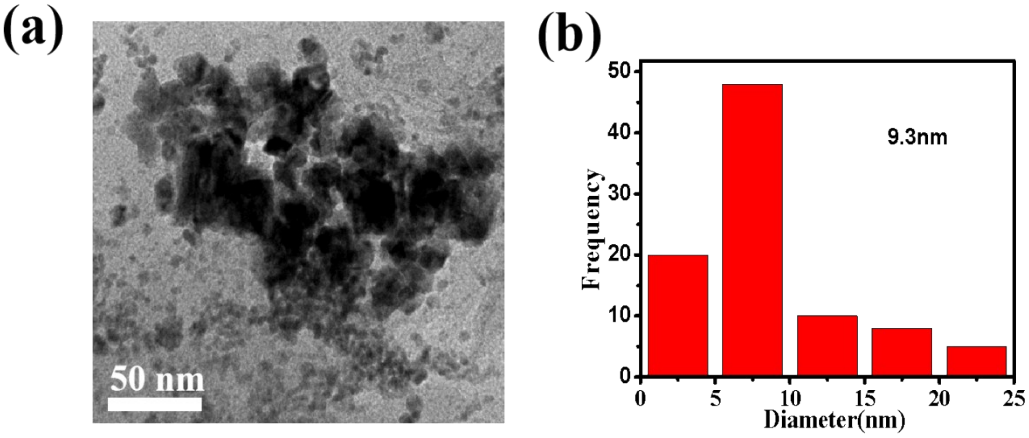


Fig. S1 TEM image of (a) PdNPs@rGO, and (b) Pd particle size distribution histogram on PdNPs@rGO.

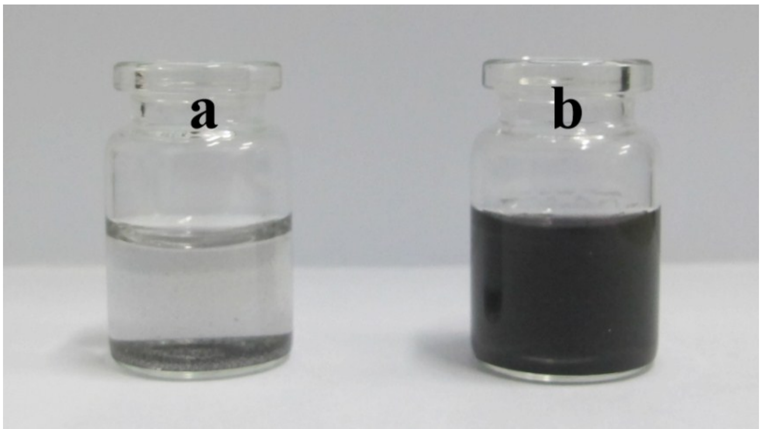
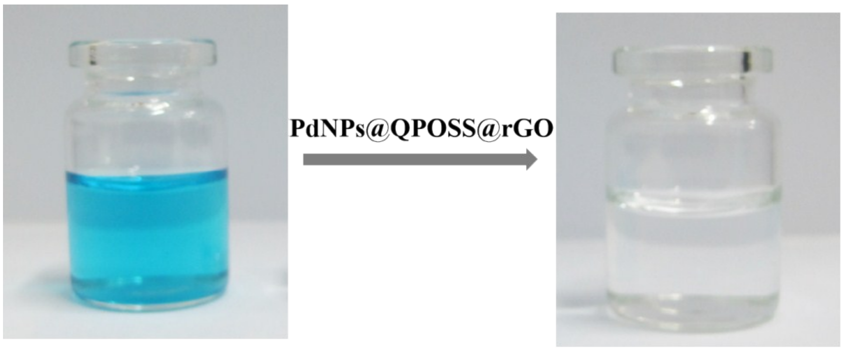


Fig. S2 Optical photographs of (a) PdNPs@rGO and (b) PdNPs@QPOSS@rGO dispersed in aqueous solution after two weeks, all of their concentrations are 0.25 mg mL^{-1}.



Methylene Blue (MB)

Leuco Methylene Blue (LMB)

Fig. S3 Optical photographs for the catalytic reduction of MB to LMB.

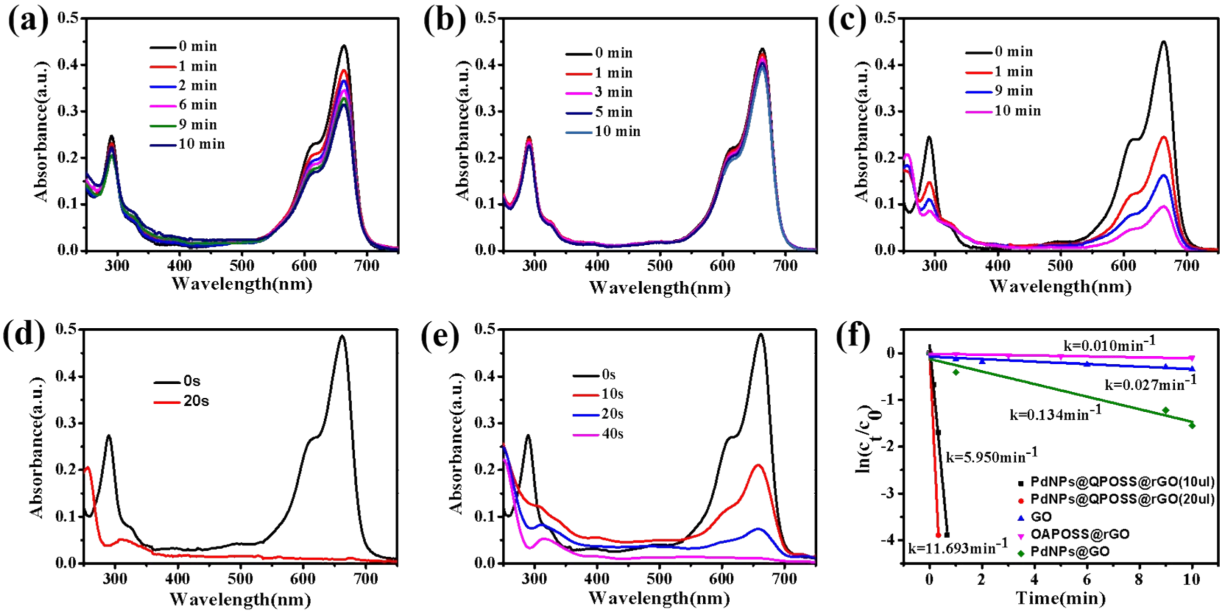


Fig. S4 Successive reduction reaction of MB using catalysts (20 μL): (a) GO, (b) OAPOSS@rGO, (c) PdNPs@rGO, (d) PdNPs@QPOSS@rGO (20 μL), (e) PdNPs@QPOSS@rGO (10 μL) and (f) Plots of ln (C_t /C_0) vs. reaction time (t) for different control catalysts (0.1 mg mL^{-1} catalyst, 2.0 mL of 0.013 mM MB and 1.0 mL of 0.5 M $NaBH_4$ were used for the reduction of MB).

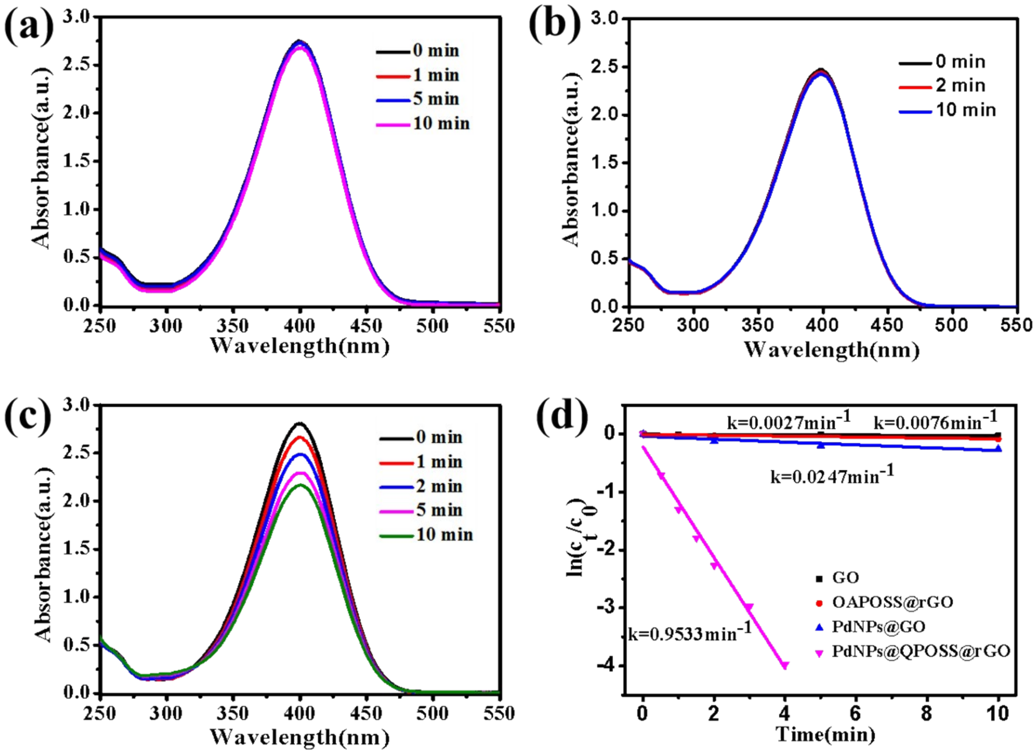


Fig. S5 Successive reduction of p-NP using (a) GO (30 μL), (b) OAPOSS@rGO (30 μL), and (c) PdNPs@rGO (30 μL) as catalysts (0.25 mg mL^{-1} catalyst, 2.0 mL of 0.325 mM p-NP and 1.0 mL of 0.2 M $NaBH_4$ were used for the reduction of p-NP). and (d) Plots of ln (C_t /C_0) vs. reaction time (t) for different control catalysts.

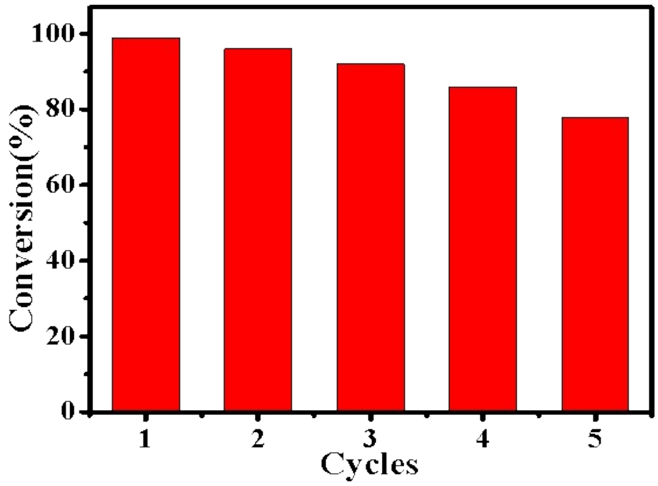


Fig. S6 The reusability of PdNPs@QPOSS@rGO catalysts in the p-NP reduction reaction.

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

Samples	Time (s)[a]	*k* (min)[b]	TOF (min)[c]	Refs
Pd-TNPs/RGO	420	0.4	1.226	1
Ag/MFC	600	0.34	-	2
Graphene-PDA-Pd	300	0.1224	-	3
Pd NPs (pc-7)	420	1.006	108.27	4
Pd-PIBrGO	30	9.563	2198.4	5
Mesoporous3D wood@Pd membrane	Rapidly	-	2.02	6
MpSi-Pd	4	0.655	1.78	7
Fe-Fe_2O_3@PDA@Pd	420	0.9	-	8
RGO/Fe_3O_4	240	-	-	9
PdNPs@QPOSS@rGO	20	11.693	2431.5	This work

[a] The reduction time of MB in the presence of catalyst. [b]Apparent rate constant. [c] Turnover frequency (TOF), defined as moles of MB molecules reduced per mole of Pd catalyst per unit time, is calculated based on the Pd contents in PdNPs@QPOSS@rGO (3.48 wt%.) determined by ICP.

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

Samples	Time(min)	*k*(min)	TOF(min)[c]	Refs
Fe_3O_4@PDA-Pd@[Cu3(btc)$_2$]	8	0.72	-	10
Pd@TP-POP	5.75	0.61	3.8	11
GO-$MnFe_2O_4$-PdNPs	4	0.768	-	12
UiO-66-NH_2/TTACP/Ni@Pd	2.5	0.852	-	13
MpSi-Pd	30	0.159	1.4	7
Au NPs@GFDP	7	0.665	7.3	14
PS@RGO@Pd	10	0.286	-	15
Pd/CNs	10	0.342	14.7	16
Graphene-PDA-Pd	9	0.283	0.03	3
PdNPs@QPOSS@rGO	4	0.95	30.6	this work

[a] Turnover frequency (TOF) is defined as the number of moles of p-NP reduced per mole of Pd catalyst per hour.

Table S3 Comparison of the ability of various catalysts for Suzuki cross-coupling reactions of bromobenzene and phenylboronic acid.

Entry	Catalyst	Solvent	T (°C)	Time (%)	Conversion (%)	Refs
1	GO-PdP_2 (0.5 mol%)	EtOH–H_2O	80	2h	88	17
2	PdNPs-IP-IL (1.0 mol%)	H_2O	100	6h	55	18
3	Pd@APGO （0.24 mol%）	EtOH–H_2O	80	6h	80	19
4	Fe_3O_4@C-Pd@mCeO_2 (0.29 mol%)	EtOH–H_2O	80	3h	95	20
5	SiO2-pA-Cyan-Cys-Pd (0.5 mol%)	H_2O	100	5.5h	88	21
6	Fe_3O_4-DA-DMG/Pd^0 (1.0 mol %)	H_2O	80	12h	97.4	22
7	3D IL-rGO/Pd (0.5 mol%)	EtOH–H_2O	80	1h	94	23
8	3D G/MWCNTs/Pd (0.5 mol%)	EtOH–H_2O	60	1h	95	24
9	Pd@GOF (1.1mol%)	EtOH	40	24h	97	25
10	Pd@Mag-Msn (1.0 mol%)	Dioxane	80	6h	77	26
11	Pd/BOFs (2.6 mol%)	H_2O	80	2h	91	27
12	PEG-Pd (1.2 mol%)	EtOH–H_2O	80	12h	93	28
13	PdNPs@QPOSS@rGO (0.3 mol%)	H_2O	80	2h	99.8	This work

Table S4 Leached amount Pd of PdNPs@QPOSS@rGO by ICP.

Entry	Element Pd Concentration in solution, mg/L (ppm)
Before four cycles	5.98
After four cycles	5.59

The turnover frequency (TOF) values of the corresponding reactions were calculated according to following equation:[29]

$$TOF = \frac{[MB] \times conversion}{[Pd] \times t} \qquad \text{Eq.1}$$

Here the concentrations of methylene blue [MB] was fixed to be 1.04×10^{-5} M, and [Pd] was determined by ICP-AES. The conversion at time *t* can be obtained from Fig. 7c. We estimated the TOF values for all the runs with the conversion of MB at 30%. The TOF values of the catalytic reactions for 4-nitrophenol were calculated according to the equation similar to MB. The molar concentration [4-NP] of substrate was 1×10^{-5} M. The Pd molar concentration [Pd] of PdNPs@QPOSS@rGO in reaction systems was calculated by ICP-AES results. The conversion at reaction time *t* can be obtained from Fig. 8d. The calculation for TOF values of the catalytic reduction of nitrophenols with the conversion of NPs at 100%.

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