Electronic supplementary information (ESI)

Controllable decoration of sub-nano palladium clusters on reduced graphene oxide with superior catalytic performance in selective oxidation of alcohols

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As the Electronic supplementary information (ESI) of the manuscript "*Controllable decoration of sub-nano palladium clusters on reduced graphene oxide with superior catalytic performance in selective oxidation of alcohols*", following materials are provided:

(1) More experimental details for the preparation of GO, rGO, and various Pd/rGO samples with different solvents and Pd precursors;

(2) More results including the TEM images and size distribution of the Pd species on the Pd/rGO samples prepared with different solvents and Pd precursors as well as those calcined in an inert atmosphere; the results of Pd 3d XPS and Pd K-edge EXAFS; a comparison of various catalysts in their performance for the aerobic oxidation of benzyl alcohol.

1. More experimental details:

Preparation of graphene oxide (GO). GO was synthesized by a modified Hummers' method.[1] Briefly, graphite powder (10 g) and sodium nitrate (5 g) were mixed with sulfuric acid (98 wt.%, 230 mL) in a beaker immersed in an ice-water bath with agitation. Potassium permanganate (30 g) was then added slowly to the mixture and the resultant mixture was kept at 35±2 °C for 30 min. After that, deionized water (460 mL) was added gradually; the water bath temperature was then increased to 98 °C and maintained at this temperature for 40 min. The resultant bright-yellow suspension was then diluted and further treated with H_2O_2 solution (30%, 30 mL). Finally, the suspension was centrifuged and washed carefully to remove the residual salt, and then dewatered at 50 °C under vacuum to obtain the graphite oxide powder. Graphene oxide was then obtained by exfoliating the graphite oxide in aqueous solution under sonication for 2 h, and followed by a vacuum drying process.

Preparation of reduced graphene oxide (rGO). The rGO used here was obtained by rapid heating-up of the above-obtained graphene oxide under high vacuum.[2] Briefly, the as-prepared GO was grounded into fine powder (300 mesh) and loaded into a quartz tube. It was then evacuated to a pressure lower than 2.0 Pa and heated quickly to 250 °C with a heating rate of 30 °C min^{-1}; the rGO sample of fluffy black powder was then generated through the abrupt expansion of GO at about 250 °C.

Deposition of Pd species on rGO with different solvents. The same protocol as that for typical Pd/rGO with ethanol as the impregnation solvent was used to prepare the Pd/rGO samples with different solvents, including methanol (M), ethanol (E), isopropanol (P), acetone (A), and water (W). For the preparation of the Pd/rGO-E-N_2H_4 catalyst, the sample impregnated from ethanol was dispersed again in an ethanol solution containing 2 ml hydrazine hydrate, stirred vigorously at room temperature for 24 h, and then filtered, followed by washed with water and ethanol for several times, and dried at room temperature.

Deposition of Pd species on rGO with $Pd(AcO)_2$ + HCl as precursor. The rGO sheets were first suspended in an ethanol solution and dispersed under ultrasound for 1 h. Subsequently, the ethanol solution of $Pd(AcO)_2$ and HCl solution (2 mL, 2 mol/L) were added into the graphene suspension under ultrasound irradiation for another 10 min. The resultant mixture was vigorously stirred for 4 h, followed by filtering and drying at room temperature for 24 h. The solid sample was eventually obtained by calcination in hydrogen

(20 mL/min) at 200 °C. Similarly, the Pd/rGO samples could be also prepared with $Pd(AcO)_2 + HNO_3$ (HBr, or HF) as the precursors.

2. More detailed results:

Table S1 Results of Pd K-edge EXAFS spectra fitted for various Pd/rGO samples

Sample	Shell	CN	N_{total}	R (Å)	ΔE (eV)	σ^2 (Å^2)	R-factor
Pd/rGO-E-100	Pd-O	-	5.2	-	-	-	0.0038
	Pd-Cl	5.2 (±0.7)		2.31 (±0.01)	2.34	0.006	
	Pd-Pd	-		-	-	-	
Pd/rGO-E-200	Pd-O	0.5 (±0.3)	5.0	2.10 (±0.03)	-1.22	0.010	0.0010
	Pd-Cl	2.5 (±1.0)		2.31 (±0.02)	8.59	0.010	
	Pd-Pd	2.0 (±0.8)		2.74 (±0.02)	-1.22	0.010	
Pd/rGO-E-300	Pd-O	0.7 (±0.3)	5.1	1.95 (±0.01)	-3.18	0.006	0.0013
	Pd-Cl	1.9 (±0.5)		2.32 (±0.02)	1.45	0.006	
	Pd-Pd	2.5 (±0.6)		2.76 (±0.03)	-3.18	0.006	
Pd/rGO-E-400	Pd-O	0.8 (±0.5)	6.1	1.90 (±0.03)	-1.82	0.005	0.0012
	Pd-Cl	1.6 (±0.4)		2.33 (±0.01)	-1.82	0.006	
	Pd-Pd	3.7 (±0.4)		2.76 (±0.01)	-1.82	0.005	
Pd/rGO-E-500	Pd-O	1.2 (±0.4)	8.9	1.97 (±0.03)	-1.82	0.006	0.0030
	Pd-Cl	0.6 (±0.4)		2.35 (±0.03)	0.06	0.008	
	Pd-Pd	7.1 (±0.4)		2.73 (±0.03)	-8.50	0.008	
Pd/rGO-E-600	Pd-O	0.7 (±0.5)	9.5	1.99 (±0.02)	9.34	0.021	0.0014
	Pd-Cl	-		-	-	-	
	Pd-Pd	8.8 (±1.5)		2.77 (±0.02)	-3.80	-0.002	
Pd/AC-E-100	Pd-O	2.0 (±1.0)	5.3	1.96 (±0.03)	-9.40	0.008	0.0023
	Pd-Cl	-		-	-	-	
	Pd-Pd	3.3 (±0.8)		2.75 (±0.02)	-4.36	0.006	

Note: CN, coordination number; ΔE, inner core correction; R, distances, σ^2, Debye-Waller Factor. (Fit range $3 < k < 11$, $1.2 < R < 3.2$, number of independent points = 9.5)

Table S2 Performances of the Pd/rGO-A (with acetone as the impregnation solvent) and Pd/rGO-W (with water as the impregnation solvent) series catalysts calcined at different temperatures in the aerobic oxidation of benzyl alcohol

Entry	Catalyst	Conv. (%)	Sel. (%)	TOF (h^{-1})	Carbon balance (%)
1	Pd/rGO-A-NR	9.4	99.9	156	99.7
2	Pd/rGO-A-50	9.8	99.9	162	99.7
3	Pd/rGO-A-100	88.9	92.3	1579	99.0
4	Pd/rGO-A-150	44.3	99.9	996	99.7
5	Pd/rGO-A-200	38.7	99.8	907	99.8
6	Pd/rGO-W-NR	4.1	99.9	58	99.6
7	Pd/rGO-W-50	4.3	99.9	60	99.4
8	Pd/rGO-W-100	5.2	99.9	75	99.9
9	Pd/rGO-W-150	5.4	99.9	61	99.7
10	Pd/rGO-W-200	6.0	99.9	72	99.6

Reaction conditions: 6 mL deionized water, 1.6 mmol benzyl alcohol substrate, 10 mg catalyst (the molar ratio of substrate/Pd was about 1200), 0.5 MPa O_2; the reaction was carried at 60 °C for 1 h with agitation (700 rpm). TOF values are obtained on the basis of reaction results for initial 0.5 h.

Table S3 Comparison of various catalysts in their performance for the aerobic oxidation of benzyl alcohol

Catalyst	Substrate/Metal molar ratio	Solvent [a]	Temperature (°C)	Time (h)	Conversion (%)	Selectivity (%) [b]	TOF (h^{-1}) [c]	Ref.
Pd/MgO	1064	TFT	70	8	12	100	16	3
Au/$Ga_3Al_3O_9$	197	Toluene	80	2	98	>99	96	4
Au/MgO	1894	Methanol	110	10	96	58 [d]	182	5
AuPd/AC	500	Water	60	3	96	94	160	6
Au/MnO_2	3940	Free	120	5	41	99	323	7
PtRu/CNT	500	Water	80	3	52.5	96.5	88	8
$Ru(OH)_x/ZrO_2$	100	Toluene	100	1	>99	>99	100	9
CM-CeO_2-Pd	5112	Free	120	16	82.1	62.9	262	10
Ru/hydroxyapatite	6	Toluene	80	3	100	>99	2	11
Au/hydrotalcite	9	Toluene	40	24	85	91.7	7	12
Ru/Al_2O_3	40	TFT	83	1	>99	>99	40	13
RuO_2/FAU	20	Toluene	80	1.5	100	>99	13	14
Au/C	1600	Water	60	12	>99	>99 [e]	133	15
Au/CuO_{co}	492	Free	80	5	58.5	98.2	56	16
Au/ZrO_2	1904	Free	130	5	50.7	87.0	193	17
Pd_{20}@Au_{80}/AC	500	Water	60	--	90	>99	1021	18
Pd/APS-TUD	25000	Free	160	1	22.3	95.2	18571	19
Au-Pd/TiO_2	--	Free	100	8	74.5	91.6	6440	20
Pd@hmC	1667	Water	80	1	48.0	77.1	2940	21
PdHAP-0	500	TFT	90	1	>99	>99	500	22
Pd/Dk1-RE	10321	Toluene	100	1	67	98	6916	23
Pd/Al_2O_3-ads	16167	Free	88	8	97	96	1952	24
Pd/AC	3000	Free	80	--	90	61	2980	25
Pd/NaX	3819	Free	100	4	66	97	626	26
Pd/SiO_2-Al_2O_3	17201	Free	70	10	97	98	--	27
Pd/AC	--	*p*-Xylene	70	--	--	85	≈1000	28
Pd/rGO-E-100	1200	Water	60	1	98.9	99.9	1960	this work
Pd/rGO-E-100	8000	Water	100	0.5	98.6	85.4	26440	this work

[a] TFT represents trifluorotoluene;

[b] Selectivity refers to benzaldehyde except that specially pointed;

[c] Turnover frequency (TOF), the number of benzyl alcohol molecules converted per active site and hour, is estimated on basis of total active metal atoms;

[d] Selectivity refers to ester;

[e] Selectivity refers to benzoic acid.

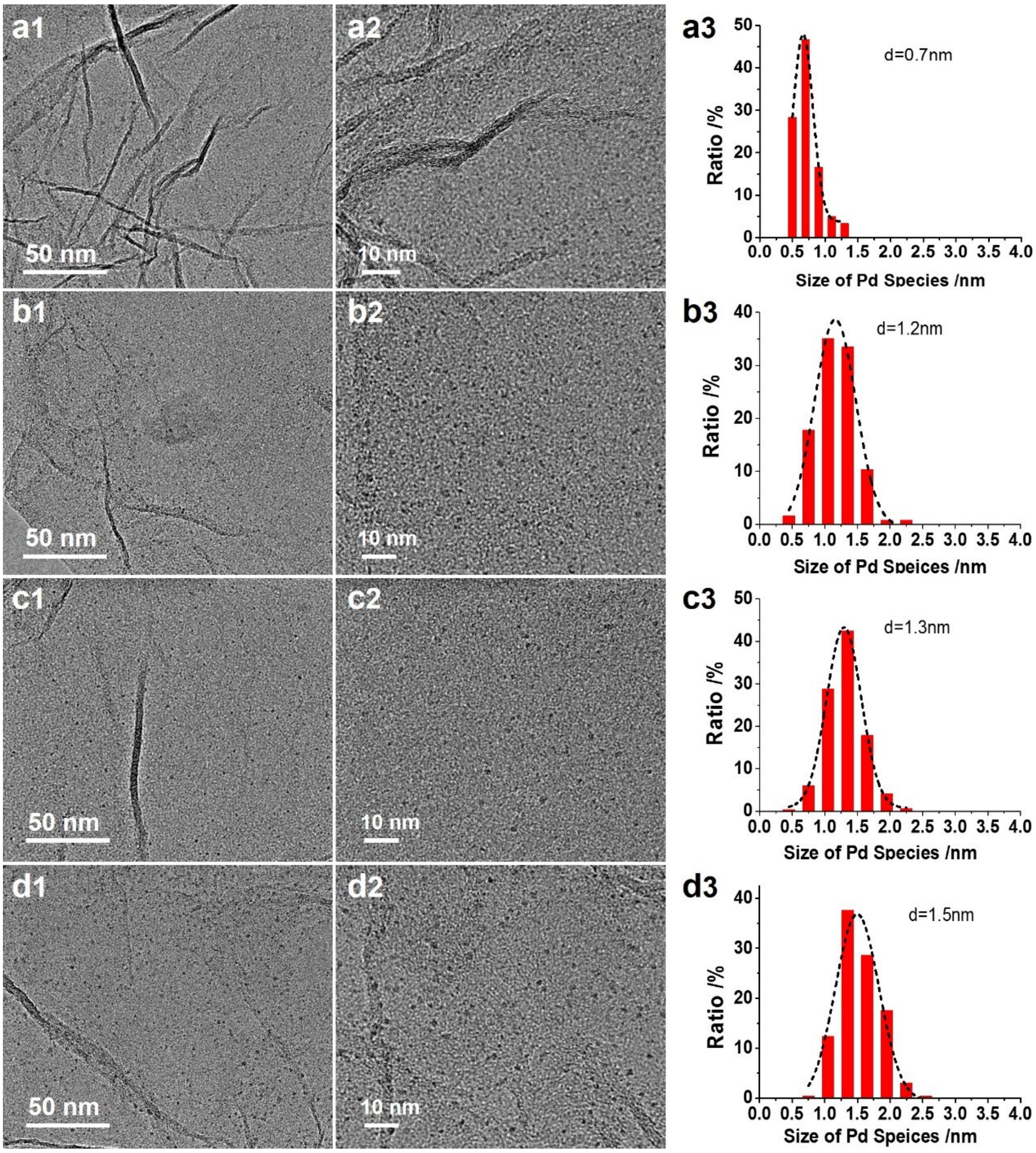

Fig. S1 TEM images (a1–d1 and a2–d2) and size distribution (a3–d3) of Pd nanoclusters immobilized on the rGO sheets by impregnation with different solvents (they all were calcined at 100 °C in hydrogen). (a1, a2, a3) acetone; (b1, b2, b3) methanol; (c1, c2, c3) isopropanol; and (d1, d2, d3) water.

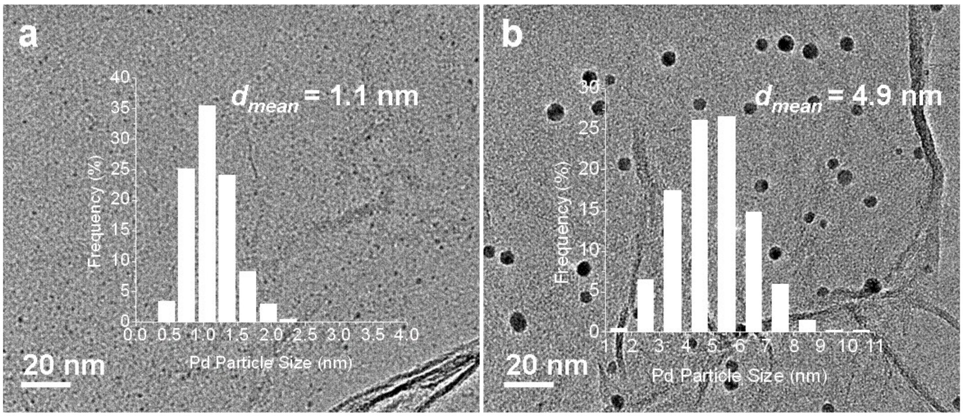

Fig. S2 TEM images and size distribution of the Pd species immobilized on the rGO sheets with different precursors. (a) $Pd(AcO)_2$ + HBr; and (b) $Pd(AcO)_2$ + HF.

Besides HCl, other halogenic acid like HBr and HF were also used to deposit the Pd species on the rGO sheets, following the same protocol as that for $Pd(AcO)_2$ + HCl as the Pd precursor. As mentioned in the main manuscript, with $Pd(AcO)_2$ as the precursor, the size of Pd particles on Pd/rGO is 7.7 nm; after HBr is added, the size of Pd species is decreased to 1.1 nm, similar to the value of 0.8 nm obtained by adding HCl. However, ultrafine Pd nanoclusters cannot be obtained through the addition of HF.

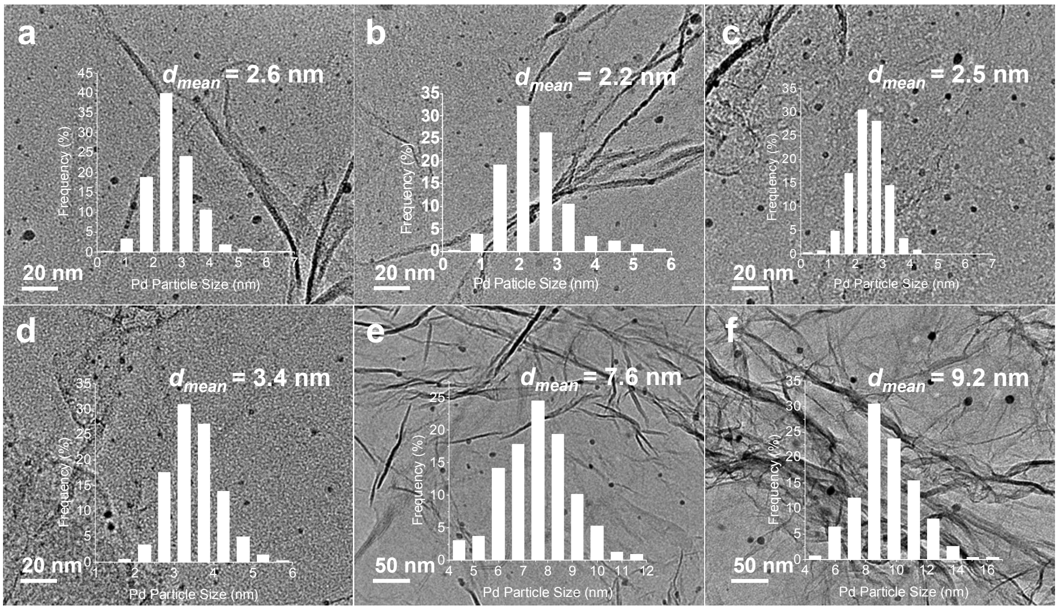

Fig. S3 TEM image and size distribution of the Pd species immobilized on the rGO sheets with $PdCl_2$ as the precursor but calcined in argon atmosphere at different temperatures: (a) 100 °C; (b) 200 °C; (c) 300 °C; (d) 400 °C; (e) 500 °C; and (f) 600 °C

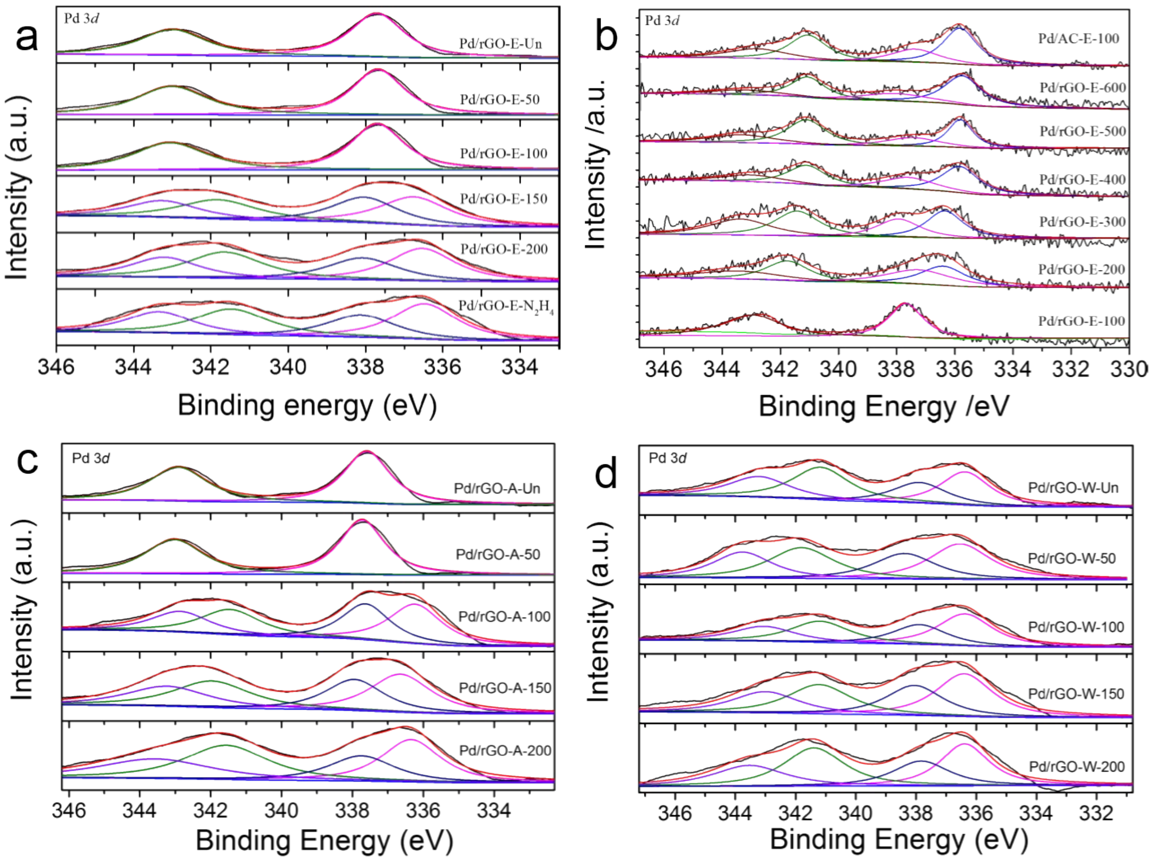

Fig. S4 Pd 3d XPS spectra of various Pd/rGO and Pd/AC samples. (a) Samples impregnated in ethanol solution then treated by different methods; (b) samples impregnated in ethanol solution then reduced at different temperatures; (c) samples impregnated in acetone solution then reduced at different temperatures; (d) samples impregnated in water solution then reduced at different temperatures.

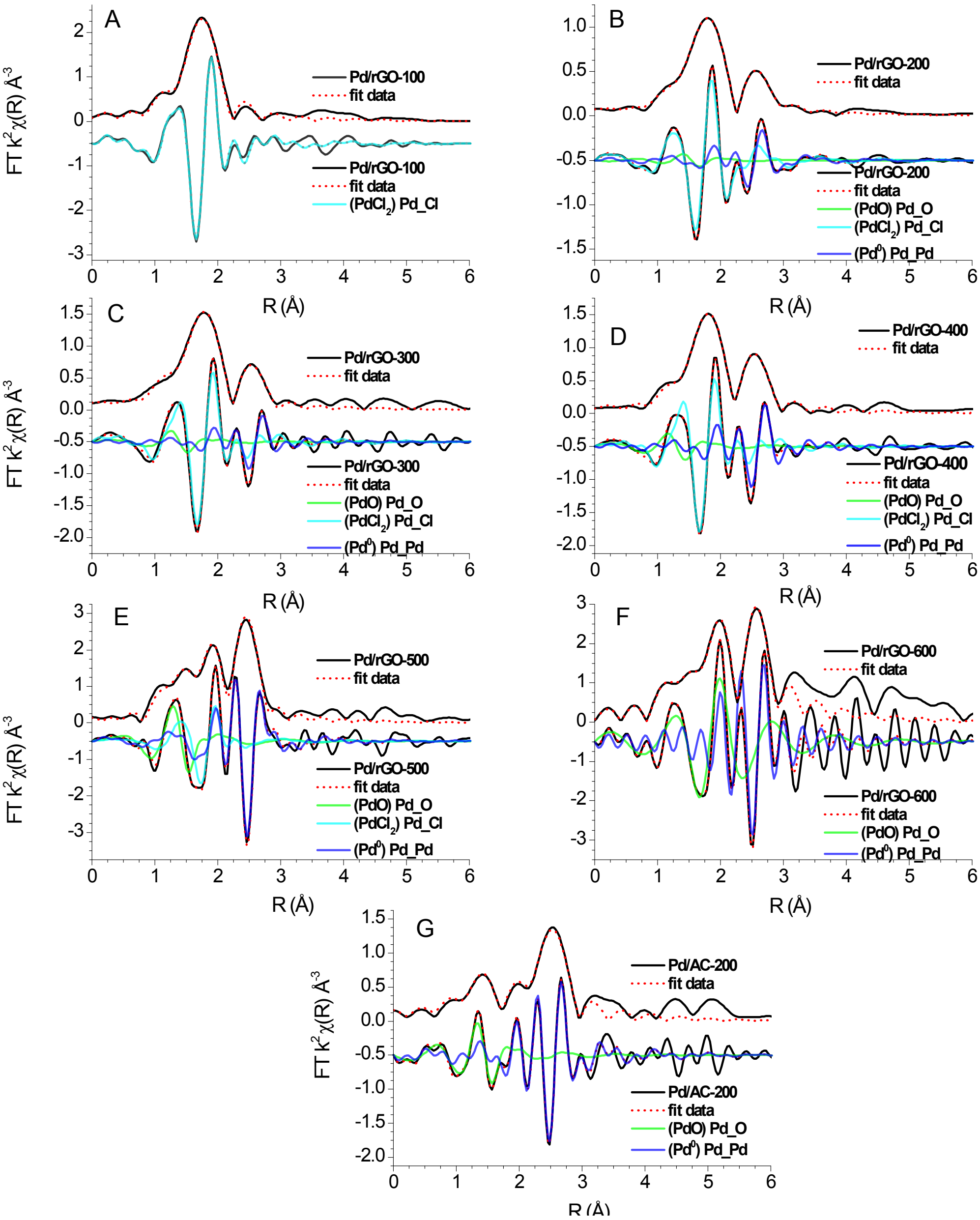

Fig. S5 Pd K-edge EXAFS spectra of the Pd/rGO-E and Pd/AC-E samples calcined at different temperatures in hydrogen, showing the magnitude and imaginary components of the k^2 weighted Fourier transform data. (a) Pd/rGO-E-100; (b) Pd/rGO-E-200; (c) Pd/rGO-E-300; (d) Pd/rGO-E-400; (e) Pd/rGO-E-500; (f)Pd/rGO-E-600; and (g) Pd/AC-E-200.

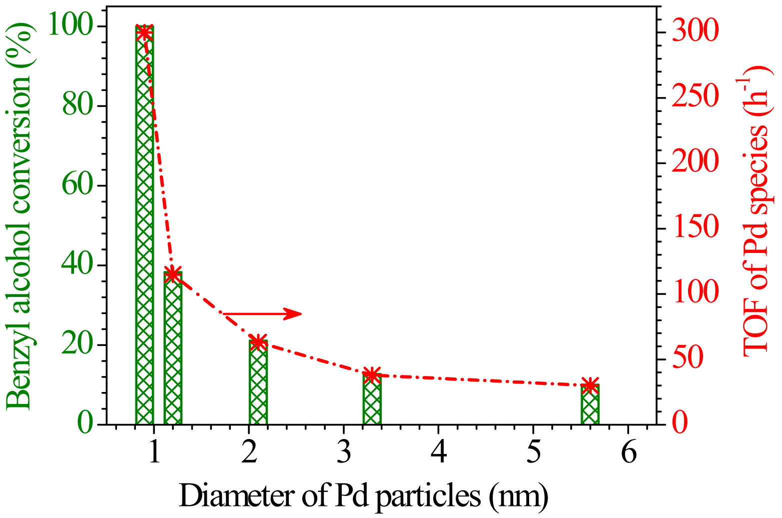

Fig. S6 Relationship between the activity in the benzyl alcohol oxidation of various Pd/rGO-E catalysts and the particle size of Pd on the rGO sheets. Reaction conditions: 6 mL deionized water, 1.6 mmol substrate, 10 mg catalyst (the molar ratio of substrate/Pd is about 1200), 0.5 MPa O_2, 60 °C, under stirring (700 rpm) for 4 h.

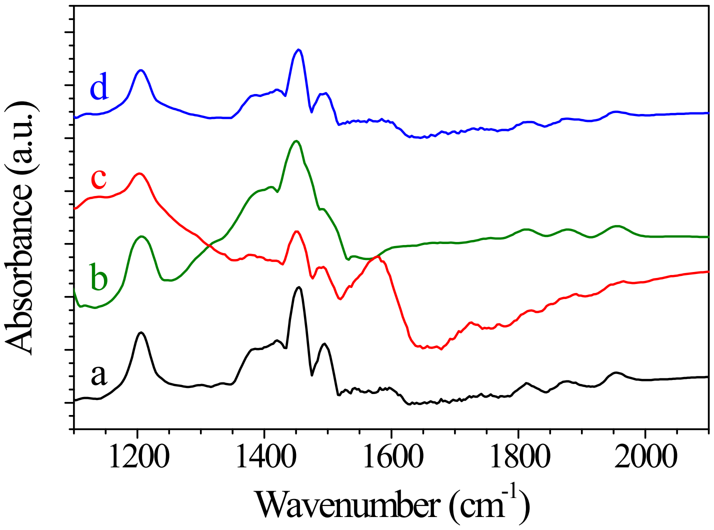

Fig. S7 IR spectra for the adsorption of benzyl alcohol on (a) Pd/rGO-E-NR, (b) Pd/rGO-E-50, (c) Pd/rGO-E-150, and (d) Pd/rGO-E-200; the spectra are collected at room temperature after introducing benzyl alcohol for 30 min.

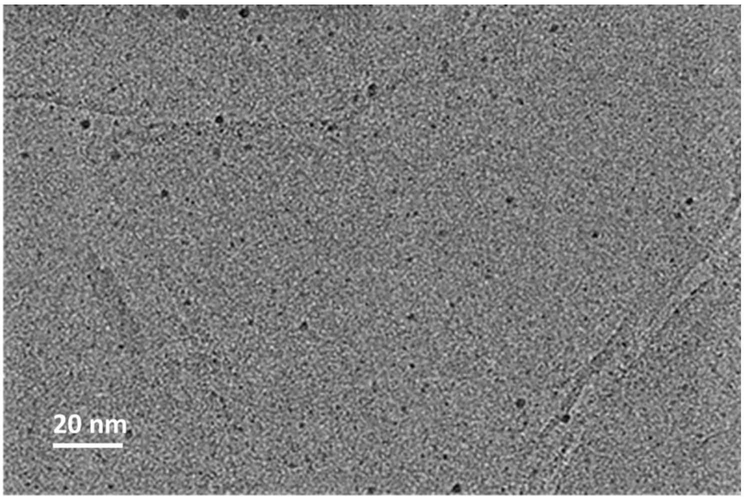

Fig. S8 Morphology of Pd species in the Pd/rGO-E-100 after five cycle reaction.

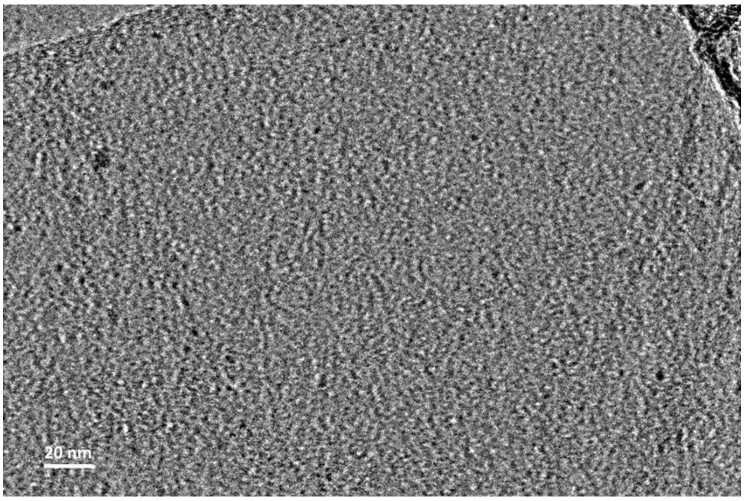

Fig. S9 Morphology of Pd species in the Pd/rGO-E-N_2H_4 obtained by reduction with hydrazine hydrate.

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