Supporting Information

Palladium Nanoparticles on Reduced Graphene Oxide for Efficient and Practical Heterogeneous Activation of Aryl Chlorides in Aqueous Media *via* Microwave-Assisted Conditions

Qingxiao Zhang,[†a] Zhan Mao,[†a] Kaixuan Wang[a], Nam Thanh Son Phan[*b], and Fang Zhang[*a]

[a] *The Education Ministry Key Lab of Resource Chemistry and Shanghai Key Laboratory of Rare Earth Functional Materials, Shanghai Normal University, 100 Guilin Rd., Shanghai, 200234, China*

[b] *Faculty of Chemical Engineering, Ho Chi Minh City University of Technology, 268 Ly Thuong Kiet Street, District 10, Ho Chi Minh City, VN 84, Vietnam.*

Table S1. Pd content of a series of Pd/rGO composites.

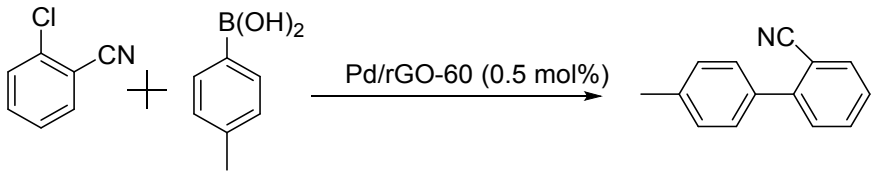
Entry	Catalyst	Pd content (mmol/g)
1	Pd/rGO-30	0.05
2	Pd/rGO-60	0.78
3	Pd/rGO-110	0.89

Table S2. Optimization of the reaction parameters in the Pd/rGO catalyzed Ullmann reaction.[a]

Entry	Catalyst	Base	Time (h)	Conversion (%)	Yield (%)
1[b]	Pd/rGO-60	CH_3COONa+KOH	1.0	2.0	1.80
2[c]	Pd/rGO-60	CH_3COONa+KOH	1.0	28.3	14.9
3[d]	Pd/rGO-60	CH_3COONa+KOH	1.0	40.8	30.9
4	Pd/rGO-60	CH_3COONa+KOH	1.0	72.3	69.5
5[e]	Pd/rGO-60	HCOONa	1.0	62.3	45.8
6[f]	Pd/rGO-60	CH_3COONa	1.0	26.5	24.5
7[g]	Pd/rGO-60	HCOONa+KOH	1.0	77.2	44.5
8[h]	Pd/rGO-60	HCOONa+NaOH	1.0	69.8	37.8
9[i]	Pd/rGO-60	CH_3COONa+NaOH	1.0	56.8	45.7
10[k]	$Pd(OAc)_2$	CH_3COONa+KOH	20	85.4	83.6
11[k]	Pd/rGO-60	CH_3COONa+KOH	2.0	10.2	5.4
12[k]	Pd/rGO-60	CH_3COONa+KOH	20	>99	85.6
13[j]	Pd/rGO-60	CH_3COONa+KOH	2.0	40.4	35.2
14[k]	Pd/rGO-60	CH_3COONa+KOH	2.0	10.2	5.4
15[k, l]	Pd/rGO-60	CH_3COONa+KOH	1.0	29.8	22.5
16[k]	$Pd(OAc)_2$	CH_3COONa+KOH	20	85.4	83.6

[a]Reaction conditions: 1.0 mmol chlorobenzene, 0.50 mmol TBAB, 1.5 mmol CH_3COONa, 2.5 mmol KOH,, 2.0 mL solvent (V_{water}:V_{MeOH}=1/1) and 0.50 mol% Pd catalyst, 100℃ (microwave heating); [b]70°C; [c]80°C; [d]90°C; [e]0.9 mmol HCOONa; [f]0.9 mmol CH_3COONa; [g]0.9 mmol HCOONa and 1.5 mmol KOH; [h]0.9 mmol HCOONa and 1.5 mmol NaOH; [i]0.9 mmol CH_3COONa and 1.5 mmol NaOH; [j]No TBAB; [k]Oil bath; [l]150°C.

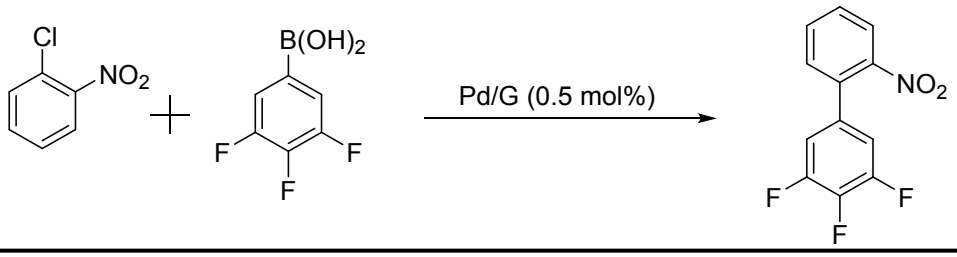
Table S3. Catalytic performances of Pd/rGO-60 catalyst in the reaction by changing for 4'-methyl-2-biphenylcarbonitrile.[a]



Entry	Time (h)	Solvent	Conversion (%)	Yield (%)
1	1	H_2O+EtOH	56.7	49.8
2	2	H_2O+EtOH	92.2	86.4
3	3	H_2O+EtOH	98.4	93.8
4	2	DMF	91.2	90.6

[a]Reaction conditions: 1.0 mmol 2-Chlorobenzonitrile, 1.2 mmol p-Tolylboronic acid, 0.50 mmol TBAB, 3.0 mmol K_3PO_4, 2.0 mL solvent (V_{water}/V_{MeOH}=1/1) and 0.50 mol% Pd catalyst, 100℃ (microwave heating).

Table S4. Optimization of reaction conditions of the synthesis of 2-nitro-3',4',5'-trifluoro-1,1'-biphenyl by using Pd/rGO-60 catalyst.[a]



Entry	Solvent	Base	Temperature (℃)	Conversion (%)	Yield (%)
1	H_2O/EtOH	K_2CO_3	80	52.8	45.2
2	EG	K_2CO_3	80	79.0	73.2
3	H_2O/THF	K_2CO_3	80	25.3	23.9
4	H_2O/DMF	K_2CO_3	80	Trace	Trace
5	H_2O/CH_3OH	K_2CO_3	80	Trace	Trace
6[b]	H_2O/EtOH	K_2CO_3	80	54.2	53.8
7	EG	NaOH	80	22.3	4.16
8	EG	K_3PO_4	80	38.2	30.3
9	EG	Na_2CO_3	80	28.9	25.1
10	EG	KF	80	40.6	37.9
11	EG	HCOONa	80	50.1	33.9
12	EG	CH_3COONa	80	66.9	56.5
13	EG	K_2CO_3	90	83.5	76.2
14	EG	K_2CO_3	100	92.1	89.7
15[c]	EG	K_2CO_3	100	91.2	85.1
16[d]	EG	K_2CO_3	100	90.3	79.5

[a]Reaction Condition: 1.0 mmol 1-chloro-2-nitro-Benzene, 1.2 mmol 3, 4, 5-trifluorophenyl-boronic acid, 0.50 mol% Pd/rGO-60, 3.0 mmol K_3PO_4, 2.0 mL solvent (V_{water}/V_{MeOH}=1/1), 1.5 h, microwave heating; [b]$Pd(OAc)_2$ as catalyst; [c]5.0 mmol 1-chloro-2-nitro-Benzene; [d]oil bath heating, 20 h.

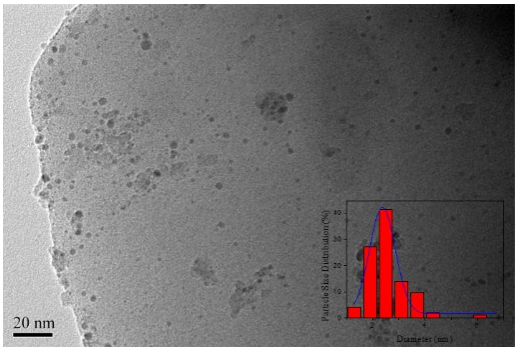


Figure S1. TEM image and particle size distribution of Pd/SiO_2 sample.

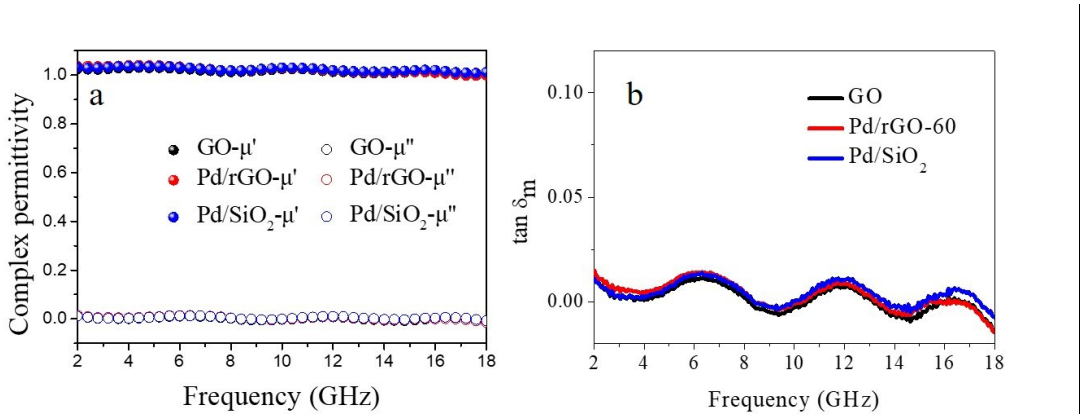


Figure S2. Frequency dependence of real part and imaginary part of permeability (a), and magnetic loss tangent (b) of rGO, Pd/rGO-60 and Pd/SiO_2 samples.

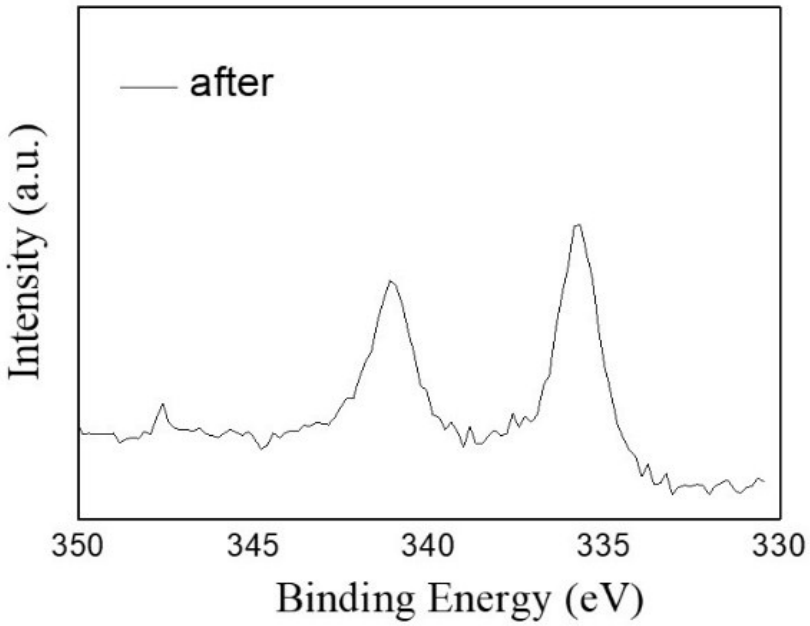


Figure S3. XPS spectrum of the reused Pd/rGO-60 catalyst after six cycles.

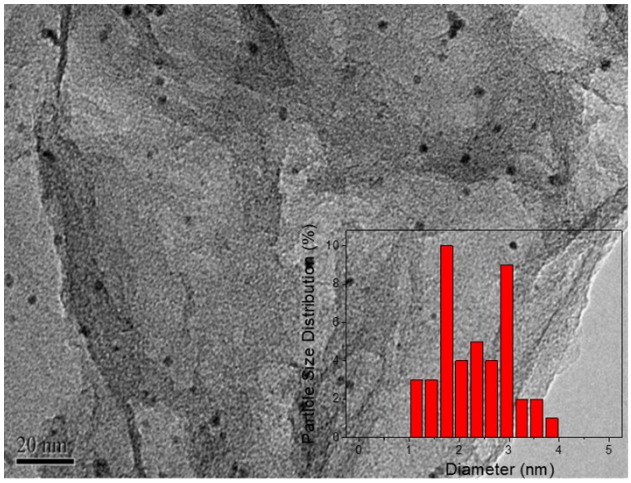


Figure S4. TEM image and particle size distribution of the reused Pd/rGO-60 catalyst after six cycles.