

Supplementary Materials

Synthesis and basic catalytic application of Pd nanoparticles supported on 3D nitrogen-doped reduced graphene oxide

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Experimental section

Materials

All chemical reagents were of analytical grade and were used as received. GO were prepared according to a modified Hummers' method.

Preparation of 3D-NrGO

In a typical experiment, 10 mL GO (10 mg L⁻¹) aqueous dispersion with 1 mL formaldehyde solution (37% wt), 200 mg melamine and 400 mg FeCl₃·6H₂O was sonicated for 20 min. Subsequently, the stable suspension was transferred and sealed into a 50 mL Teflon-lined stainless steel autoclave, heated at 180 °C for 24 h, and then cooled to room temperature naturally. After that, the obtained three-dimensional graphene hydrogel was treated by freeze-drying for 12 h. After heating the freeze-dried graphene gel at 850 °C for 2h with a heating speed of 5 °C/min under Ar atmosphere, the 3D nitrogen-doped reduced graphene oxide composite (3D-NrGO) was obtained by removing the Fe₂O₃ with 8M HCl and washing the residue until pH is equal to 7.0.

Preparation of 3D-NrGO/Pd

In a typical experiment, 2 mL H_2PdCl_6 solution (5 mg/mL) was added into 20 mL PEG200 to form a homogeneous mixture, and then the above 50 mg 3D-NrGO was added into the above mixture and dispersed. The dispersion was kept for 24 h at 100 °C. After steps of rinsing with ethanol and drying in air, the resultant Pd NP-decorated 3D-NrGO composite was obtained, and denoted as 3D-NrGO/Pd. The product was collected by centrifugation and washed with EtOH three times. The content of Pd was estimated to be 8.1 wt% based on ICP-MS.

Suzuki Reduction Catalyzed by 3D-NrGO/Pd

Aryl halide (1.0 mmol), arylboronic acid (1.2 mmol), K_2CO_3 (2.5 mmol), and 1.5 mg of 3D-NrGO/Pd were added to the vessel with 6 mL water/EtOH (v/v=1/2). The mixture was continuously stirred at 60 °C for the desired time until complete consumption of the starting aryl halide. The reaction progress was monitored by GC at a fixed time interval. After the reaction, the catalyst was filtered from the mixture, washed by deionized water and absolute alcohol, and then dried in vacuum at 60 °C overnight. The product was extracted with diethyl ether and determined by GC, which using n-decane as the internal standard.

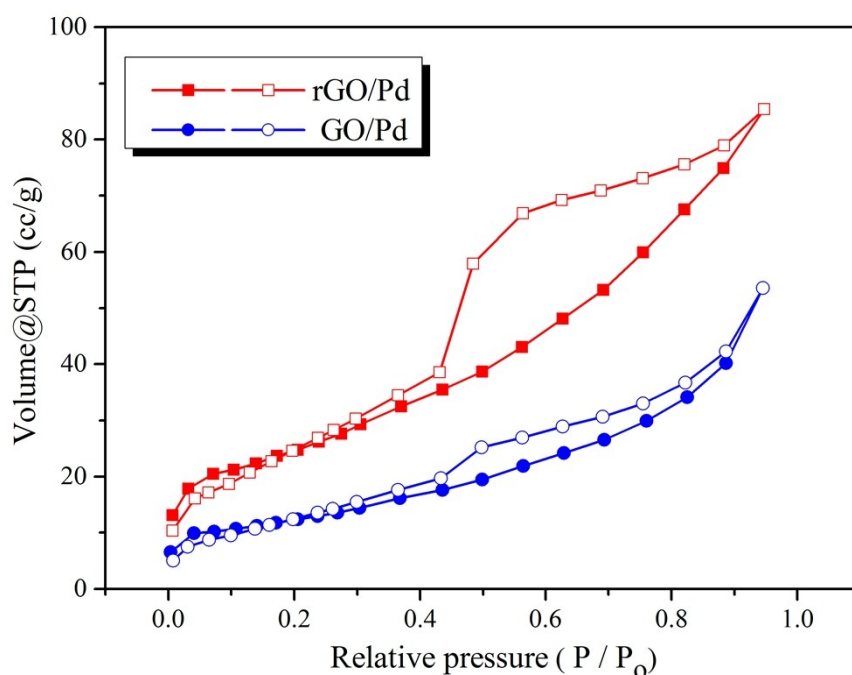


Fig. S1 (a) N_2 adsorption-desorption isotherms of rGO/Pd and GO/Pd composites

Characterization of Products

4-nitrobiphenyl (Table 2, entry 1, 4 and 8):

Pale yellow solid, ^1H NMR (300 MHz, CDCl_3): δ (ppm): 8.30 (d, $J = 8.2$ Hz, 2H), 7.73 (d, $J = 8.9$ Hz, 2H), 7.64-7.61 (m, 2H), 7.53-7.42 (m, 3H).

(Known compound, CAS 92-93-3, see: V. Percec, G.M. Golding, J. Smidrkal, O. Weichold, *J. Org. Chem.*, **2004**, *69*, 3447.).

Biphenyl (Table 2, entry 2 and 9):

White solid; mp 69-70 °C (lit. 72 °C), ^1H NMR (300 MHz, CDCl_3): δ 7.38 (t, $J = 7.2$ Hz, 2H), 7.47 (t, $J = 22.0$ Hz, 4H), 7.63 (d, $J = 8.0$ Hz, 4H).

(Known compound, CAS 92-52-4, see: Oncel, Nurdal et al. *Journal of Organometallic Chemistry*, 2016, 811, 81-90).

4-methoxybiphenyl (Table 2, entry 3):

White solid, ^1H NMR (300 MHz, CDCl_3): δ (ppm): 7.57-7.52 (m, 4H), 7.45-7.40 (m, 2H), 7.33-7.26 (m, 1H), 6.98 (m, 2H), 3.86 (s, 3H).

(Known compound, CAS 613-37-6, see: E. Shirakawa, Y. Hayashi, K.I. Itoh, R. Watabe, N. Uchiyama, W. Konagaya, S. Masui, T. Hayashi, *Angew. Chem. Int. Ed.*, **2012**, *51*, 218.).

4-Cyanobiphenyl (Table 2, entry 5)

White solid; mp 83-85 °C (lit. 83-84 °C); ^1H NMR (300 MHz, CDCl_3): δ 7.39-7.45 (m, 1H), 7.45-7.53 (m, 2H), 7.55-7.63 (m, 2H), 7.64-7.77 (m, 4H).

(Known compound, CAS 2920-38-9, see: Garel, Claire et al. *Applied Catalysis, A: General*, 2015, 504, 272-286)

3-Methyl-biphenyl (Table 2, entry 6)

^1H NMR (300 MHz, CDCl_3): δ 7.58 (d, $J = 7.6$ Hz, 2H), 7.42 (m, 4H), 7.33 (t, $J = 7.4$ Hz, 2H), 7.16 (d, $J = 7.4$ Hz, 1H), 2.42 (s, 3H).

(Known compound, CAS 643-93-6, see: Giacalone, Francesco et al. *ACS Nano*, 2016 10(4), 4627-4636)

2-Methyl-biphenyl (Table 2, entry 7)

^1H NMR (300 MHz, DMSO): δ 7.45 (t, $J = 7.3$ Hz, 2H), 7.41-7.22 (m, 6H), 7.22-7.15 (m, 1H), 2.23 (s, 3H).

(Known compound, CAS 643-58-3, see: Oncel, Nurdal et al. *Journal of*

Organometallic Chemistry, 2016, 811, 81-90)