

Graphene oxide/carbon nanotubes-Fe₃O₄ support Pd nanoparticles for hydrogenation of nitroarenes and C-H activation

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1. Materials

All chemicals were used as received without further purification: graphite powder (200 mesh) (Alfa Aesar, Johnson Matthey Company); Multi-walled carbon nanotubes (Beijing Cnano Technology Limited Purity: > 95%, average length: 10 μm , average diameter: 11 nm); iron (II) oxalate dihydrate (Aladdin Industrial Corporation); palladium acetate (Wako Pure Chemical Industries, Ltd); 1-butyl-3-methylimidazolium-tetrafluoroborate ([BMIM]BF₄); cuprous iodide (Tokyo Chemical Co., Ltd); nitrobenzene, 4-nitroanisole, 4-nitrotoluene, cesium fluoride (Sinopharm Chemical Reagent Co., Ltd); 8-nitroquinoline, benzoxazole (Energy Chemical); 1,3-dinitrobenzene, p-nitrobenzoic acid, o-nitrobenzoic acid, methyl 4-nitrobenzoate (Xiya Chemical Industry Co., Ltd); 4-nitrobenzotrile, p-nitroacetophenone, iodobenzene, p-nitrophenol, o-nitrophenol, silver oxide, phenylacetylene (J&K Scientific Co., Ltd); potassium permanganate, ethanol, hydrogen peroxide, tetrahydrofuran, sulfuric acid, phosphoric acid, N,N-dimethylformamide, ammonium chloride, magnesium sulphate (Beijing Chemical Works).

2. A schematic illustration of plasma system

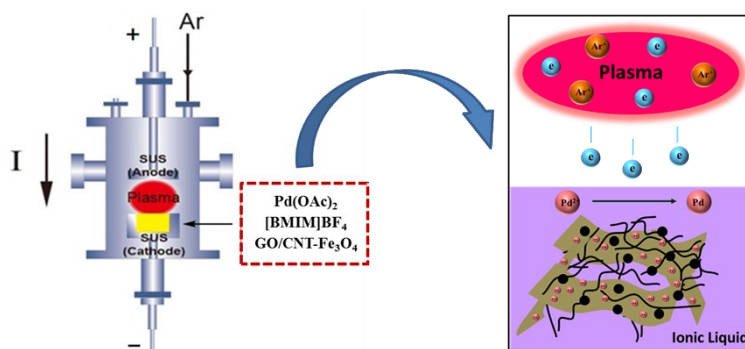


Fig. S1. A schematic illustration of plasma system.

3. SEM and TEM images of Pd-1, Pd-2, Pd-4 and Pd-5

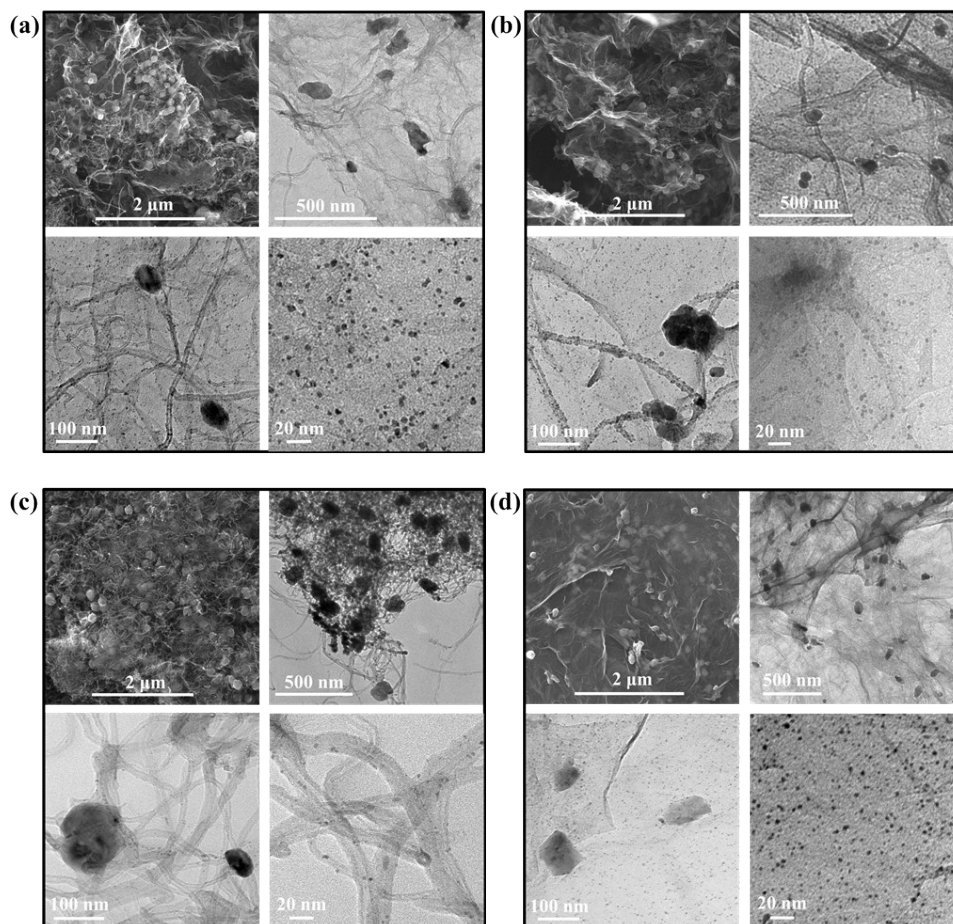


Fig. S2 SEM and TEM images of Pd-1 (a), Pd-2 (b), Pd-4 (c) and Pd-5 (d).

4. The size distribution of Pd nanoparticles

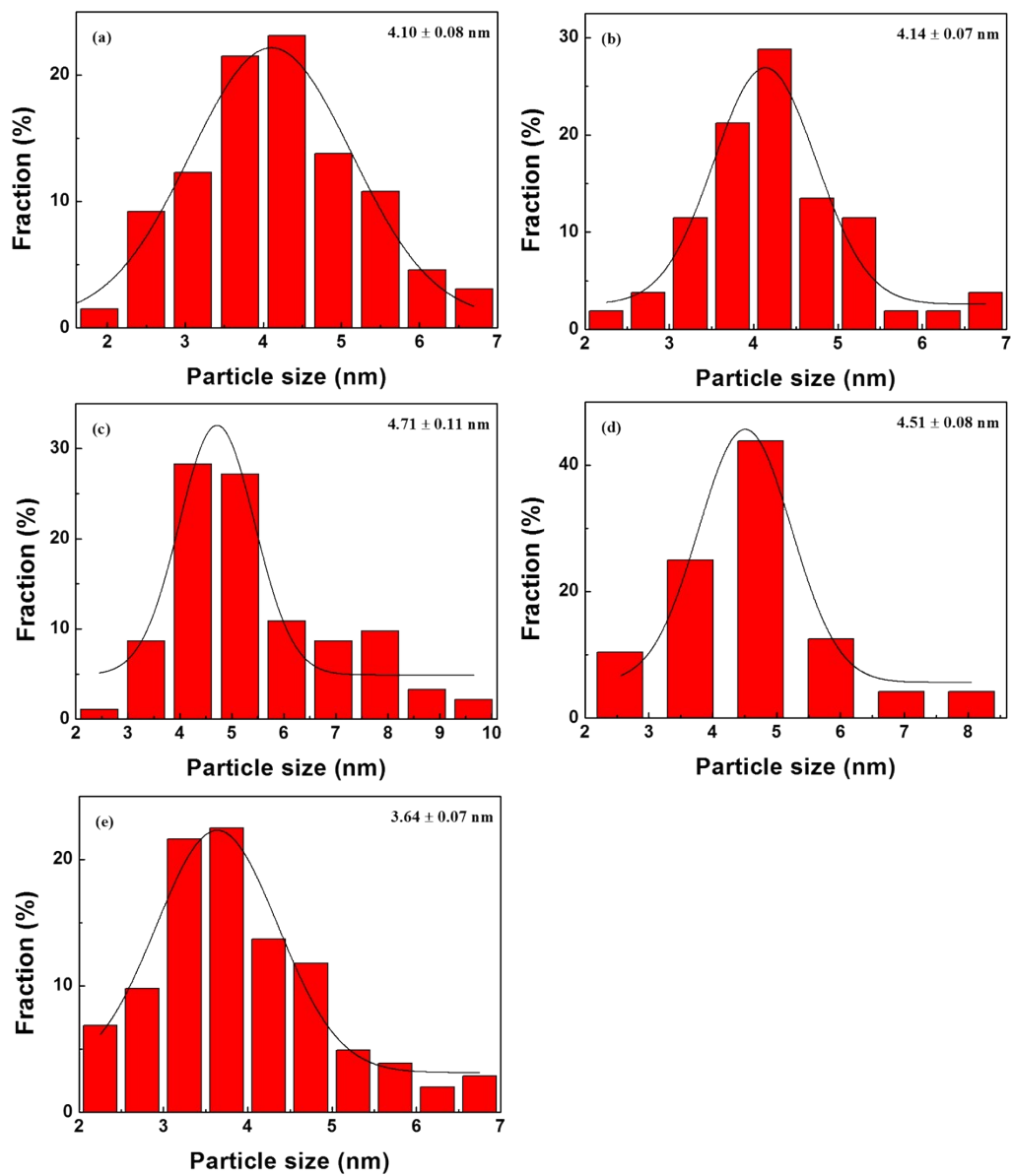


Fig. S3 Particle size distribution of Pd-1 (a), Pd-2 (b), Pd-3 (c), Pd-4 (d) and Pd-5 (e).

5. High resolution XPS spectra of Pd 3d of Pd-3

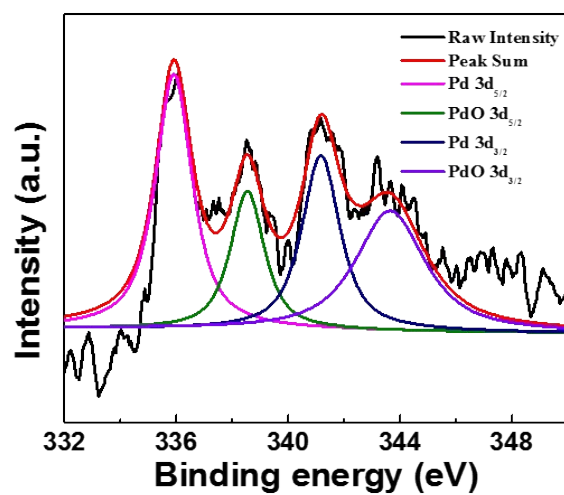


Fig. S4 High resolution XPS spectra of Pd 3d of Pd-3.

6. Water contact angles of Pd-n

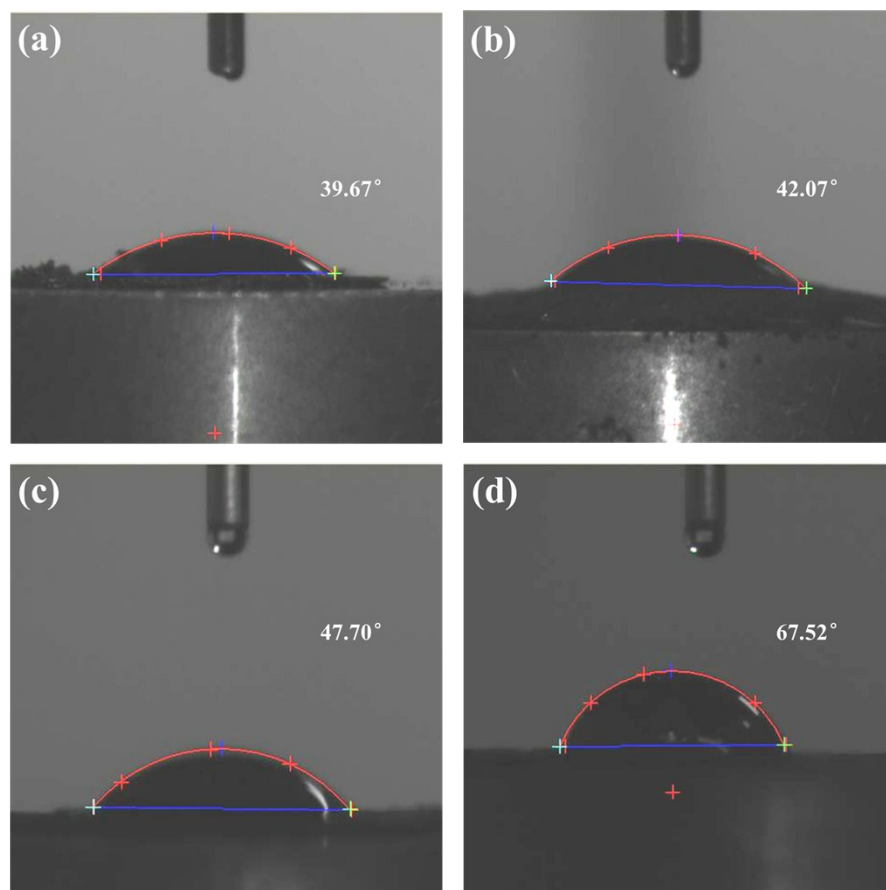


Fig. S5 Water contact angles of Pd-5 (a), Pd-1 (b), Pd-2 (c), and Pd-3 (d).

7. XRD patterns of reused catalyst

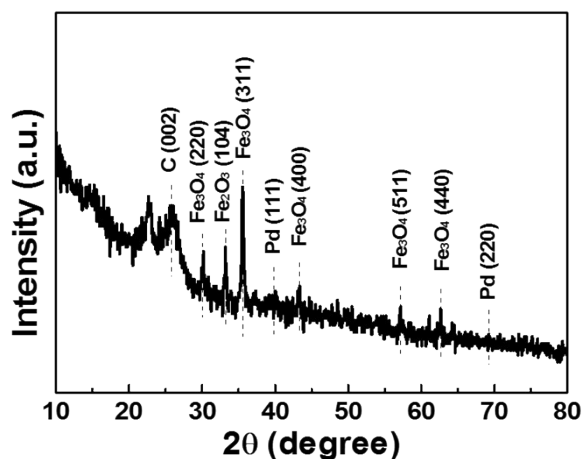


Fig. S6 XRD patterns of reused catalyst.

8. General procedure for C-H bond functionalization reactions

8.1. Arylation of benzoxazole

To an micro-reaction vial was added CsF (2.5 equiv., 189.9 mg), Pd-3 catalyst (3 mol% , 22 mg) and CuI (2 equiv., 190.5 mg). To this was added benzoxazole (0.5 mmol, 50 μ L), iodobenzene (1 mmol, 112 μ L) and DMF (2 mL). The reaction mixture was heated to 140 °C with stirring for 18 h. To the reaction mixture was added satd aq NH₄Cl (20 mL) and the mixture was stirred in air. The mixture was then extracted into ethyl acetate. The organic layers were combined, dried over MgSO₄, filtered and the solvent removed under reduced pressure. The resulting brown residue was dry-loaded onto silica gel, and purified by flash chromatography eluting with EtOAc in petroleum ether solvent systems to give the product [1-3].

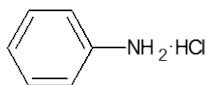
8.2 Glaser coupling reaction of phenylacetylene

To a mixture of Pd-3 catalyst (2 mol%, 14.7 mg) and Ag₂O (0.5 mmol, 115.9 mg) in THF (2.0 mL) was added phenylacetylene (0.5 mmol, 55 μ L), and then the mixture was stirred at 60 °C for 12 h [4]. The reaction progress was monitored by TLC. After the phenylacetylene consumed, the solvent was removed under a reduced pressure. The product was filtered through a short silica column with

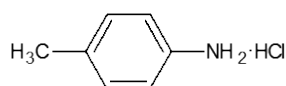
petroleum ether (60-90 °C) to remove catalyst and then was purified with a silica column using petroleum ether (60-90 °C) as eluent, giving 1,4-diphenylbutadiyne as a white solid.

9. ¹H NMR spectra data

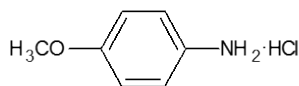
Aniline hydrochloride: ¹H NMR (300 MHz, CD₃OD) δ 7.62-7.45 (m, 3H), 7.41 (d, *J* = 8.4 Hz, 2H).



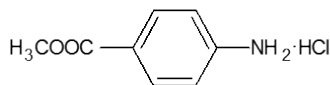
4-Methylaniline hydrochloride (Table 3, entry 1): ¹H NMR (400 MHz, CD₃OD) δ 7.25 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 8.3 Hz, 2H), 2.29 (s, 3H).



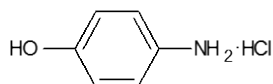
4-Methoxyaniline hydrochloride (Table 3, entry 2): ¹H NMR (300 MHz, CD₃OD) δ 7.41-7.25 (m, 2H), 7.14-6.99 (m, 2H), 3.83 (s, 3H).



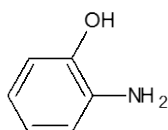
4-Aminobenzoic acid methyl ester hydrochloride (Table 3, entry 3): ¹H NMR (300 MHz, CD₃OD) δ 8.24-8.10 (m, 2H), 7.57-7.50 (m, 2H), 3.93 (s, 3H).



4-Aminophenol hydrochloride (Table 3, entry 4): ¹H NMR (300 MHz, CD₃OD) δ 7.24 (d, 2H), 6.92 (d, *J* = 8.7 Hz, 2H).

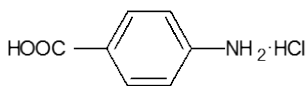


2-Aminophenol (Table 3, entry 5): ¹H NMR (300 MHz, , CD₃OD) δ 6.75-6.55 (m, 4H).

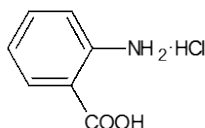


4-Aminobenzoic acid hydrochloride (Table 3, entry 6): ¹H NMR (300 MHz, MeOD) δ 8.34-7.84 (m,

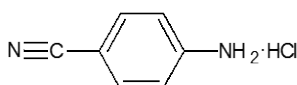
2H), 7.74-7.26 (m, 2H).



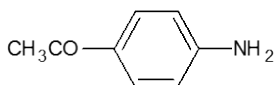
2-Aminobenzoic acid hydrochloride (Table 3, entry 7): ^1H NMR (300 MHz, CD_3OD) δ 8.22 (d, J = 7.8 Hz, 1H), 7.76 (t, J = 7.0 Hz, 1H), 7.68-7.42 (m, 2H).



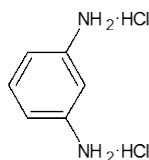
4-Aminobenzonitrile (Table 3, entry 8): ^1H NMR (300 MHz, CD_3OD) δ 7.92-7.79 (m, 2H), 7.62-7.39 (m, 2H),.



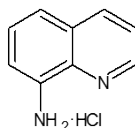
4-Aminoacetophone (Table 3, entry 9): ^1H NMR (300 MHz, CDCl_3) δ 7.77 (d, J = 8.6 Hz, 2H), 6.61 (d, J = 8.6 Hz, 2H), 4.15 (br, 2H), 2.47 (s, 3H)



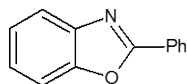
1,3-Diaminobenzene (Table 3, entry 10): ^1H NMR (300 MHz, CD_3OD) δ 7.77-7.52 (m, 1H), 7.50 (d, J = 1.9 Hz, 3H).



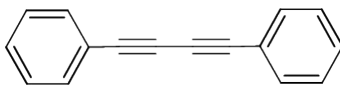
8-Aminoquinoline (Table 3, entry 11): ^1H NMR (300 MHz, CD_3OD) δ 9.05 (dd, J = 4.7, 1.6 Hz, 1H), 8.71 (dd, J = 8.4, 1.5 Hz, 1H), 7.98-7.88 (m, 1H), 7.82 (dd, J = 8.4, 4.7 Hz, 1H), 7.78-7.68 (m, 2H).



2-phenylbenzoxazole (5a): ^1H NMR (400 MHz, CDCl_3) δ 8.23-8.13 (m, 2H), δ 7.73-7.55 (m, 1H), δ 7.55-7.33 (m, 1H), δ 7.31-7.21 (m, 3H), δ 7.15 (m, 2H).



1,4-diphenylbutadiyne (7a): ^1H NMR (400 MHz, CDCl_3) δ 7.55-7.51 (m, 4H), δ 7.38-7.30 (m, 6H).



References

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