

Electronic Supplementary Information

Efficient covalent modification of graphene by diazo chemistry

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Experimental Section

1. Synthesis of diaryldiazo for graphene modification

A suspension of 4,4'-bis(dimethylamino)benzophenone (1.5 g, 5.6mmol) in ethanol (30 mL) was treated with hydrazine hydrate (4.06 mL, 84mmol). The resulting mixture was heated to a gentle reflux for 48 h, cooled, and concentrated under vacuum. The residue was washed with propan-2-ol (10 mL) and the resulting solid collected by filtration and dried under vacuum to get the product (yield: 91%). m.p. 176 °C.

Added 0.25 g (0.89mmol) 4, 4'-bis(dimethylamino)benzophenone-hydrazone, 0.154 g (2.5 mmol) MnO₂, 0.32 g Na₂SO₄ and 0.1 ml EtOH (KOH saturated solution) into 5 ml dry THF. The mixture was stirred in dark for 3 hours. The reaction was traced with MS spectra to check whether or not there was complete consumption of starting materials. IR was used to check whether or not there was a characterized peak for =N₂ group (2028 cm⁻¹). The mixture was filtered through a celite plug, and dried under vacuum to give a dark green powder product (yield: 89%).

2. Treatment of graphene with diaryldiazo

Graphite oxide was synthesized by the modified Hummers method. Aqueous suspensions of graphene oxide (GO) was prepared by 30 min sonication of graphite oxide. Diaryldiazo (0.25 g) was dissolve in 5 ml Et₂O, then the GO was added into the solution. The solvent was removed under vacuum. The mixture was heated at 100-120 °C. The color was changed from dark green to light yellow in 20 min. The final product (DC-GO) is washed with acetone and water for several times.

3. Synthesis of diazonium salts and diazonium functionalization to graphene

A range of diazonium salts were prepared by reaction of the amines with sodium nitrite and hydrochloric acid in THF/H₂O at -5 - 0 °C. The standard procedure was shown below. A stirring solution of the amine (1 eq) in THF/H₂O was cooled to -5 °C then 3M hydrochloric acid (2 eq) was added to the mixture was stirred for up to 5 minutes. NaNO₂ (1.1 eq) was dissolved in 1 ml water, cooled down, and then added into the above mixture. The solution was stirred for up to 30 minutes. H-acid confirmed presence of the diazonium salt. NaOAc (2 eq) was added to neutralize the solution. The diazonium salts were used immediately.

The DC-GO was reduced by typical reduction procedure using hydrazine hydrate¹. Then, the DC-rGO (100 mg, 1 eq) was immersed in a solution of diazonium salt (1.65 mmol, 2 eq). The reaction was left to stand at 5 °C for 18 hours. The product DC-rGO-DNS was filtered through sinter funnel and washed with water and acetone until the washing was colorless then DC-rGO-DNS was dried under vacuum.

4. Characterization and measurement

Characterization of organic compounds was done using the following equipment and settings. Infrared (IR) spectra were recorded on Bruker Tensor 27 FT-IR spectrometers. ¹H NMR and ¹³C NMR were recorded on Bruker AVF400 (400 MHz) spectrometer. Mass spectra (m/z) were obtained with a Fisons Platform spectrometer with electrospray ionisation (ESI).

FT-IR (Bruker, Tensor 27) and Raman spectra (Horiba JobinYvon, France) were used to characterize the functionalized graphene. XPS was performed on a lab built spectrometers at 10⁻⁹ - 10⁻¹⁰ Torr, with an Al K-α X-ray source (1486.6 eV). TEM (JEOL, JEM-2100F) was used to characterize the morphology and structure of the samples.

Supporting data

1. The characterization of diaryldiazo

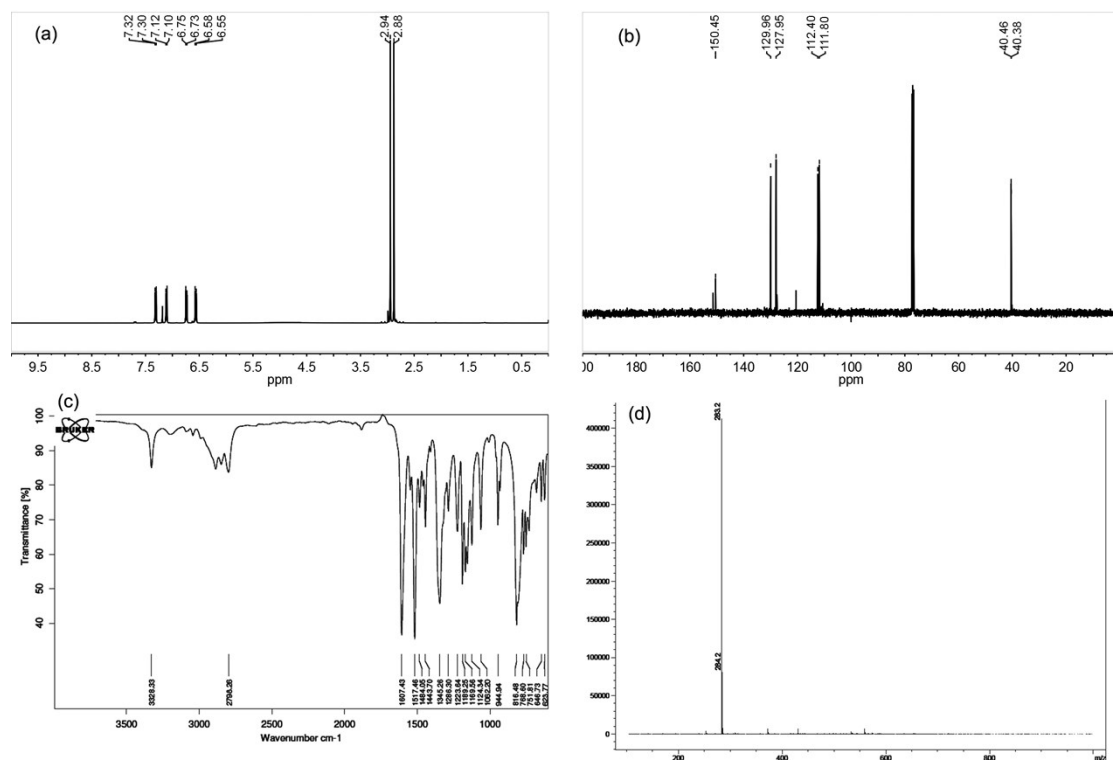


Fig. S1 (a) ^1H NMR, (b) ^{13}C NMR, (c) FTIR, (d) MS spectra of 4, 4'-bis(dimethylamino)benzophenone-hydrazone

^1H NMR (d₆-DMSO, 400 MHz, δ): 2.88 (s, 2H), 2.94 (s, 2H), 6.55 (d, 2H), 6.75 (d, 2H), 7.10 (d, 2H), 7.30 (d, 2H). ^{13}C NMR (d₆-DMSO, 400 MHz, δ): 40.4, 111.8, 112.4, 127.6, 128.0, 129.9, 150.5. IR: 3228, 1607, 1517, 1345, 1189 cm^{-1} . MS m/z (%): 283.2 (100).

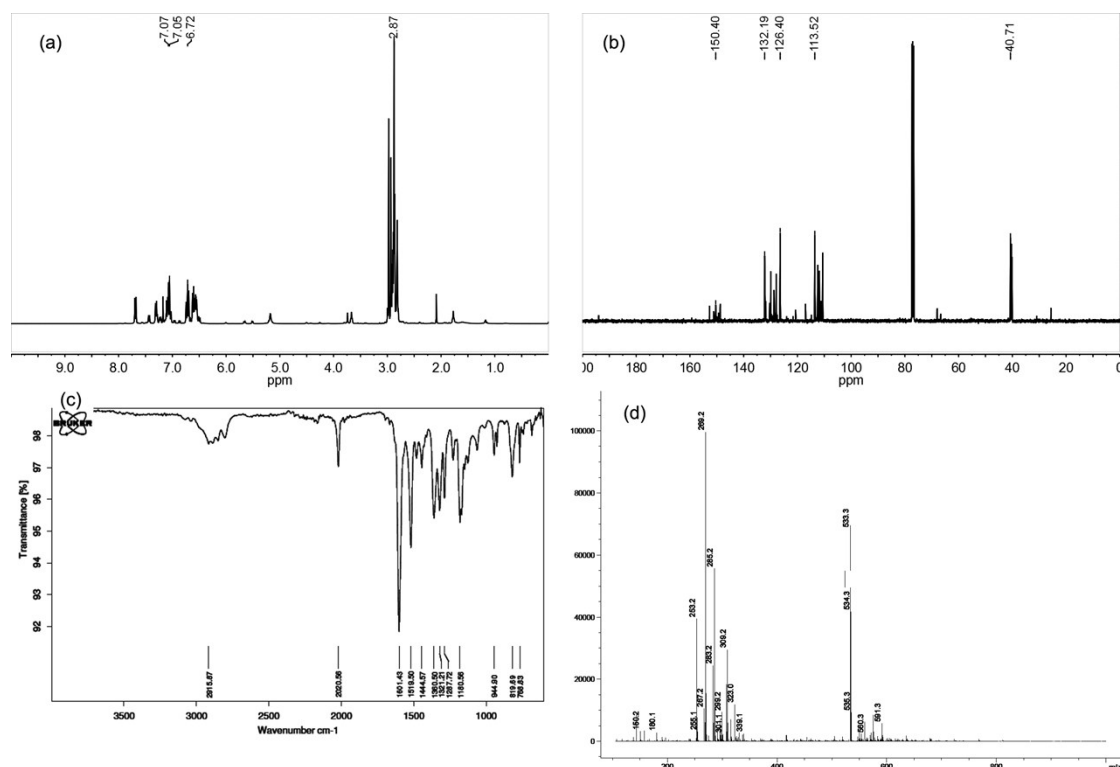


Fig. S2 (a) ^1H NMR, (b) ^{13}C NMR, (c) FTIR, (d) MS spectra of diaryldiazo

^1H NMR (CDCl_3 , 400 MHz, δ): 2.87 (s, 12H), 6.72 (d, 4H), 7.07 (d, 4H). ^{13}C NMR (CDCl_3 , 200 MHz, δ): 40.7, 113.5, 126.4, 132.1, 150.4. IR: 2020, 1601, 1519, 1360 cm^{-1} . MS m/z (%): 269.2 (100).

2. The XPS spectra of graphene

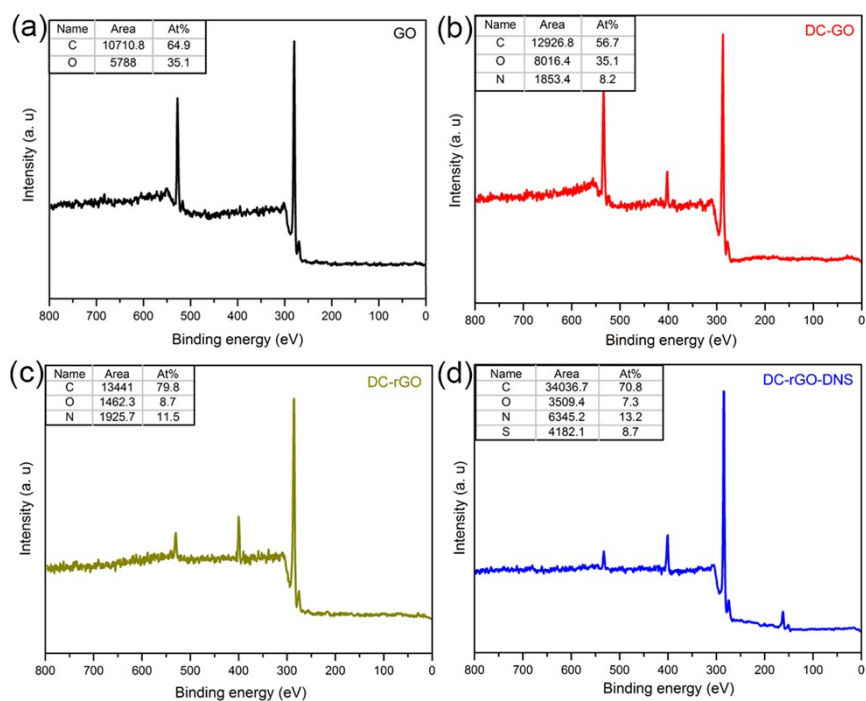


Fig. S3 The XPS survey spectra of (a) GO, (b) DC-GO, (c) DC-rGO and (d) DC-rGO-DNS.

References

1. S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S. T. Nguyen and R. S. Ruoff, *Carbon*, 2007, **45**, 1558-1565.