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Synthesis of conjugated covalent organic frameworks/graphene composite for supercapacitor electrode

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Chemicals and Regents

1,3,5-Triformylbenzene was synthesized as reported elsewhere.[S1] Graphene oxide (GO) was prepared via a modified Hummers method.[S2] Amine modified reduced graphene oxide (NH_2-rGO) was prepared by one-pot solvothermal process with GO as raw material in the presence of ammonia.[S3] All other reagents were of analytical grade and used as purchased without further purification.

Synthesis of conjugated covalent organic frameworks/graphene composite, COFs and NH_2-rGO-CHO.

NH_2-rGO (48mg) was weighed into a small vial and disperse in 6.0 mL of 1,4-dioxane. After being stirred for 0.5 h, 1,3,5-triformylbenzene (48mg), 1,4-diaminobenzene (48 mg) and acetic acid aqueous (0.6 mL 3.0 mol/L) was added to the above dispersion successively under mild stirring. All the above dispersion transferred into a Teflon-lined autoclave and heated at 120 ^oC for 2 days. Afterwards, the obtained dark green solid was isolated by centrifugation, washed with N,N-dimethylformamide (3×10 mL) and tetrahydrofuran (3×10 mL), and dried at 80 ^oC under vacuum for 12 h to yield a new composite COFs/NH_2-rGO (Scheme 1). In order to compare the energy storage properties of COFs/NH_2-rGO, COFs was prepared with the same method for fabricating COFs/graphene without adding NH_2-rGO into the reaction. In order to confirm the formation of imine bonds between graphene and COFs, NH_2-rGO was treated with 1,3,5-triformylbenzene in the presence of acetic acid to obtained a sample NH_2-rGO-CHO.

Characterization

The products were visualized using a JSM-7001F field emission scanning electron microscopy (FE-SEM). X-ray diffraction (XRD) spectra were obtained on a Bruker D8 Advance X-ray diffractometer. Fourier transform infrared (FT-IR) analysis was conducted on a BRUKER TENSOR FT-IR spectroscopy. Solid-state ^{13}C CP-MAS NMR spectra were carried out on a Varian infinity-plus 400 spectrometer. The X-ray photoelectron spectroscopy (XPS) was performed on VG ESCALAB HP photoelectron spectrometer. Raman spectra were measured using a Renishaw inVia Raman microscope with 532 nm wavelength excitation.

Electrochemical studies were carried out in a three-electrode system with a Na_2SO_4 electrolyte solution (1 mol L^{-1}). Freshly prepared material on nickel mesh, a platinum electrode, and a saturated calomel electrode (SCE) were used as the working, counter, and reference electrodes, respectively. The working electrode was fabricated by mixing 80 wt% prepared material, 10 wt% poly(tetrafluoroethylene) binder, and 10 wt% Ketjenblack (EC-600JD) in an agate mortar. An appropriate amount of ethanol was then added to this mixture to make slurry, which was subsequently coated on Ni foam (1×1 cm^2) and dried in an oven at 110 °C for 2 h. The Ni foams with active materials were finally pressed under 10 MPa to obtain the working electrodes. Cyclic voltammetry (CV) was carried out on a CHI 660E electrochemical workstation. Galvanostatic charge–discharge cycle tests were performed on a CT2001A-LAND cell test system.

References

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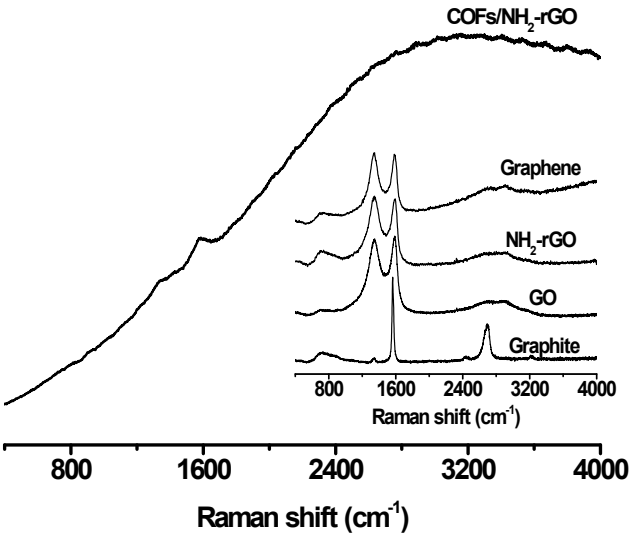

Fig. S1 Raman spectra of Graphite, GO, NH_2-rGO, Graphene and COFs/NH_2-rGO.

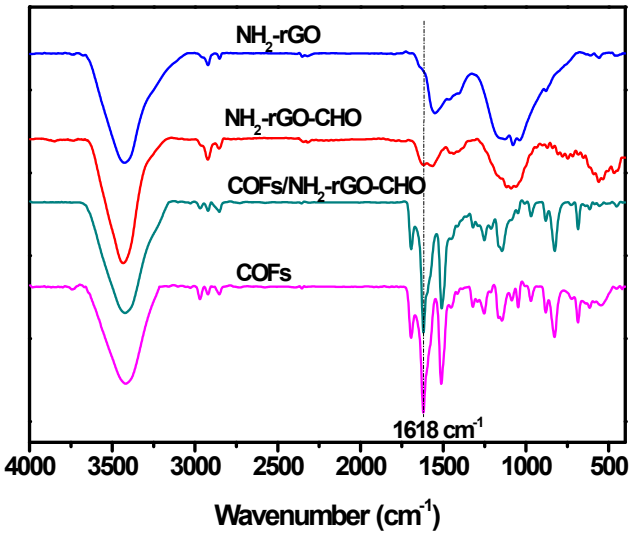

Fig. S2 IR spectra of NH_2-rGO, NH_2-rGO-CHO, COFs/NH_2-rGO and COFs.