Electronic Supplementary Material (ESI) for Nanoscale

Electronic supplementary information

Tunable Photoluminescence and Spectrum Split from Fluorinated to Hydroxylated Graphene

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1. TEM, HRTEM spectra and element analysis of the prepared FG samples

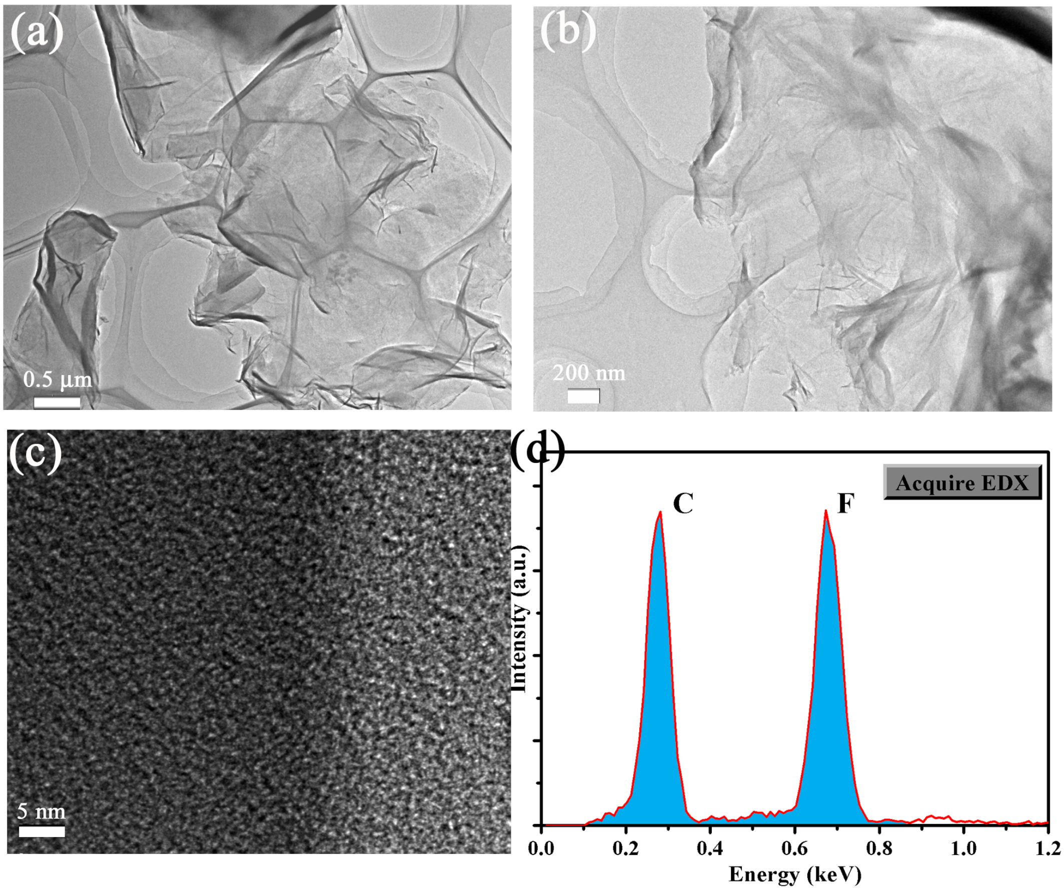

Figure. S1 (a) A wide-field image of the obtained FG sheets. (b) A closer look at the thin FG sheets with wrinkling surface and optical transparency. (c) HRTEM image of FG displays diminished hexagonal structure and disordered morphology as a result of the invasion of fluorine atom. (d) Energy dispersive X-ray (EDX) spectrum of the obtained FG sheets, showing that no other element than carbon and fluorine can be detected on the FG sheets.

2. The formula and yield of the prepared hydroxyl-functionalized FG sheets

Table S1 The formula and yield details of samples from FG-0 to FG-7

	FG-0	**FG-1**	**FG-2**	**FG-3**	**FG-4**	**FG-5**	**FG-6**	**FG-7**
FG/mg	100	100	100	100	100	100	100	100
NaOH/mg	0	66.41	132.82	199.23	265.64	332.05	398.46	464.87
KOH/mg	0	92.92	185.84	278.76	371.68	464.60	557.52	650.44
Yield (%)	97	20	37	42	65	77	87	90

To conduct the reaction, the as prepared FG (100 mg) was blended with NaOH–KOH mixture powder at different ratios according to the above Weight Ratio Table. To ensure as large contact area among the mixture as possible, the initial NaOH and KOH pellets were first milled into powder using a quartz mortar, and then blended uniformly with FG. Meanwhile, in order to obtain liquid eutectic alkali and mobile hydroxyl anion the weight ratio of NaOH should be kept around 43.1%. For the control sample, no alkali was added. The mixture was then heated at 180 ^{o}C for 6 h in air.

After cooling down to room temperature, the product was dispersed in 100 mL Milli-Q water and sonicated at 40% power for 1 h dissolve alkali and further exfoliate the obtained graphene sheets. After the residual FG that flows on the surface of the solution was carefully pipetted, the product was vacuum filtered onto a microporous membrane (0.45 μm), followed by being rinsed with Milli-Q water (until the PH value reaches neutral) and dried through vacuum freeze drying for 48 h. Finally, the product was collected for yield calculation and following characterizations.

3. FTIR and XRD spectra of the samples

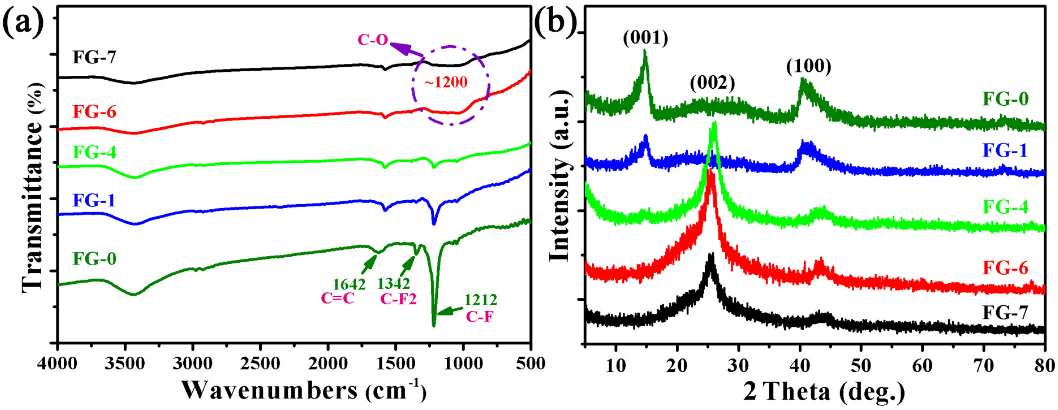

Figure. S2 (a) FTIR spectra and (b) XRD patterns of progressively hydroxyl-functionalized FG sheets.

In Fourier transform infrared (FTIR) spectra analyses (Figure 2a), the peaks located at 1212 cm^{-1} can be ascribed to the stretching vibration of the C–F covalent bonds, and absorption at 1342 cm^{-1} is assigned to the stretching vibration of the CF$_2$ moieties in the rings located at the edges.[1-2] And the characteristic stretching vibrations of C=C at 1642 cm^{-1} could be observed in all the samples. However, the intensity of the CF$_2$ functional groups gradually decreases with increased weight ratio of alkali/FG, and disappears completely after the ratio reaches 6 (sample FG-6). Such changes also occur within the covalently bound C–F functional groups. Meanwhile, a broad absorption located around 1200 cm^{-1} gradually gains intensity and becomes obvious from sample FG-6; as discovered in previous reports,[3-5] such a vibrational absorption is characteristic of C-OH groups on graphene skeleton.

The (001) peaks in XRD spectra, which are a reflection in a hexagonal system particularly for compounds possessing a very high fluorine level, weaken distinctly accompanying with the increased alkali ratio and also disappear from FG-6. In contrary, the (002) reflection narrows and a d-spacing of 0.35 nm can be deduced, indicating a more perfect C sp^2 structure with fewer defects are gradually restored.

4. XPS spectra of the progressively hydroxyl-functionalized FG sheets

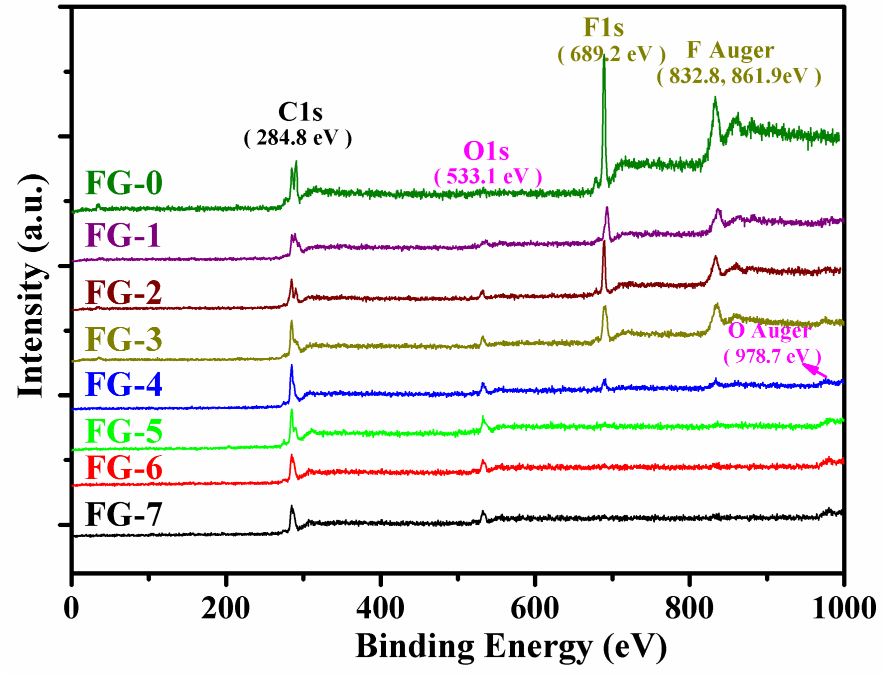

Figure. S3 XPS survey spectra of samples from FG-0 to FG-7

To present more detailed compositional analysis of the as-prepared samples, XPS investigation was performed to monitor the changes of element concentration. The corresponding results are shown in Fig. S3. Agree well with our previously prepared FG, no detectable nitrogen or oxygen element can be found in the initial FG-0, showing the high purity of the sample. With the alkali weight increases, the concentration of fluorine decreases while the concentration of oxygen first increases to maximum at O/C=0.30 (FG-5) and then stables at about 0.15 (FG-7), suggesting successful substitution of fluorine for hydroxyl.

5. XPS survey spectrum and corresponding C1s high-resolution XPS spectrum of FGi

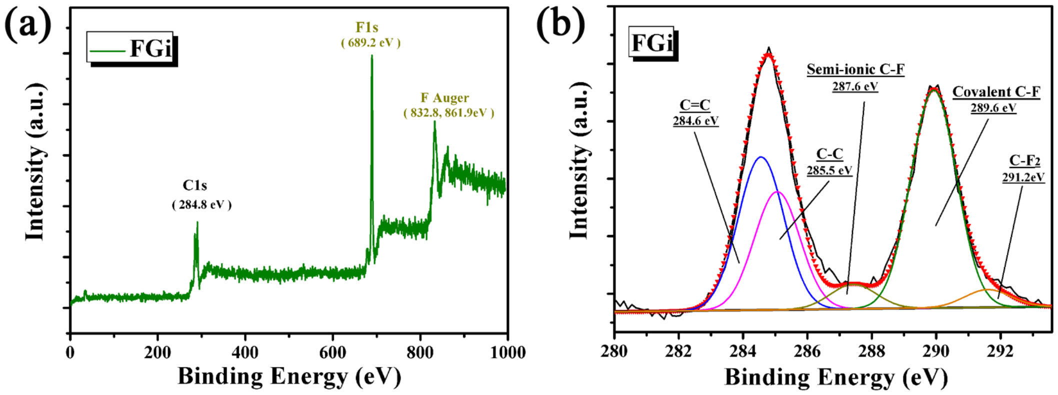

Figure. S4 (a) XPS survey spectrum of FGi, and (b) C1s high-resolution XPS spectrum of FGi and corresponding Gaussian fitting result.

The chemical composition and bond nature of the raw material (FGi) were also measured, and the relating results are shown in Fig. S4. The Gaussian fitting result of C1s high-resolution XPS indicates that three types of C-F bonds can be found on the structure of FGi. After sonication, while some fluorine loses during the process (from F/C≈0.63 of FGi to about F/C≈0.43 of FG-0)[1], the obtained FG sheets inherit the C-F bond nature of FGi, which also has the same three bonds. Thus FGi and FG share the similar electronic structure due to fluorine invasion, both of which exhibit hybridized structure consisting of sp^2 and sp^3 carbon on the plane. Meanwhile, compared with FGi, the sp^2 structure of FG is gradually restored due to the loss of fluorine atoms.[1]

6. Dispersibility of hydroxylated FG in commonly-used solvents

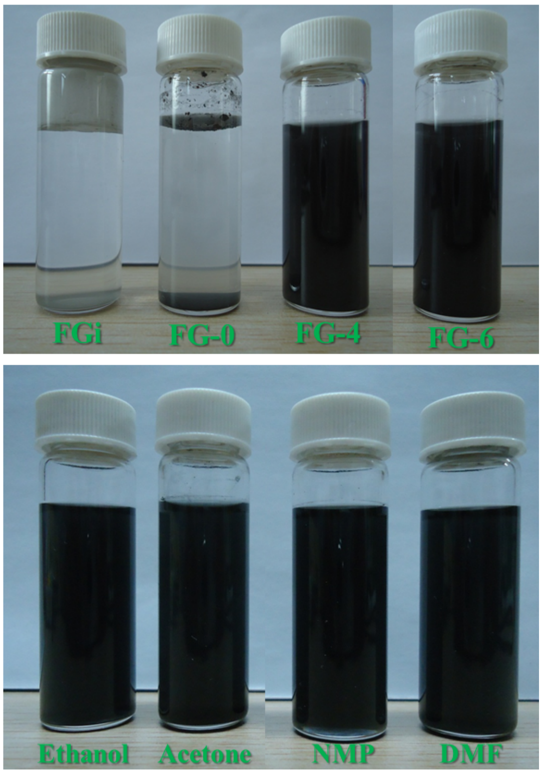

Figure. S5 Digital images of hydroxyl-functionalized FG dispersed in water, ethanol, acetone, NMP, and DMF.

To investigate the dispersibility of HOG (FG-6), 2 mg of the sample was dispersed in 6 mL of solvents. FGi and FG is difficult to be dispersed in water due to the hydrophobic nature of fluoride; while for the hydroxyl-functionalized graphene sheets, they can be easily dispersed in various solvents as a result of the introduction of hydrophilic hydroxyl groups, especially in water.

References and Notes

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