

Electronic Supplementary Information (ESI)

Experimental Information

Materials: Potassium ferricyanide and potassium ferrocyanide were purchased from Sigma-Aldrich Co. (St. Louis, USA). All other chemicals were of analytical grade or higher and used without purification. Double distilled water was used throughout to prepare solutions.

Apparatus: All electrochemical measurements were performed with a CHI660B electrochemical workstation (CH Instruments Co., Shanghai, China). The experiments were carried out at room temperature using a three-electrode configuration in 10 mL glass cell. A platinum wire was used as auxiliary electrode and a Saturated Calomel Electrode (SCE) worked as reference electrode. The working electrode was a glassy carbon (GC) electrode coated with graphene.

The images of transmission electron microscope (TEM) were recorded using a JEM-2100F transmission electron microscope (JEOL, Japan) operating at 200 kV. Raman spectra were recorded using a Jobin-Yvon spectrometer set to an excitation wavelength of 484 nm. The X-ray diffraction (XRD) pattern was obtained with a Philips powder diffraction system (model PW 1830) using a Cu K α source operating at 40 kV. Fourier-transform infrared (FT-IR) characterization was carried out on a Magna 560 FT-IR spectrometer within the range of 1000-2000 cm⁻¹. X-ray photoelectron spectroscopy (XPS) measurements were conducted with an ESCALAB-MKII spectrometer (VG Co., U.K.) with an Al K α X-ray radiation as the excitation source and a chamber pressure of 3.5 \times 10⁻⁷ Pa.

Synthesis of graphene: The as prepared graphene (a-GR) were prepared according to the chemical reduction of graphene oxide (GO) which was fabricated from natural graphite powder via a modified Hummer's method.¹⁻² Briefly, 32 mg GO was dispersed into 170 mL water then ultrasonic agitate for 0.5 h to obtain a suspension. Following this, 55 μ L 85% hydrazine solution and 385 μ L ammonia were added into the suspension. The solution was refluxed at 95 °C for 1 h. After that, the mixture was filtrated and washed with water several times then dried overnight under vacuum.

Purification of graphene: The based washed graphene sheets (b-GR) were prepared according to the following procedures. In brief, 16 mg graphene were added into a flask which contains 8 mol dm⁻³ NaOH followed by refluxing at 100 °C for one hour, resulting in a suspension solution consists of colorless liquid containing debris and black particles. After cooling to room temperature the mixture was centrifuged for 3 mins at 12,000 rpm for several times. The supernatant liquid was decanted and put on one side. The black pellet was then re-acidified with HCl of an equivalent concentration to the NaOH and then washed with enough water.³⁻⁴

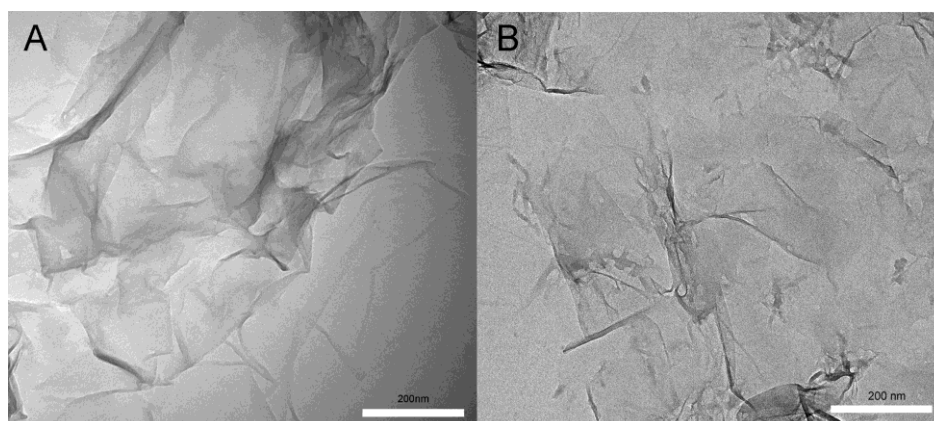
Preparation of r- graphene: For comparison, we fabricate a material which restores debris onto BGS with hydrochloric acid (r-GR) as following method. The separated b-GR was re-dispersed in the earlier mentioned supernatant liquid which contained carbonaceous debris and the mixture was subject to acidic adjustment with HCl. After continuously stirring for 1 hour, the suspension was followed by centrifugation and washed with doubly distilled water until the filtrate reached a neutral pH. The solid filtrate was then dried under vacuum. We defined the resulting graphene sample as

r-graphene (r-GR).

Preparation of graphene modified GC electrodes: The modified electrodes were prepared by casting 5 μL of the suspension (1 mg mL^{-1} dispersed in DMF) onto the surface of the GC electrode which was polished with 0.05 mm alumina slurry and then successively cleaned in ethanol and distilled water. The electrode was allowed to dry under an infrared lamp to evaporate the solvent.

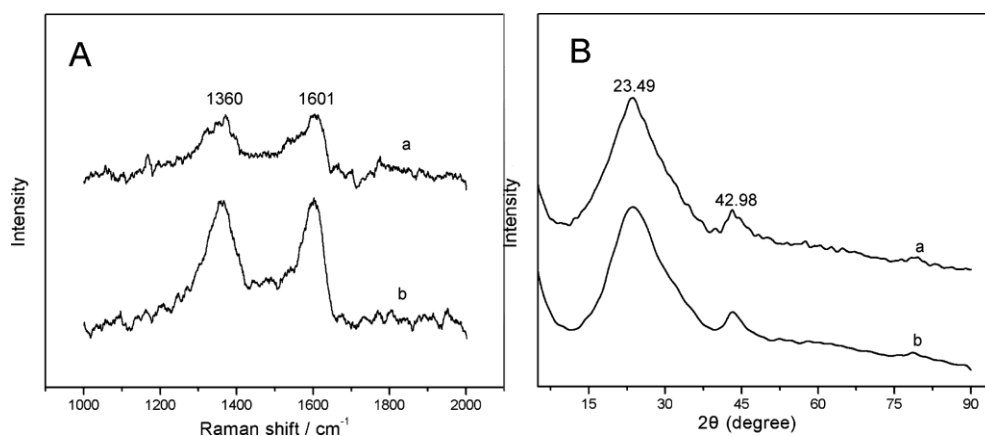
Characterization of a-GR and b-GR

Transmission electron microscopy (TEM): The TEM images of a-GR and b-GR are shown in SI Figure 1. We can observe that both of them exhibit few layer stacked structures indicating the exfoliation of graphite oxide. However, it is noteworthy that the electrochemistry performance of few layer graphene is similar to that of monolayer graphene.⁵⁻⁶ Moreover the sheets are not flat but corrugation and entangled with each other, the edge of graphene sheets looks crumpled and folded and look like crumpled silk veil waves.⁷⁻⁸ These observations are in accordance with previous literatures. The image of b-GR is similar with a-GR, which confirms that the structures of sheets themselves are not changed appreciably during the process of base washing.



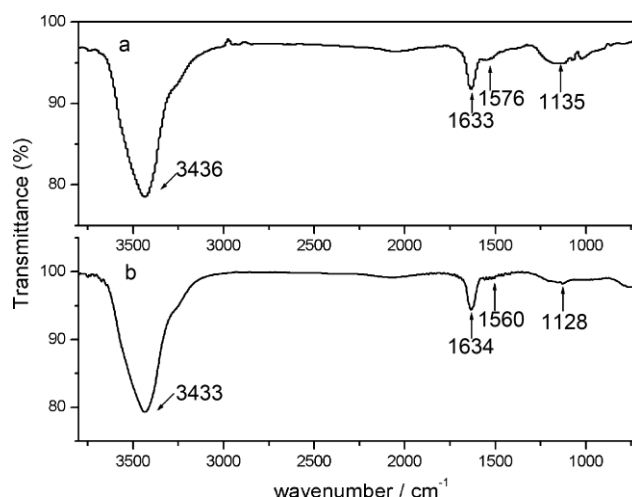
SI Figure 1 A high-resolution TEM image of a-GR (A) and b-GR (B).

Raman Spectroscopy and X-ray Diffraction (XRD): SI Figure 2A shows the Raman spectroscopy which is an important tool to analysis the ordered and disordered crystal structures of carbon materials. Two distinct peaks can be observed at 1360 cm^{-1} and 1601 cm^{-1} respectively, corresponding to the D-band and G-band. The D-band can be attributed to the breathing mode in C-C ring structures, which indicate of defects. The G-band is due to the stretching vibrations of sp^2 -bonded carbon atoms.³ As for GR, the spectrum shows a broad D and G peaks, with the intensity ratio (I_D/I_G) of D-band and G-band up to 1.61. However, the sample of b-GR exhibits a similar response to a-GR, with the ratio at 1.59. The distinction can be considered as instrument error. The XRD patterns are shown in SI Figure 2B. It can be seen that the a-GR and b-GR exhibit a nearly identical response. A broadened peak can be observed at $2\theta = 23.49^\circ$, corresponding to the (002) diffraction of a-GR. Another small peak at $2\theta = 42.98^\circ$ is indexed to (100) planes of a-GR. After base washing, the degree and peak intensity have not changed obviously as seen from the spectrum. Therefore, the Raman and XRD analyses not only confirm the successfully synthesized of graphene, but also demonstrate that the graphene structures are not damaged with base washing, which is in agreement with the conclusion of TEM.



SI Figure 2 Raman (A) and XRD (B) spectra of a-GR (a) and b-GR (b)

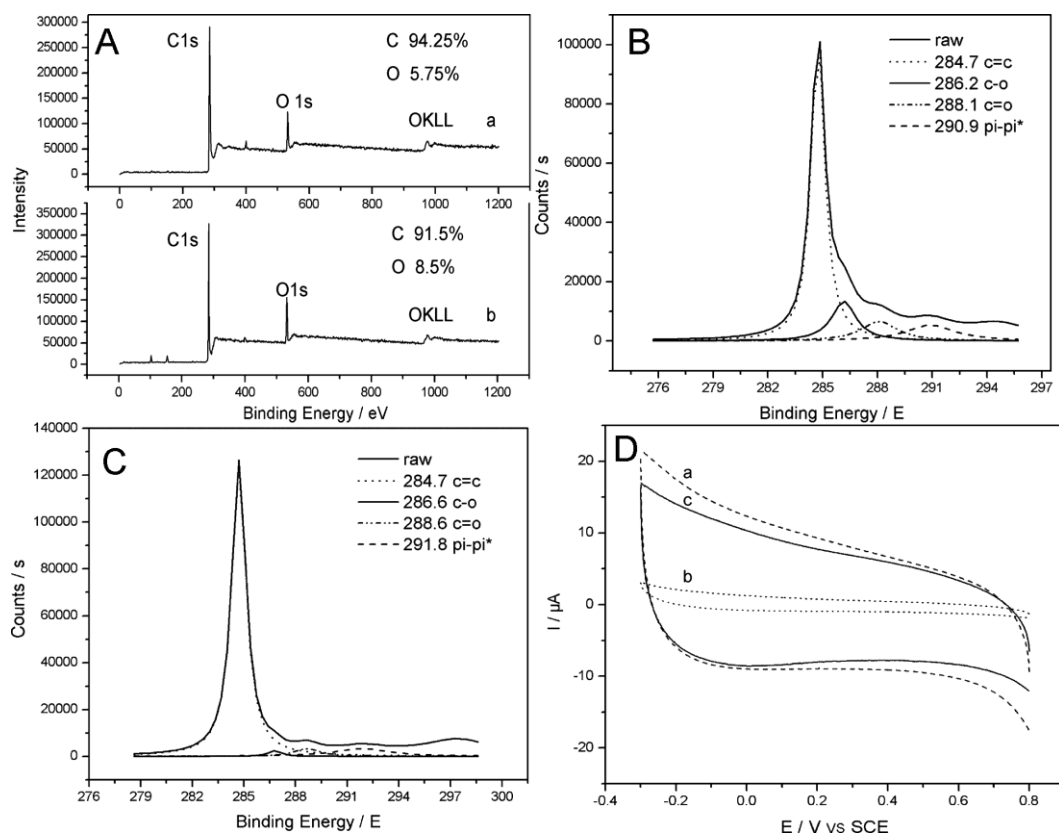
Fourier Transform Infrared Spectroscopy (FT-IR): The variations in FT-IR and XPS spectra of both graphene samples indicate the decreased oxygen-containing groups from a-GR to b-GR owing to the removal of carbonaceous debris. The FTIR spectrum was shown in SI Figure 3, a broad feature at around 3400 cm⁻¹ related to O-H stretching or chemisorbed water. The peak at 1633 cm⁻¹ and 1576 cm⁻¹ is likely due to the C=C stretching vibration and C-C (aromatic) skeleton stretching vibration. The broad peak at 1103 cm⁻¹ may C-(CO)-C stretching and bending for ketones, C-O-C asymmetric and symmetric stretching for ethers or C-O stretching for alcohols and phenols.⁹ This absorption peak at b-GR decreased dramatically compared with a-GR. As for the tiny peak at 1576 cm⁻¹ which can be observed at a-GR and impurities but the intensity decreased apparently at b-GR, indicating that the carbonaceous debris mainly consists of oxygen containing polycyclic aromatic compounds are heavily covalently functionalized with similar groups to a-GR, yet can be eliminated with base washing.



SI Figure 3 FTIR spectra of a-GR (a) and b-GR (b)

X-ray Photoelectron Spectroscopy (XPS): SI Figure 4A show a typical XPS survey scan spectrum, with a strong C 1s peak at 284.7 eV, a small O 1s peak at 532.2 eV and a weak O KLL Auger band at around 978 eV. The ratio of the C and O reduced obviously after base washing, indicating that the impurities, which consist of many aromatic hydrocarbons and oxygen function groups, indeed have been derived from graphene sheets. A single peak at 284.7 eV and an asymmetrical tail at higher energies can be observed at the spectrum of a-GR (Figure 4B). The C 1s signal of a-GR can be separated into four peaks via a function of lorentzian, representing sp²-hybridized carbon atoms (284.7 eV), the alcohol/ether groups (286.2 eV), the carbonyl/carboxylic acid groups (288.2 eV) and the π - π^* shake up satellite band (290.9 eV), which is typical for sp²-hybridized carbon atoms, demonstrated the existence of aromatic/conjugated systems.¹⁰⁻¹¹ However the spectrum of b-GR is featureless (Figure 4C), a drastic decrement of intensities for the alcohol/ether groups (286.6 eV) and carbonyl groups (288.6 eV) can be observed at b-GR compared with a-GR, nearly out-of-sight. This is in accord with the FTIR spectrum, revealing that the

impurities contain of oxygen function groups, indeed have been derived from graphene sheets.



SI Figure 4 High-resolution XPS of (A) the survey spectrum of a-GR (a) and b-GR (b), (B) C 1s spectrum for a-GR, (C) C 1s spectrum for b-GR, (D) CV curves recorded in 1 M Na₂SO₄ using a-GR (a, dashed line), b-GR (b, dotted line) and r-GR (c, solid line) electrodes respectively.

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