Supporting Information

Highly efficient electrolytic exfoliation of graphite into graphene sheets based on Li ions intercalation-expansion-microexplosion mechanism

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I. Experimental details

Synthesis of graphene by electrolytic exfoliation.

As schematically shown in Figure S2, the molten salt electrolysis experiments were performed in a cylindrical stainless steel reactor. The upper cover of the reactor was equipped with graphite rod cathode up-down feedthroughs, view window, thermocouple and steel cavity for water cooling. A cylindrical graphite crucible anode (external: 110 mm height and 50 mm diameter; internal: 70 mm height and 25 mm diameter, Graphite technologies, high purity grade) was positioned vertically inside a programmable tubular electric furnace. The interior of the furnace was continuously purged with argon during electrolysis. About 70 g of anhydrous lithium hydroxide (LiOH) was thermally pre-dried inside the graphite crucible at 300 °C for at least 2 h, and then gradually heated to 600 °C under an argon flow (80 cm^3/min). Afterwards, a high-purity graphite rod cathode of 5 mm in diameter was inserted to a depth of 15 mm in the melts by means of a screw mechanism. The electrolysis was controlled by a constant current of 15 A at 600°C, which is higher than its melting point (471°C). The electrolysis duration was about 30 min. After electrolysis, the graphite rod cathode was removed from the

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crucible and the electrolyte was left to solidify overnight under a slow flow of argon. The solidified electrolyte was added to distilled water under ultrasonic conditions in order to react with the residual lithium metal within carbonaceous products, where a microexplosion occurs in the interlayer space of graphene layers and instantly releases a large amount of hydrogen. These gaseous products could lead to the detached graphene layers or stacks being further exfoliated. At last, the few-layers graphene with low density of defects were collected *via* centrifugation, washed with distilled water and dried for characterization.

Characterization of graphene.

The X-ray diffraction (XRD) patterns of the samples were tested by X'Pert Pro diffractometer using Cu Kα radiation (λ = 0.15418 nm). The morphologies of the samples were examined by scanning electron microscopy (SEM, Hitachi S4700). Transmission electron microscopy (TEM) images were collected on a FEI Tecnai G^2 F30 system. Atomic force microscopy (AFM) images of graphene sheets were taken in tapping mode using an AFM (Veeco, Dimension® Edge™). The graphene sheets were homogeneously dispersed in 2-propanol under ultrasonication for 30 min. Next, a few drops of the suspension were pipetted onto silicon substrates. The air-dried substrates were placed directly under the AFM tip for the morphology analysis. Raman scattering spectra was recorded at room temperature using a Renishaw InVia Raman Spectrometer under a backscattering geometry (λ = 532 nm). Fourier transformed infrared (FT-IR) spectrum was tested by a Nicolet 6700 FT-IR spectrometer (Thermo). The X-ray photoelectron spectroscopy (XPS, AXIS UTLTRADLD equipped with a dual Mg Kα - Al Kα anode for photoexcitation) sample was prepared by drop-casting the dispersion of the sample on a Si wafer.

II Supplemental Figures

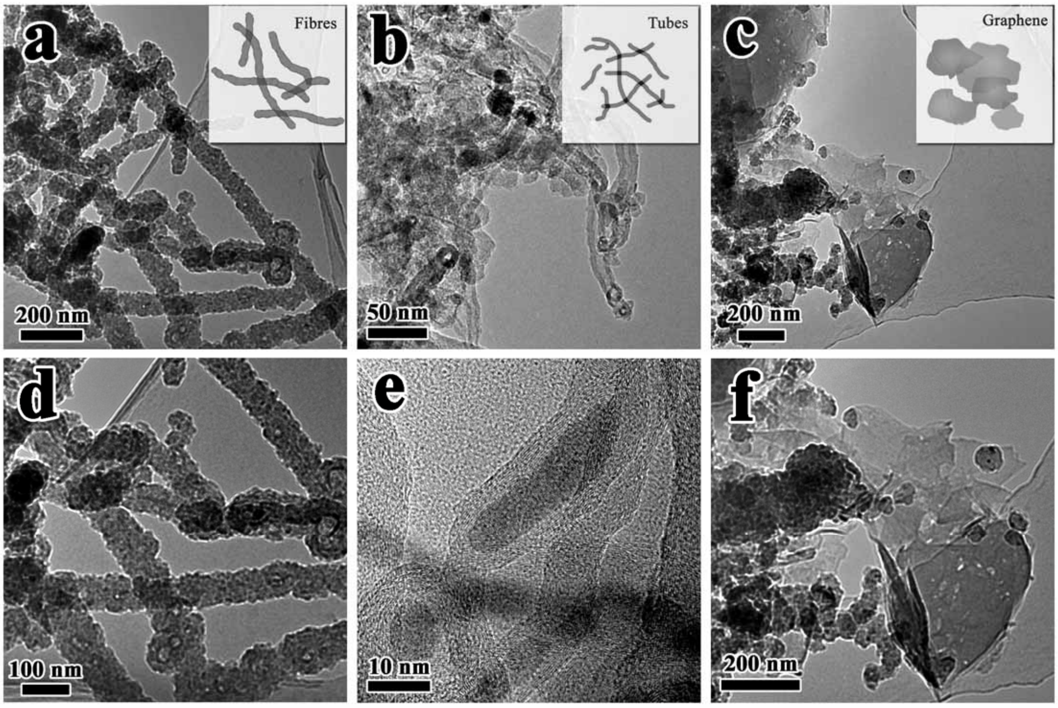

Figure S1. The TEM images of the carbon-based constituents produced from the LiCl electrolyte. (a) and (d) carbon fibres; (b) and (e) carbon nanotubes; (c) and (f) Graphene and graphite fragments.

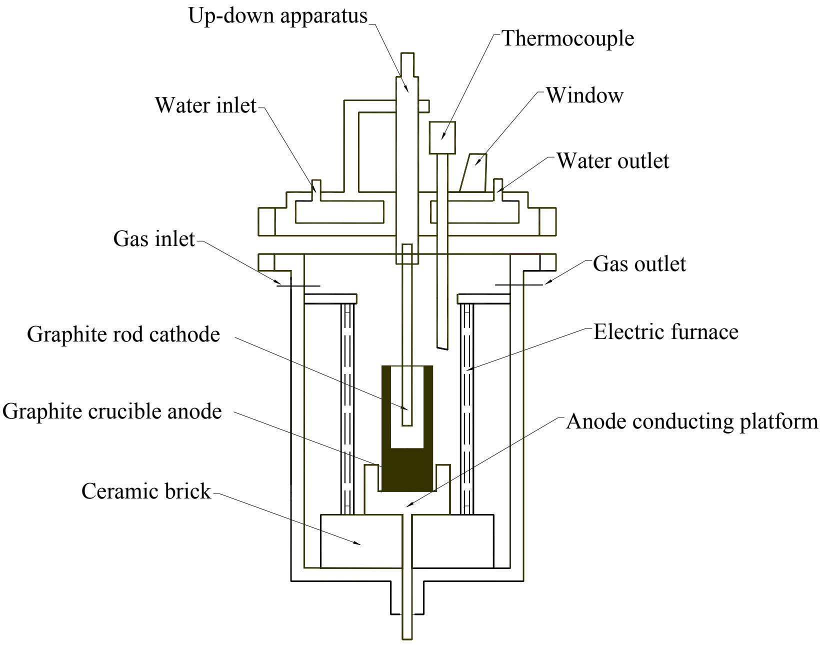

Figure S2. A schematic diagram of the experimental set-up for molten salt electrolysis method.

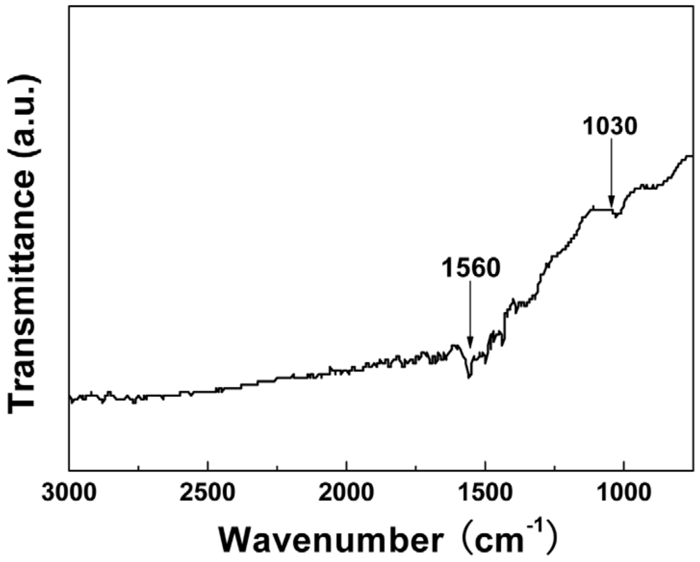

Figure S3. FT-IR spectrum of the as-prepared graphene.