

Electronic Supplementary Information (ESI) for

Cu₂O@reduced graphene oxide composite for removal of contaminants from water and supercapacitor

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Experimental Section

Synthesis of Graphene oxide. Graphene oxide (GO) was prepared from purified natural graphite according to the Hummers method.^{S1,2} In detail, graphite powder (1.0 g), NaNO₃ (0.5 g) and KMnO₄ (3.0 g) were slowly added into concentrated H₂SO₄ (23 ml) cooled by ice bath and the mixture was vigorously stirred at 35±3 °C for 30 min. On completion of the reaction, water (46 ml) was added, and the temperature was kept at 98 °C for 15 min. Then the temperature was reduced to 60 °C with the addition of warm water (140 ml), H₂O₂ (30%, 10 ml) was added and the reaction was further stirred for 2 h. The above mixture was filtrated to collect the solid product and washed with 4% HCl solution (5 times), and then washed repeatedly with deionized water (three times). Finally the material was dried in vacuum to obtain a loose brown powder.

Materials Synthesis. GO (150 mg, equal to 50 mg reduced graphnene oxide) and water (300 ml) was ultrasonicated in a beaker for 2 h. A aqueous solution (40 ml) of Cu(CH₃CO₂)₂·H₂O [1265 mg, equal to 450 mg Cu₂O], ang glucose (1150 mg) was added into the above beaker. The mixture was stirred for 4 h to complete ion exchange, followed by adding aqueous solution (50 ml) of NaOH (506 mg, 1.0 equivalent) dropwise. The brown GO-Cu(OH)₂ was separated from the mixture by filtration and then was added into aqueous solution (30 ml) of and glucose (1150 mg). The mixture was transferred to and sealed in a Teflon-lined autoclave (50 ml), heated to 90 °C and kept at this temperature for 8 h. After cooled to room temperature naturally, the black solid was separated by filtration and washed with deionzied water (3×10 ml) and ethanol (3×10 ml) and Cu₂O@reduced Graphene Oxide composite (CGC) were obtained. The designed weight ratio of rGO to Cu₂O is 1:9. Prue Cu₂O were obtained by similar prosses in the absence of GO.

Materials Characterization. Fourier transform infrared (FT-IR) spectroscopy measurements were carried out on a NICOLET 560 Fourier transform infrared spectrophotometer. Raman spectra were recorded on a Renishaw RM-1000 with excitation from the 514 nm line of an Ar-ion laser with a power of about 5 mW. The phase structures of as-prepared products were characterized with X-ray diffraction (XRD, Bruker D8 advance) with Cu K_α radiation ($\lambda = 1.5418 \text{ \AA}$). X-ray photoelectron spectra (XPS) were recorded on a PHI quantera SXM spectrometer with an Al K_α = 280.00 eV excitation source, where binding energies were calibrated by referencing the C1s peak (284.8 eV) to reduce the sample charge effect. The morphology of as-prepared products was studied by using transmission electron microscope (TEM, Hitachi H-7650B, operating at 80.0 kV). For atom force

microscopy (AFM) measurement, the samples were coated on Si surface and AFM studies were performed using a Digital Instruments Dimension 3100 microscope in the tapping mode. N₂ adsorption–desorption was tested on TriStar II 3020 (Micromeritics Instrument Corporation, USA).

Adsorption Measurement. The adsorption experiments are conducted with CGC as adsorbent for Rhodamine B (RhB, 1.0×10⁻⁵ M), and Methylene blue (MB, 2.0×10⁻⁵ M) solution in bottle (20 ml) and at room temperature. For filtration experiments, the CGC was pressed into a 13 mm round plate and pressed into membrane, then the membrane was fixed in a filter. Solution of RhB (1.0×10⁻⁵ M) was impelled to pass through the membrane under a constant rate of 0.1 ml min⁻¹. The concentration of RhB in the filtrate was measured with a UV–VIS recording spectrophotometer (UNIC Corp. UV–2102PC). For recycling of CGC after adsorption of MB, CGC was washed by EtOH (10 ml) for 8 h and reused for adsorption of RhB.

The most popular methods of surface area calculation are those based on gas adsorption isotherm technique. Adsorption is the process of the attachment of atoms or molecules to the surface of a solid, which can be divided into either physical or chemical adsorption.^{S3} Physical adsorption is very useful to measure the specific surface area (SSA) and pore volume in mesopores (2–50 nm) or micropores (< 2 nm) materials. The standard method for measuring surface area is consigned to the BET method and involves N₂ (or Ar) physical adsorption and desorption as a function of heating a known weight of material.^{S4} The BET equation (1) is as follows:^{S3}

$$\frac{P}{V(P_0-P)} = \frac{P/P_0}{V(1-P/P_0)} = \frac{1}{cV_m} + \frac{c-1}{cV_m}(P/P_0) \quad (1)$$

where P is the actual gas pressure at the equilibrium experiment state, P_0 is the saturation pressure at the selected temperature, P/P_0 is relative pressure, V is the standardized experimental volume of the adsorbed gas per gram of adsorbent, V_m is the volume of the adsorbate monolayer per gram of adsorbent, c is a constant which reflects the interaction between adsorbent and adsorbate molecules.

The total surface area S (the surface of complete monolayer coverage) can be obtained by X_m :

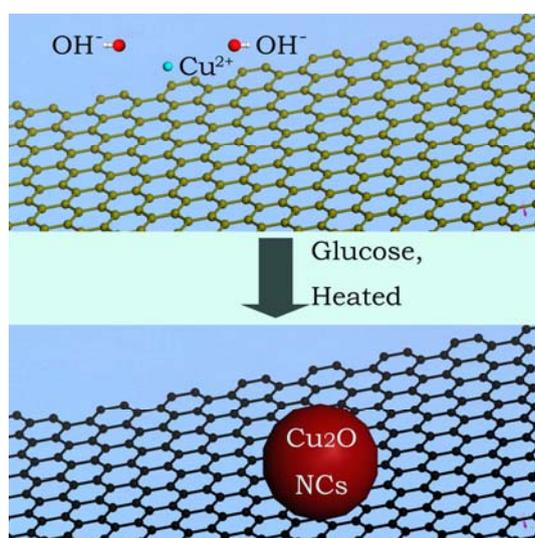
$$S = \left(\frac{X_m}{M} \right) \times N_A \times A_m \quad (2)$$

where X_m is the adsorbance (or adsorptive capacity, in kg) of adsorbate monolayer, M is the molar mass of adsorbate, N_A is Avogadro constant (6.022×10²³ mol⁻¹), A_m is the area of one gas molecule (0.162 nm² for N₂). So the specific surface area S_{SSA} (i.e., surface-to-mass ratio, m² kg⁻¹) is calculated by equation (3):

$$S_{SSA} = \frac{S}{M_x} \quad (3)$$

where M_x is the mass of adsorbent.^{S5}

Electrochemical Measurement. For supercapacitor measurement, CGC (10 mg) was compressed into foam nickel plates (13×13 mm) under 12 MPa pressure. CGC electrode was immersed into solution of a saturated KCl solution for 8 h and then used as the working and counter electrode. The galvanostatic charge-discharge experiments were performed on the Newware battery testing system (Shenzhen Newware Technology Co., Ltd.). The specific capacitance was obtained from: $C_m = I/(\Delta E/\Delta t)m$, where $(\Delta E/\Delta t)$ was the average slope of the discharge curve in the potential range ΔE , Δt was the discharge time and I was the current.



Scheme S1 Illustration of synthesis of CGC from GO with glucose as a reductant.

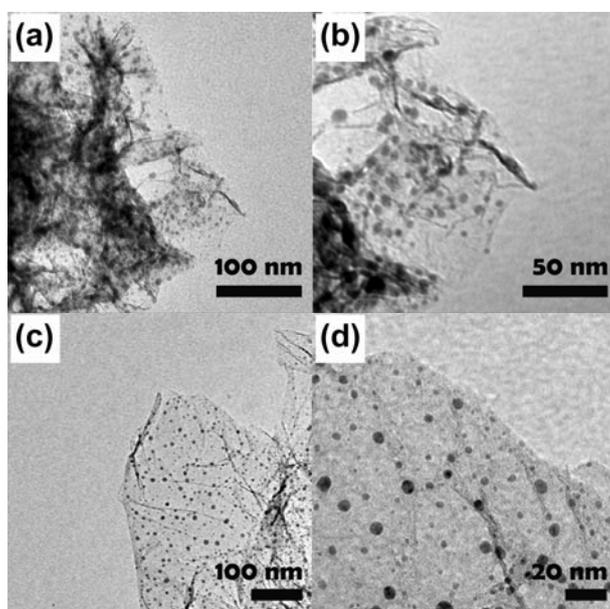


Fig. S1 (a-d) TEM images of CGC.

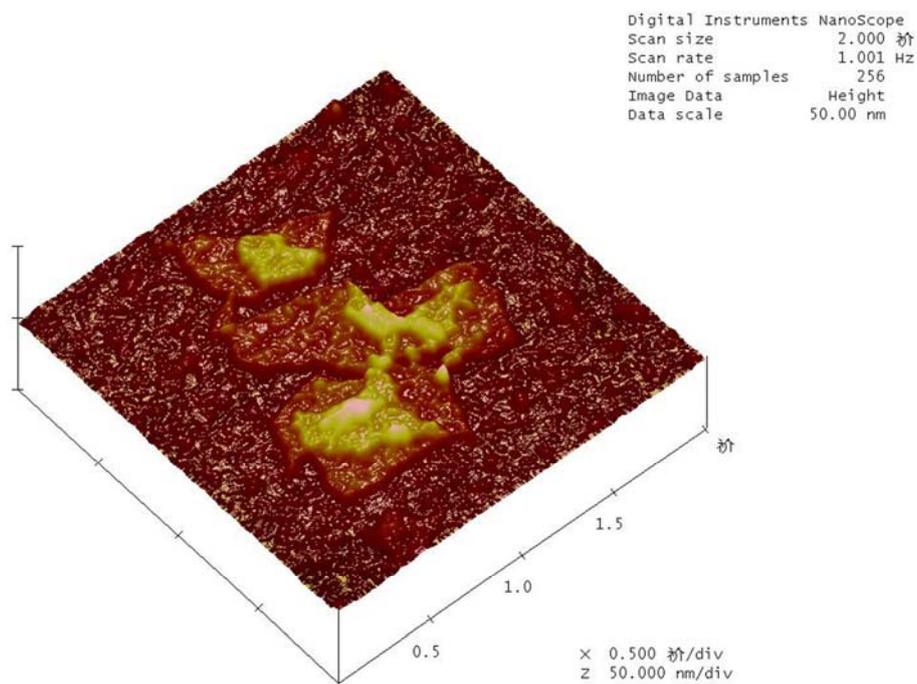


Fig. S2 (a-d) Three dimensional AFM images of CGC.

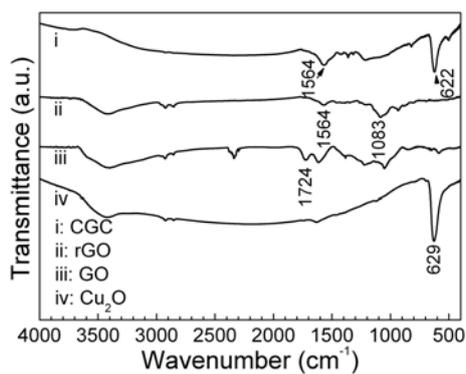


Fig. S3 (a) FT-IR spectra of CGC, rGO, GO, and Cu_2O .

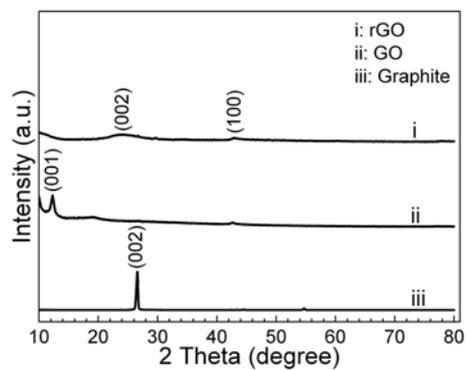


Fig. S4 (a) XRD patterns of rGO, GO, and Graphite.

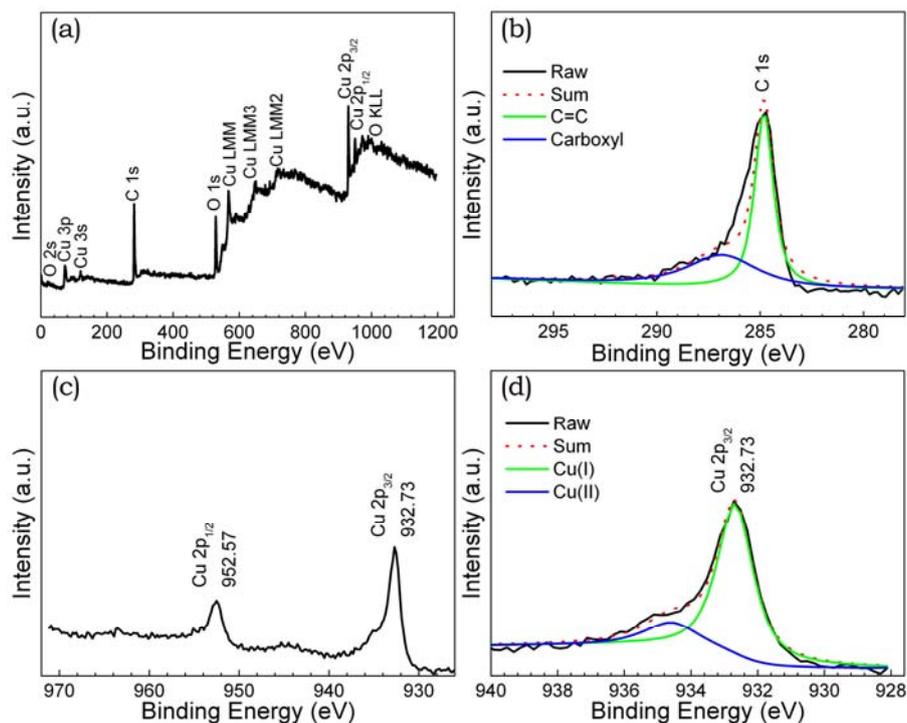


Fig. S5 XPS spectrum of (a) the CGC, and the refine scanning spectrum of (b) C1s, and (c, d) Cu2p spectra.

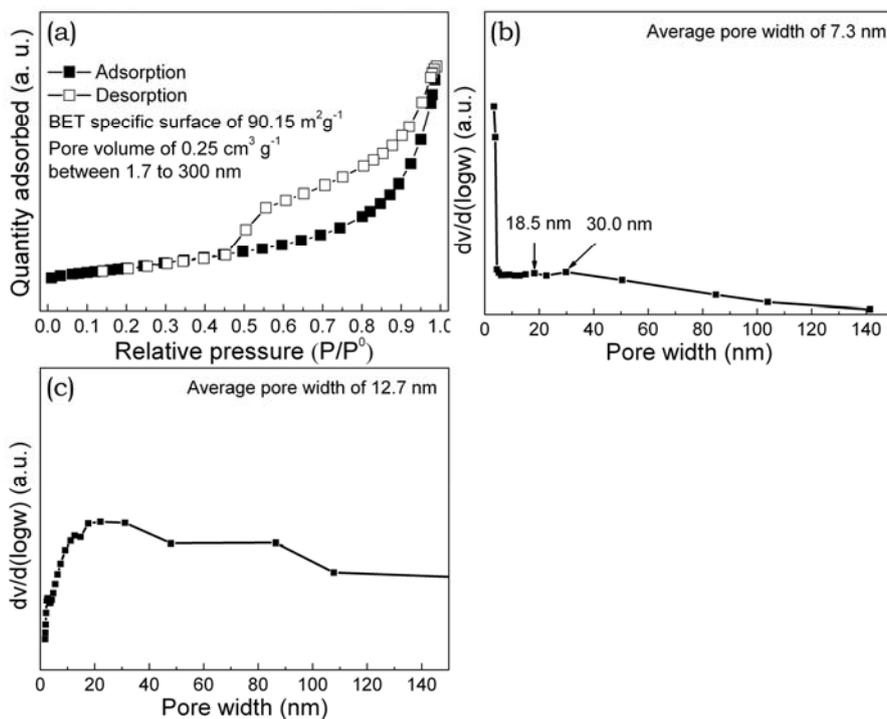


Fig. S6 (a) N₂ adsorption–desorption isotherms at 77 K, and the pore width distribution of CGC calculated from (b) desorption branch and (c) adsorption branch.

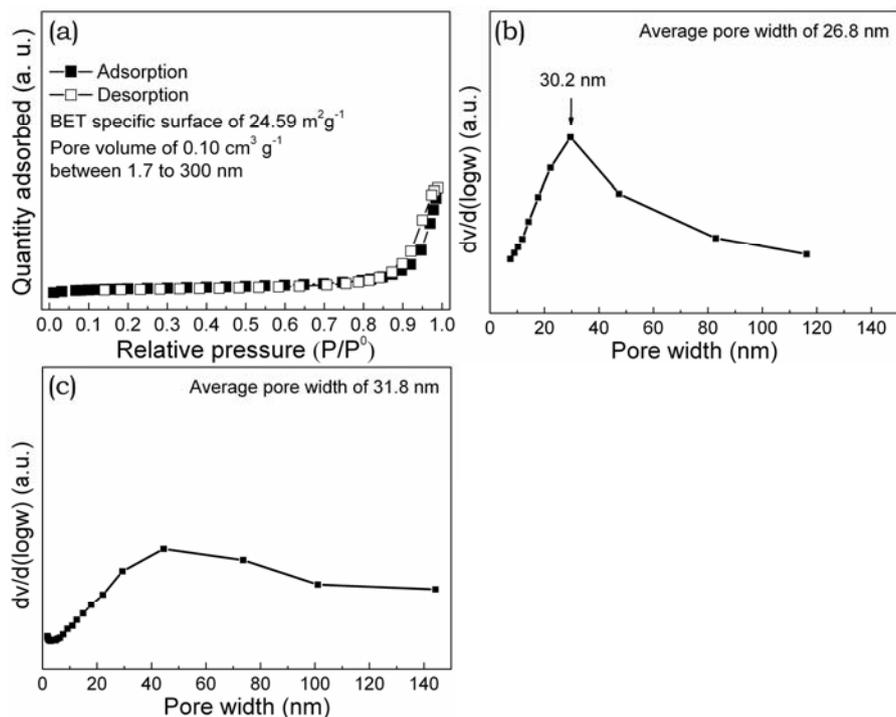


Fig. S7 (a) N_2 adsorption–desorption isotherms at 77 K, and the pore width distribution of Cu_2O calculated from (b) desorption branch and (c) adsorption branch.

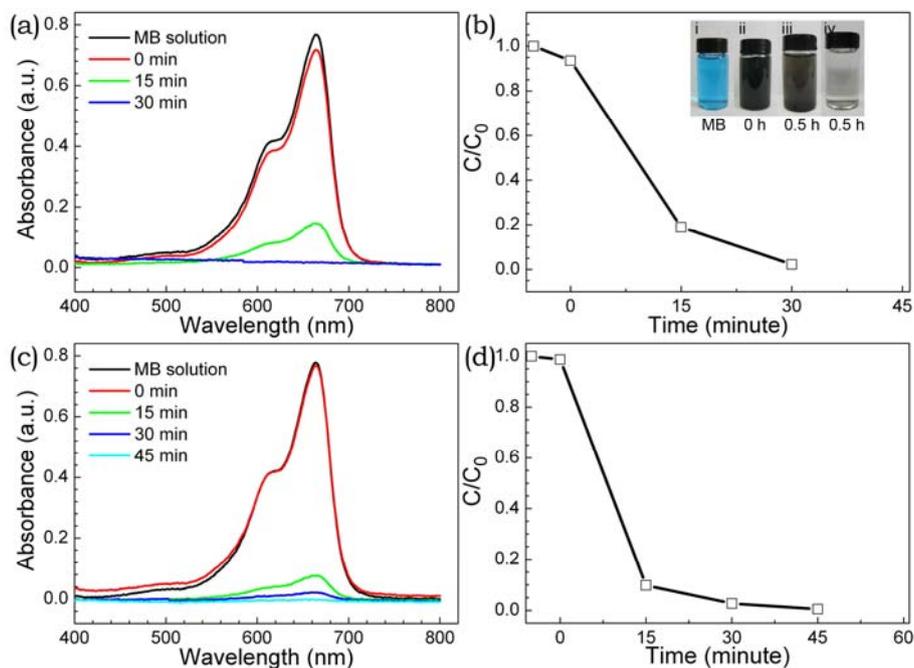


Fig. S8 (a) UV–Vis spectra, of the original ($2.0 \times 10^{-5} \text{ M}$, 20 ml) and after treatment in MB solutions with CGC (100 mg) for various times, and (b) C/C_0 curve of MB concentration versus time. The insets in (b) are photo images of corresponding solution, and (iv) Water after adsorbents removed. (c) UV–Vis spectra, of the original ($2.0 \times 10^{-5} \text{ M}$, 20 ml) and after treatment in MB solutions with reused CGC (100 mg) for various times, and (d) C/C_0 curve of MB concentration versus time. The reused CGC was obtained from the used CGC by washing with ethanol (10 ml).

References

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