

Carbon based dots for electrochemical production of hydrogen peroxide

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Materials

Natural graphite whose mean diameter is about 500 μm was purchased from Qingdao Yanxin Graphite Co. Ltd., China. Vulcan XC-72 carbon black was obtained from Cabot Corporation, USA. All chemicals were of analytical grade and used without further purification. Deionized (DI) water was used throughout the experiment.

Instrumentation

The size and morphology of the samples were measured using transmission electron microscopy (Tecnai G2 F20S-TWIN) at operation voltage of 200 kV. AFM images were obtained by tapping-mode on Nanoscope IIIa Digital Instruments with NSC15 tips (silicon cantilever, MikroMasch). Raman spectra were measured using a

Renishaw 1000 microspectrometer (excitation wavelength of 633 nm). XPS analysis was carried out using an ESCALab 250 XPS system having an Al K source. FTIR spectra were obtained on an FT-IR spectrophotometer (Thermo Nicolet 360). XRD patterns were measured from a Rigaku D/max-3C (Japan) using Cu K α radiation.

Preparation of CDs

Single-layer CDs were synthesized by chemical oxidizing XC-72 carbon black according to a previous work.¹ In a typical experiment, 5 g XC-72 carbon black mixed with 200 mL concentrated HNO₃ (8 M) was refluxed at 130 °C for 48 h. After the reaction, the resulted suspension was cooled to room temperature, and followed with a separation with a 0.22 μ m filter membrane. The obtained filtrate was well dried by reduced pressure distillation to remove water and the residual HNO₃. Then single-layer CDs could be obtained by collecting the reddish brown powder.

Synthesis of G/CDs

G/CDs were prepared by ultrasonic exfoliation of natural graphite using single-layer CDs as the intercalators.² As shown in Figure 1, 50 mg graphite and 50 mg single-layer CDs were mixed in 30 mL deionize (DI) water, which the pH value of the solution was regulated to 8 using 0.1 M NaOH. Then, the mixture was ultrasound for 5 hours. After that, the as-obtained suspension was firstly centrifuged at 3000 rpm to remove the unexfoliated graphite nanoparticles. Subsequently, the supernatant was further centrifuged at about 12000 rpm to remove the residual CDs. The sediment (G/CDs) was well washed with DI water three times through centrifugation at 12000

rpm. Finally, the washed G/CDs was re-dispersed in 3 mL DI water and stored at 4 °C for further study.

Chemical reduction of G/CDs

The G/CDs was chemical reduced by NaBH₄.³ In brief, 1 mL G/CDs solution mentioned above was diluted to 5 mL, which was heated to 80 °C. Then, 20 mg NaBH₄ was added into the solution under stirring. The heating was kept for about 3 h, making sure that NaBH₄ has been decomposed completely. The reduction product was well washed with DI water through centrifugation at 12000 rpm. The sediment (reduced G/CDs, R-G/CDs) was re-dispersed in 1 mL DI water and stored at 4 °C before use.

Electrochemical characterization

G/CDs was dispersed in DI water to achieve a catalyst concentration of ~1 mg mL⁻¹, accompanying with 5 wt% Nafion. After sonication of 10 min, 5 µL of the catalyst ink was drop-dried on a glassy carbon disc electrode (area: 0.196 cm²). CV measurements were performed using a computer-controlled potentiostat (CHI 760D, CH Instrument, USA) with a three-electrode system, including a glassy carbon working electrode (5 mm in diameter), a Pt wire (0.5 m in diameter) counter electrode and an Ag/AgCl reference electrode. Measurements on rotating disk electrode (GC, 5 mm in diameter) and rotating ring-disk electrode (disc area: 0.2475 cm², ring area: 0.1866 cm²) were carried out on a MSRX electrode rotator (Pine Instrument) and the CHI 760 D potentiostat at a scan rate of 10 mV s⁻¹.

Calculation of H₂O₂ selectivity of the G/CDs

H₂O₂ selectivity of the G/CDs was measured by the rotating ring-disk electrode, according to the equation as follow:

$$\text{H}_2\text{O}_2 \text{ yield: } \text{H}_2\text{O}_2 (\%) = 200 \times (I_R/N)/(I_D + I_R/N)$$

in which I_R is the disk current and N is the collection efficiency (0.22). A potential of 1.2 V (*vs* RHE) was applied on the Pt ring of the working electrode at a speed of 1600 rpm during the entire testing process.

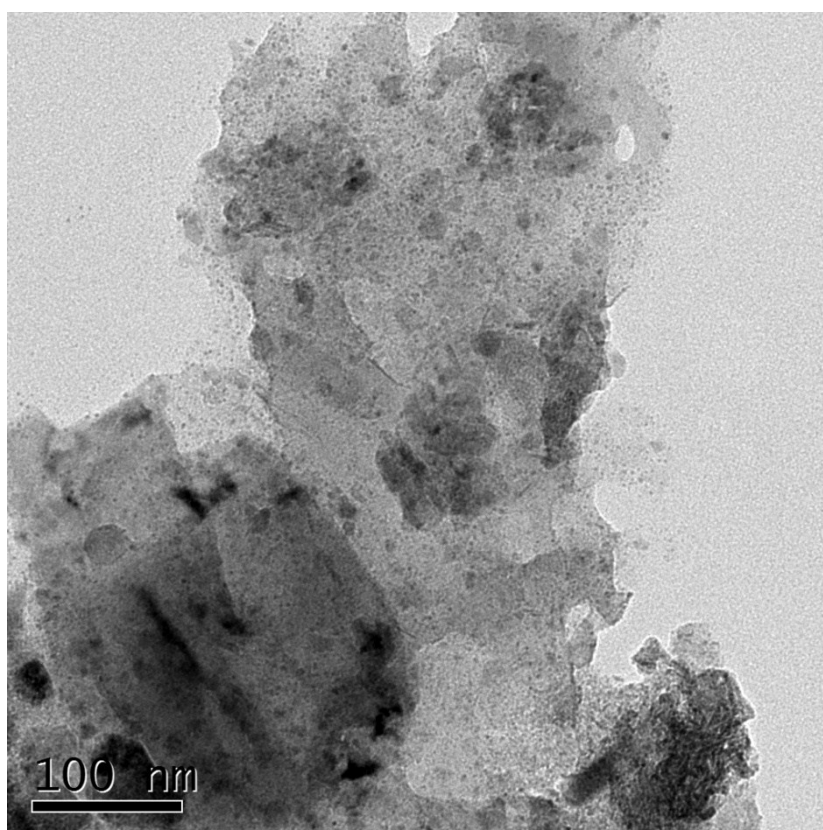


Figure S1. TEM image of G/CDs.

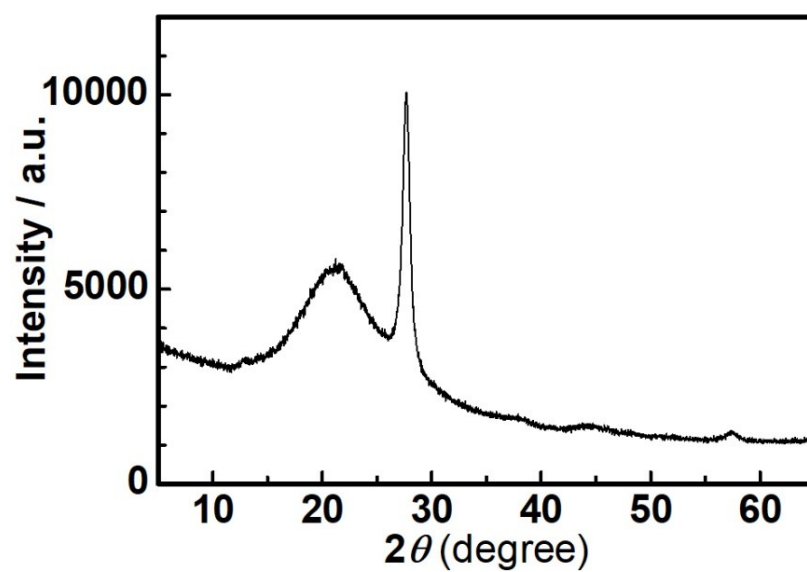


Figure S2. XRD pattern of G/CDs

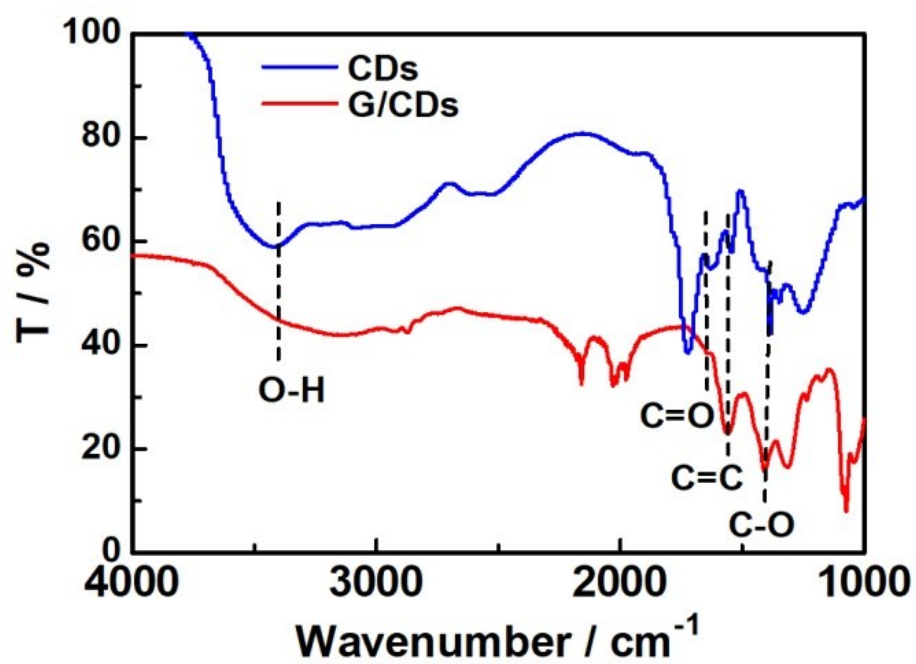


Figure S3. FTIR spectra of CDs and G/CDs

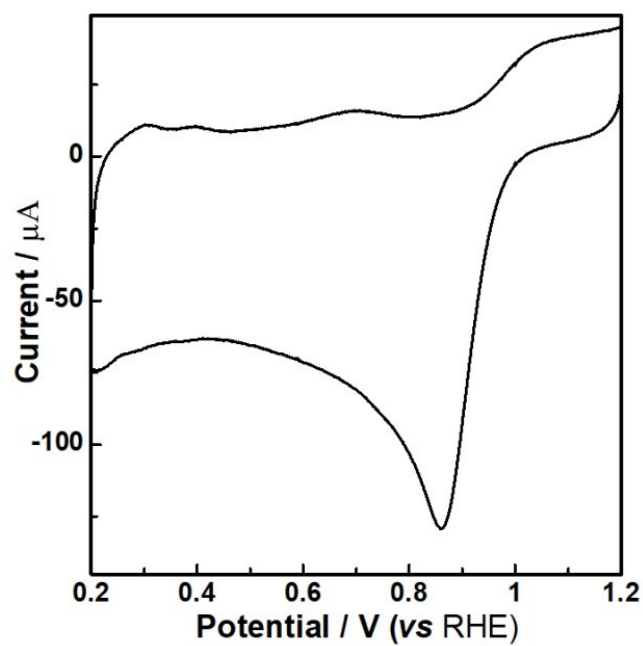


Figure S4. CV of commercial Pt/C catalyst on a GC electrode in O₂-saturated 0.1 M KOH at a scan rate of 50 mV s⁻¹.

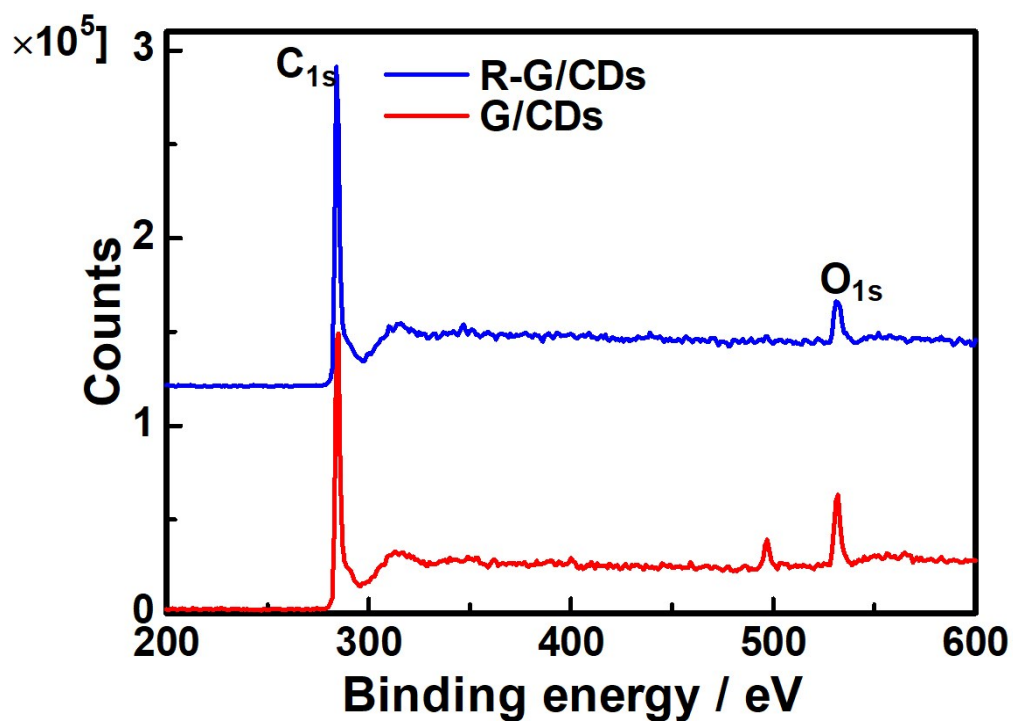


Figure S5. XPS spectra of G/CDs and R-G/CDs.

The density functional theory (DFT) calculations are performed using the Gaussian 09 package.⁴ A finite model was cut from graphene and dangling bonds were capped with hydrogens to represent a single layer of CDs (Figure S6). In some models, some hydrogens were replaced with COOH groups to study their effects on oxygen reduction reaction (ORR). The geometries was optimized without imposing symmetry constraints at the M062X density functional level using the 6-31g (d,p) basis set.⁵ The minima was confirmed with all real frequencies. The vertical electron affinity (VEA) is the energy difference between neutral and anion states at optimized neutral structures.

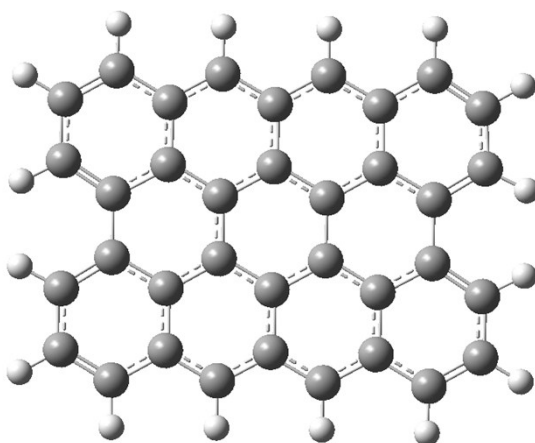


Figure S6. The finite model used in this work to represent a single layer CDs.

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