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Synergistically enhanced activity of graphene quantum dot/multi-walled carbon nanotube composites as metal-free catalysts for oxygen reduction reaction

Xuemei zhou,^a Zhimin Tian,^a Jing Li,^a Hong Ruan,^a Yuanyuan Ma,^a Zhi Yang^{*b} and Yongquan Qu^{*ac}

^a Center for Applied Chemical Research, Frontier Institute of Science and Technology, Xi'an Jiaotong University, Xi'an, 710049, China. *E-mail:* yongquan@mail.xjtu.edu.cn

^b Nanomaterials and Chemistry Key Laboratory, Wenzhou University, Wenzhou, 325027 (P. R. China). *E-mail:* yang201079@126.com

^c Institute of Chemistry for New Energy Materials, Department of Chemistry, Xi'an Jiaotong University, Xi'an, China 740049.

Experimental methods

Synthesis of graphene quantum dots (GQDs): GQDs were prepared by chemical oxidation and cutting of pitch graphite fibers. Briefly, pitch graphite fibers (0.3 g) were added into concentrated H₂SO₄ and HNO₃ (v/v = 3:1) and sonicated for two hours. The mixture was then stirred for 24 hours at 100 °C. After cooling down to room temperature, the reaction mixture was diluted with MQ water (800 mL, 18.2 MΩ cm). The pH was adjusted to 8 with Na₂CO₃. The final product solution was further dialyzed in a dialysis bag with the molecular-weight cut-off of 2000 Da for 3 days. A GQDs solution of 0.14 mg/mL was stocked for the future characterization and use.

Surface-treated MWCNTs: Pristine MWCNTs were first purified by annealing at 500 °C for 10 min in a tube furnace in air to remove amorphous carbon. Then, the products were refluxed in HCl and HNO₃ (v/v = 3:1) mixed solution for 30 min at room temperature to remove residual metal catalysts. The treated MWCNTs were filtered through a 0.45-μm filter, rinsed with deionized water until the pH of the filtered solution reached 7.0, and dried in an oven at 80 °C.

Preparation of GQDs-MWCNTs Composites: All GQDs-MWCNTs composites were

synthesized by sonication and stirring. Briefly, 5 mg MWCNTs dispersed in 5 ml water and then were added in different volumes of GQDs (1 mL, 3 mL, 5 mL and 20 mL), respectively. The solution was ultrasound for 1 hour and stirred for overnight. The mixture was then centrifuged off at 10, 000 rpm and washed with a large amount of water and dried at 60 °C in a box oven overnight.

Fabrication of electrodes: Glassy carbon (GC) electrodes (3 mm diameter, CH instrument Inc.) were polished with a 0.05 and 0.3 μm alumina slurry (CH Instrument Inc.) on a microcloth, and subsequently rinsed with ultrapure water and ethanol. The electrodes were then sonicated in MQ water for 5 min to remove any bound particles, rinsed thoroughly with ultrapure water and dried under a gentle nitrogen stream. For each electrocatalyst, 4 mg of catalyst was individually ultrasonically dispersed in 1 mL H_2O . Then, 10 μL of the suspension was dropped onto the GC surface and dried at room temperature. For comparison, a commercially available Pt/C-modified GC electrodes (10 wt% Pt supported on carbon black, fuel cell grade from Sigma) was prepared in the same way.

Electrochemical measurements: All electrochemical measurements, including cyclic voltammograms (CV), rotating-disk electrode voltammograms and chronoamperometry, were performed at room temperature in 0.1 M KOH solution, which was purged with high purity nitrogen or oxygen for at least 30 min prior to each measurement. CV measurements were performed within a potential range between -0.8 to +0.2 V (*vs.* Ag/AgCl reference electrode) at a scan rate of 100 mV s^{-1} . Rotating-disk electrode voltammograms were recorded within a potential range between +0.2 to -0.8 V (*vs.* Ag/AgCl reference electrode) at a scan rate of 10 mV s^{-1} . Chronoamperometry was performed at -0.25 V (*vs.* Ag/AgCl reference electrode). Electrochemical impedance spectroscopy (EIS) was performed in the frequency range from 0.01 Hz to 100 KHz, with 5 mV as the amplitude and open circuit potential.

Characterizations: X-Ray photoelectron spectroscopy (XPS) measurements were carried out with an ultra-high vacuum setup, equipped with a monochromatic Al $\text{K}\alpha$ X-ray source and a high resolution Thermo Fisher Scientific analyzer. Transmission electron microscopy (TEM) images were recorded with JEM-2100F (200 kV) instrument. The UV-vis and FL spectra of the sample were recorded by a PerkinElmer Lambda 35 UV-vis spectrophotometer and Hitachi F-4600 fluorescence spectrophotometer at room temperature, respectively.

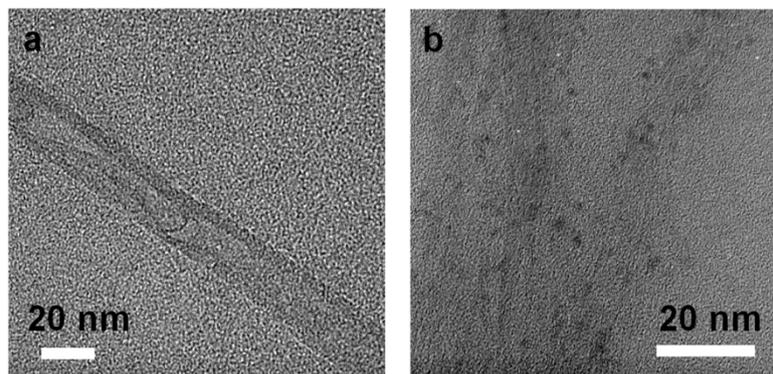


Fig. S1 TEM images for (a) purified MWCNTs and (b) GQDs-MWCNTs.

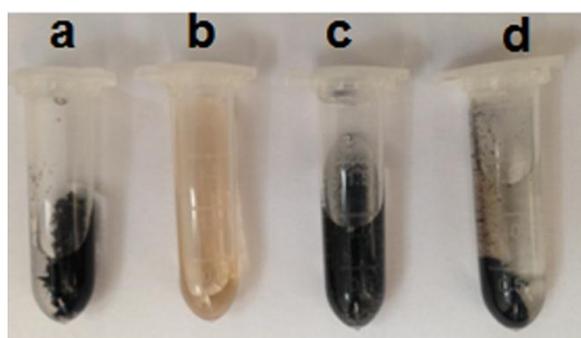


Fig. S2 The optical photographs of (a) MWCNTs; (b) GQDs solution after centrifugation at a rate of 10,000 rpm; (c) and GQDs-MWCNTs; and (d) GQDs-MWCNTs after centrifugation at a rate of 10,000 rpm.

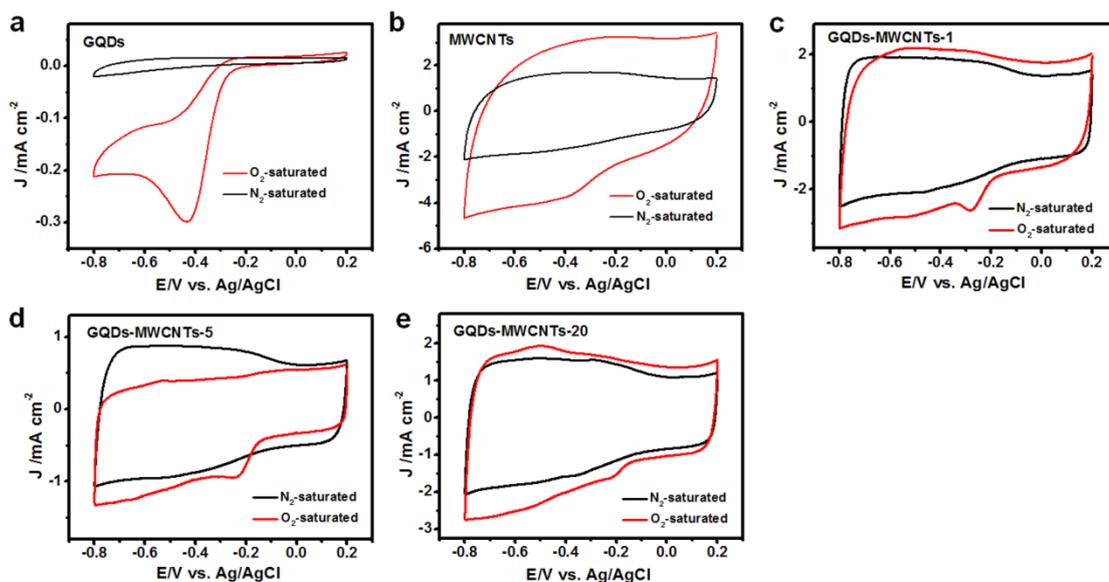


Fig. S3 CVs for the ORR at 100 mV s⁻¹ for (a) GQDs, (b) MWCNTs, (c) GQDs-MWCNTs-1, (d) GQDs-MWCNTs-5, (e) GQDs-MWCNTs-20 on the glass carbon electrode in N₂-saturated 0.1 M KOH,

O₂-saturated 0.1 M KOH solutions.

Rotating disk voltammetry measurements: To further study the ORR procedures with respect to GQDs-MWCNTs, we performed rotating-disk electrode (RDE) experiments. The RDE current-potential curves, at various rotating speeds, are shown in Fig. S4. The limited diffusion currents are dependent on the rotation rates. The number of electrons involved in the ORR can be calculated from the Koutecky-Levich (K-L) equation:

$$(1) J^{-1} = J_L^{-1} + J_K^{-1} = (B\omega^{1/2})^{-1} + J_K^{-1}$$

$$(2) B = 0.62nFC_0(D_0)^{2/3}\nu^{-1/6}$$

$$(3) J_K = nFkC_0$$

Where J is the measured current density, J_K and J_L are the kinetic- and diffusion-limiting current densities, ω is the angular velocity of the disk ($\omega = 2\pi N$, N is the linear rotation speed), n is the overall number of electrons transferred in the oxygen reduction, F is the Faraday constant ($F = 96485 \text{ C mol}^{-1}$), C_0 is the bulk concentration of O₂, ($C_0 = 1.2 \times 10^{-6} \text{ mol cm}^{-3}$), ν is the kinematic viscosity of the electrolyte ($\nu = 0.01 \text{ cm}^2 \text{ s}^{-1}$), and D_0 is the diffusion coefficient of O₂ in 0.1 M KOH ($1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$).

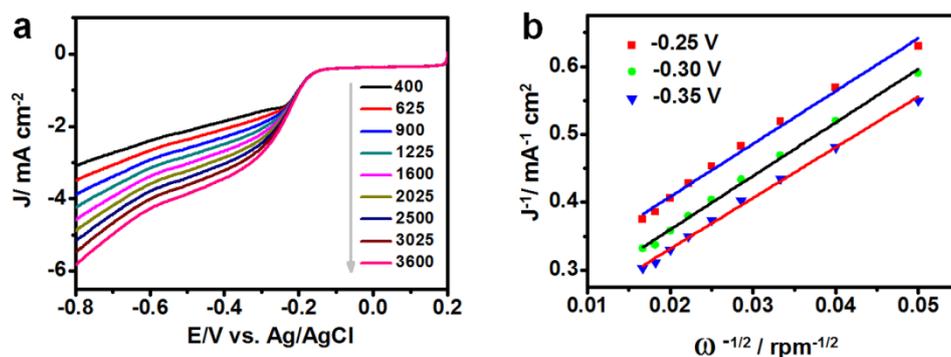


Fig. S4 (a) Rotating-disk voltammograms recorded for the GQDs-MWCNTs-3 electrode in an O₂-saturated 0.1 M solution of KOH at a scan rate of 10 mV s⁻¹ and different rotation rates. (b) Koutecky-Levich plot of J^{-1} versus $\omega^{-1/2}$ at different electrode potentials and the experimental data were obtained from Fig. S4a.

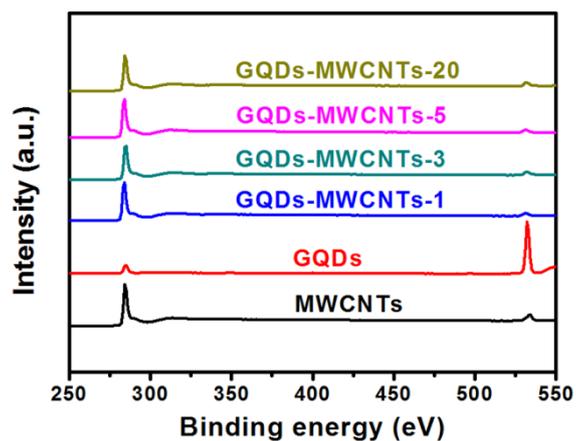


Fig. S5 XPS survey spectra of MWCNTs, GQDs, GQDs-MWCNTs-1, GQDs-MWCNTs-3, GQDs-MWCNTs-5 and GQDs-MWCNTs-20.

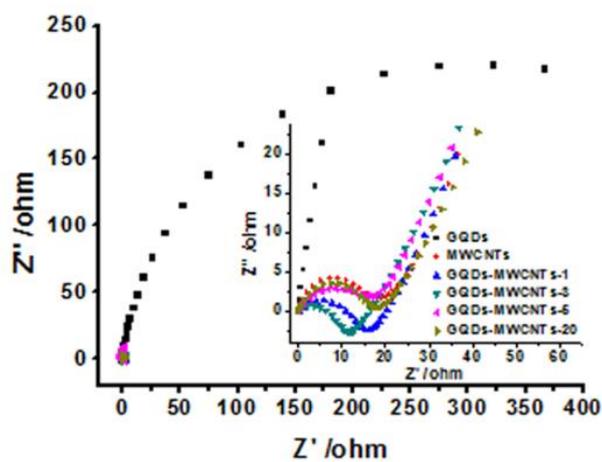


Fig. S6 Electrochemical impedance spectroscopy plots of various carbon materials.

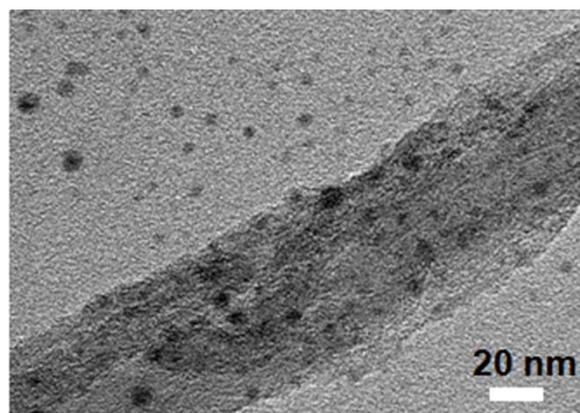


Fig. S7 TEM image of GQDs-MWCNTs-5.