Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary materials for

Synergistically enhanced activity of graphene quantum dots/graphene hydrogel composite: a novel all-carbon hybrid electrocatalyst for metal/air batteries

Experimental Section

Synthesis

The GQDs were derived from graphitized carbon nanofibers (Sigma Aldrich Corporation). In a typical process, 0.5 g graphitized carbon nanofibers were dispersed in 75 mL concentrated sulfuric acid and 25 mL concentrated nitric acid. The mixture then sonicated for 0.5 h followed by 24 h refluxing at 120 ^{o}C. After cooling to the room temperature, the 6 M KOH was employed to adjust PH to ~7. The reaction mixture was filtered using a 22 μm filter membrane to acquire the liquid supernatant and sediment. Subsequently, the supernatant was further dialyzed in a dialysis bag (Mw 1000) for 48 h to remove residual acids, and then it was concentrated to obtain the dry GQD powders. Graphene oxide (GO) was synthesized by exfoliating graphite which was purchased from Tianjin Kemiou Chemical Reagent Co. (China) through Hummers method.

The graphene quantum dot/graphene hydrogel composite was synthesized as follows: 60 mL 6 mg/mL of graphene oxide were added into 60 mL deionized water, followed by addition of 90mg of GQD powder. The mixture was homogeneous mixed and loaded into a Teflon-lined stainless steel autoclave and heated at 180 ^{o}C for 12 h. The product was washed with water and ethanol, and freeze-dried. The final product was labeled as GH-GQD-90. The GQD concentration's effect on the as-prepared electrochemical performance was studied by taking the addition of 0, 45mg and 180mg GQD as comparison, which were named as GH, GH-GQD-45 and GH-GQD-180.

Physicochemical Characterization

The morphology of samples was characterized with scanning electronmicroscopy (SEM, JSM-6360LV, JEOL), transmission electronmicroscopy (TEM, Tecnai G2 20ST). X-ray photoelectron spectroscopy (XPS, ESCA LAB 250Xi) was used to characterize the chemical state of the metal element in the material. UV-vis absorption spectra (Abs) were recorded on a UV-vis spectrophotometer (UV-1801). Photoluminescence (PL) spectra were measured using a fluorescence spectrophotometer (F-4600). N_2 adsorption/desorption measurements were employed by using a Quantachrome instrument (Quabrasorb SI-3MP). The surface area was evaluated by the Brunauere Emmette Teller (BET) method and the pore size distribution was obtained by the desorption branch using the BarretteJoynereHalenda (BJH) method. Raman spectra was measured using a laser Raman spectrometer (LabRAM HR800, JY).

Electrochemical Characterization

The ORR activities of the as-prepared sample GQD-GH were evaluated on an electrochemical workstation (Solartron 1470E) at room temperature using rotating disk electrode (RDE) technique. The linear sweep voltammetry (LSV) measurement was carried out using a catalyst loaded glassy carbon, spiral platinum wire and Ag/AgCl electrode as the working, counter and reference electrode in the range of 0.1-1.0 V, respectively. The working electrode was prepared as follows: 80 μL of 5wt % nafion solution was added to 2 mL of 3:1 v/v water/ethanol, and then, 8 mg of the catalyst was dispersed in it by sonicating to obtain a homogeneous ink. Then, 5 μL of the catalyst ink was loaded onto a glassy carbon electrode of 5 mm in diameter (the catalysts loading was ~100 μ g cm^{-2} for all samples). The electrochemical catalytic activity was tested in the O_2-saturated alkaline solution (0.1 M KOH).

The rotating ring-disk electrode RRDE measurement was carried out to clarify the electron transfer number and peroxide percentage of GH-GQD. Catalyst inks and electrode were prepared by the same method as RDE's. The disk electrode was scanned cathodically at a rate of 5 mV s^{-1} and the ring potential was constant at 0.40 V vs. Ag/AgCl. The $\%HO_2^-$ and the electron transfer number (n) were determined by the followed equations:

$$\%HO_2{}^- = 200 \times \frac{I_r/N}{I_d + I_r/N}$$

$$\mathrm{n} = 4 \times \frac{I_d}{I_d + I_r/N}$$

where I_d is disk current, I_r is ring current and N is current collection efficiency of the Pt ring. N was determined to be 0.40 from the reduction of $K_3Fe[CN]_6$[1].

In order to better describe the electrochemical performance of the GQD-GH, the as-prepared sample was evaluated by loading the sample onto the air electrode. The air electrode contained three layers: air diffusion layer, nickel mesh and catalytic layer. The catalytic layer was fabricated by catalysts, active carbon and acetylene black, as conductive additive, polytetrafluoroethylene emulsion (PTFE, 60 wt %), as binder, were mixed uniformly in a weight ratio of 3:3:1:3.

The zinc/air batteries were fabricated with three parts: pure zinc plate (anode), 6.00 M KOH aqueous solution (electrolyte) and air electrode (cathode), in the home-made cell model. The air cathode was fixed on the side with a circular hole while the metal plate was fixed on another side. The air diffusion layer is a membrane which is used to prevent electrolyte from leaking and let air go through at the same time. The air diffusion layer was fabricated by rolling press the acetylene black and polytetrafluoroethylene hybrid slurry (mass ratio: 1:5) which were dispersed in ethanol.

The constant-current discharge measurement was carried out by estimating the electrochemical performance of the air cathode in the application of zinc/air batteries. The discharge measurement was carried out using a LAND CT2001A battery-testing instrument. All battery testing measurements were operated under atmospheric air.

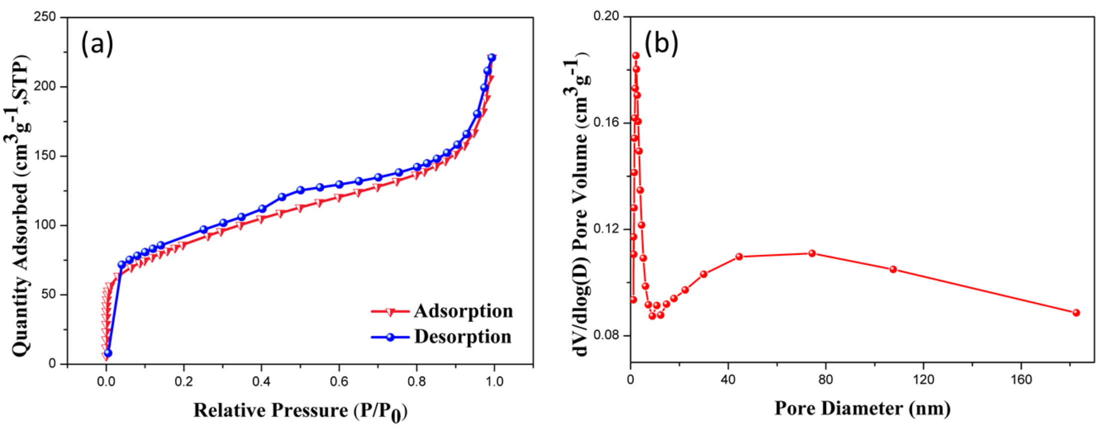


Fig. S1 (a) Nitrogen adsorption and desorption isotherms of freeze-dried GH-GQD-90; (b) pore size distribution image of GH-GQD-90

Sample	**The atom ratio of C**	**The atom ratio of O**
GH	83%	17%
GH-GQD-45	83.27%	16.73%
GH-GQD-90	83.97%	16.03%
GH-GQD-180	87.57%	12.43%

Table 1. the elemental (C, O) composition of the GH-GQD catalysts

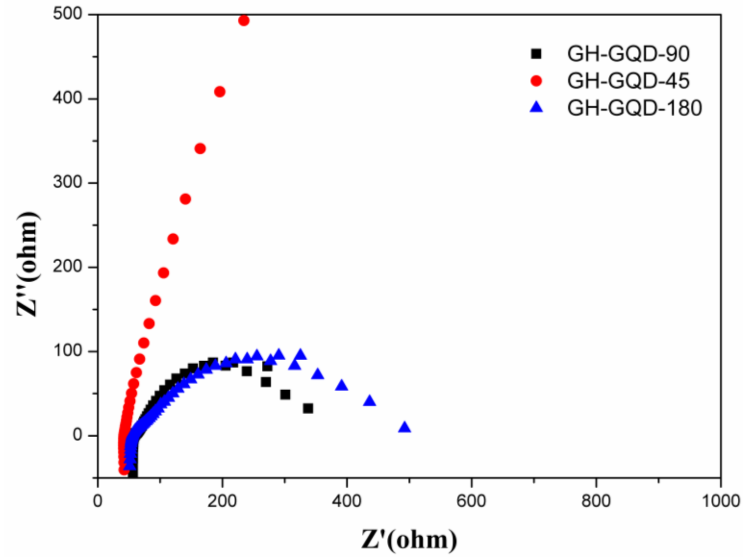


Fig. S2 Impedence spectra of GH-GQD-45,GH-GQD-90 and GH-GQD-180

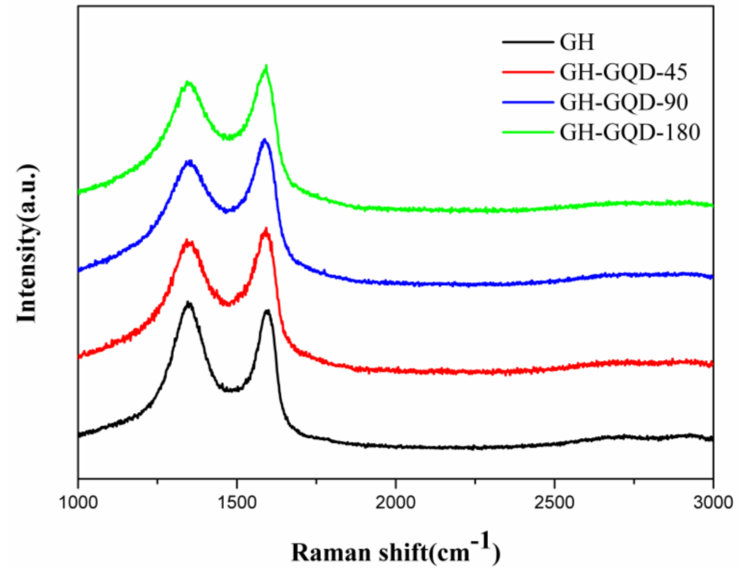
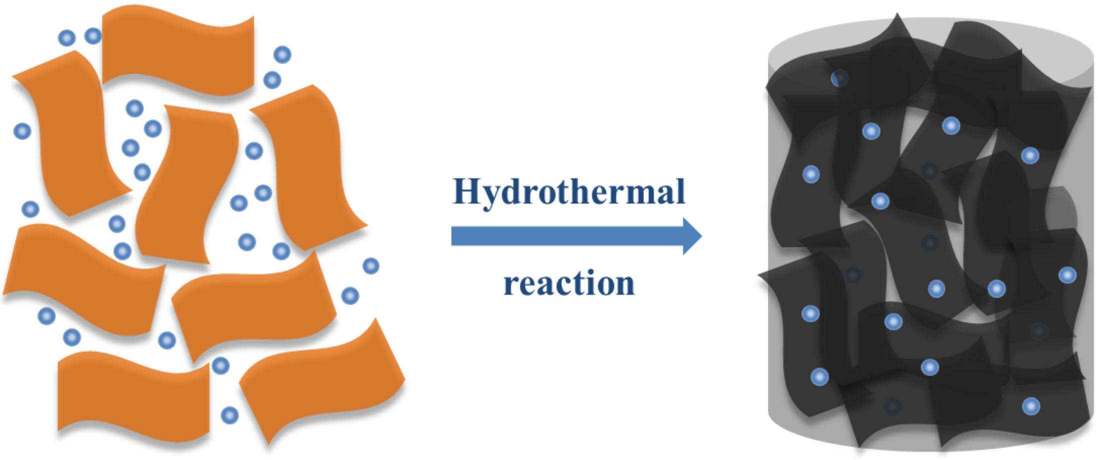


Fig. S3 Raman spectra of GH-GQD-45, GH-GQD-90 and GH-GQD-180

Sample	**I_D/I_G**
GH	1.0482
GH-GQD-45	0.9346
GH-GQD-90	0.8854
GH-GQD-180	0.9097

Table 2. the I_D/I_G of the as-prepared catalysts



Schem.1 The proposed formation mechanism for GH-GQD.

[1] Liang, Y.; Li, Y.; Wang, H.; Zhou, J.; Wang, J.; Regier, T.; Dai, H., Co_3O_4 nanocrystals on graphene as a synergistic catalyst for oxygen reduction reaction. Nature materials 2011, 10, (10), 780-6.