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Supporting Information for

Nitrogen-doped carbon dots decorated onto graphene: a novel all-carbon hybrid electrocatalyst for enhanced oxygen reduction reaction

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Experimental Details

Synthesis. The carbon source, coal, was first crushed and sieved to smaller than 150 μm, then mixed with coal tar and pressed into a tube mould under a pressure of 1.0-5.0 MPa to form rods that were then carbonized at 900 °C for 2 h yielding conductive and self-supporting carbon rods. The coal-based carbon rods were electro-oxidized at +9 V (vs. SCE) in 0.1 M NaOH aqueous solution with 0.5 M ammonia. The electrolyte was neutralized with hydrochloric acid (0.1 M). The N-CDs was collected by centrifugation of the supernatant at 9,000 rpm for 10 min and then loaded into dialysis bags for dialysis against DI water for 3 d. For comparison, the nitrogen-free CDs were also prepared under the same conditions, but etched from the coal-based rod in 0.1 M NaOH electrolyte without ammonia.

The N-CDs/G hybrid was synthesized as follows. 2 mL 4 mg/mL of graphene oxide were added into 6 mL of DI water, followed by addition of 2 mL of N-CDs hydrosol. The mixture was homogeneous mixed and loaded into a Teflon-lined stainless steel autoclave and heated at 180 °C for 12 h. The productwas washed with water and ethanol, and freeze-dried.

Characterization. The morphology and structure of the samples were investigated using a transmission electron microscopy (TEM, Philips Tecnai G2 20) at an acceleration voltage of 100 kV. Samples for the TEM measurements were prepared by dispersing in alcohol with ultrasonic treatment. The X-ray photoelectron spectra (XPS) were obtained using a Thermo ESCALAB 250 spectrometer with an Al-Kα X-ray source. Raman spectra were recorded on a DXR Raman Microscope (Thermo Scientific) with an excitation wavelength of 532 nm.

Electrode preparation and electrochemical measurements. Cyclic voltammetry (CV) measurements were performed using a computer-controlled potentiostat (CHI 760 D, Shanghai Chenhua) in a standard three-electrode cell. Electrocatalysts loaded on a glassy carbon disk (diameter: 5 mm) were used as working electrode, a Pt wire as counter electrode, and an Ag/AgCl (3.5 M KCl filled) electrode as reference electrode. Measurements on rotating disk electrode (RDE) were carried out on a MSR electrode rotator (Pine Instrument) and CHI 760 D potentiostat. For all CV and RDE measurements, an aqueous solution of KOH (0.1 M) was used as the electrolyte. Ar or O_2 was used to purge the solution to achieve the oxygen-free or oxygen-saturated electrolyte solution. The voltammetric stability test of N-CDs/G was performed in O_2-saturated 0.1 M KOH for 20,000 s, at a rotation speed of 1,000 rpm. Commercial 20 wt.% Pt/C (Johnson Matthey, Hispec 3000) catalyst was purchased and used for comparison. All electrochemical data were obtained at the temperature of 10 °C.

The working electrode was prepared as follows: Glassy carbon (GC) electrode was polished before each experiment with an alumina slurry (0.3 μm and 0.05μm) in sequence, and moderately ultrasonically cleaned with pure water. Then, 10 μL of catalyst suspension (1 mg/mL) in water and 5 μL of 0.1 wt.% Nafion solution in alcohol were sequentially dropped onto the surface of the clean GC electrode, and dried at the ambient temperature.

Electron transfer number was analyzed on the basis of Koutecky-Levichequations:

$$j^{-1} = j_L^{-1} + j_K^{-1} = (B\omega^{1/2})^{-1} + j_K^{-1} \qquad (1)$$

$$B = 0.2nFC_0(D_0)^{2/3}v^{-1/6} \qquad (2)$$

Where j is the measured current density, j_L and j_K are the diffusion- and kinetic-limiting current densities, ω is the angular velocity of the disk (rpm), n is the overall number of electrons transferred in oxygen reduction, F is the Faraday constant (F=96485 C mol^{-1}), C_0 is the bulk concentration of O_2, (C_0=1.2×10^{-6} mol cm^{-3}), v is the kinematic viscosity of the electrolyte (v=0.01 cm^2 s^{-1}), D_0 is the diffusion coefficient of O_2 in 0.1 M KOH (1.9×10^{-5} cm^2 s^{-1}). According to Equation (1) and (2), the number of electrons transferred (n) can be calculated to be 4.0 at -0.7 V, which indicates the N-CDs/G lead to a four-electron-transfer reaction to reduce directly oxygen into OH^-.

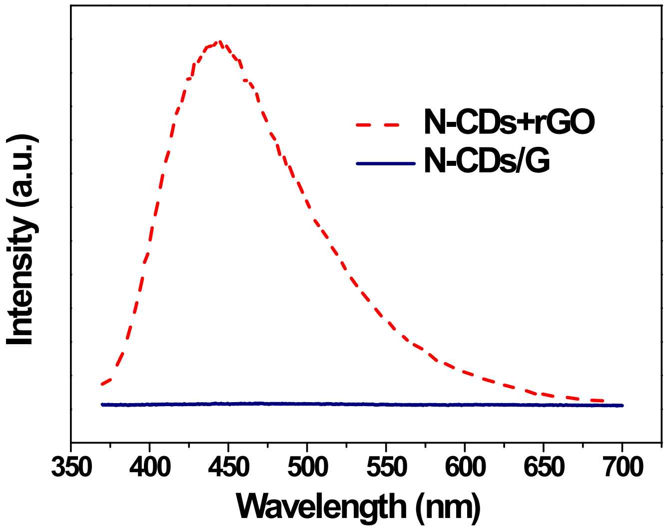

Fig. S1 Photoluminescence (PL) response of N-CDs and rGO under two different types of interactions. The mixture of N-CDs and rGO shows a notable PL emission (dashed line) at excitation of 340 nm, whereas the PL of the N-CDs/G hybrid (solid line) is quenched, implying the well-bonded interactions between N-CDs and rGO.

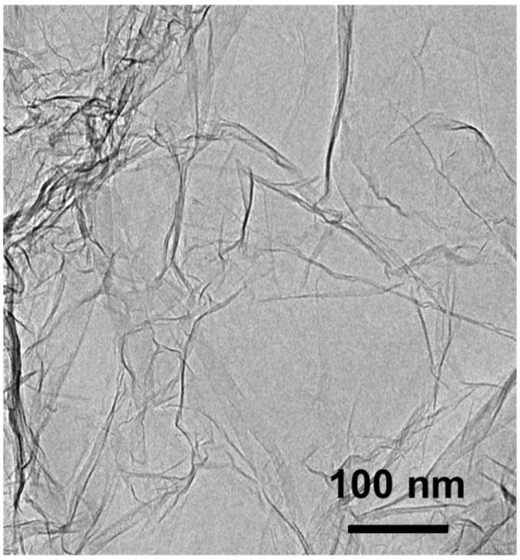

Fig. S2 TEM image of the reduced graphene oxide (rGO).

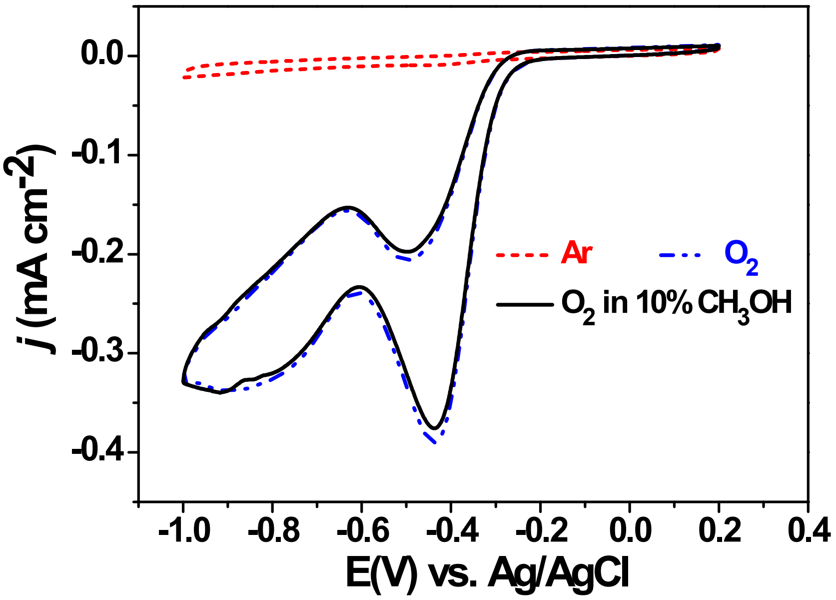

Fig. S3 Typical cyclic voltammogram for ORR at the bare glassy carbon electrode in an Ar-saturated 0.1 M KOH, O_2-saturated 0.1 M KOH, and O_2-saturated 10% (v/v) CH_3OH solutions.

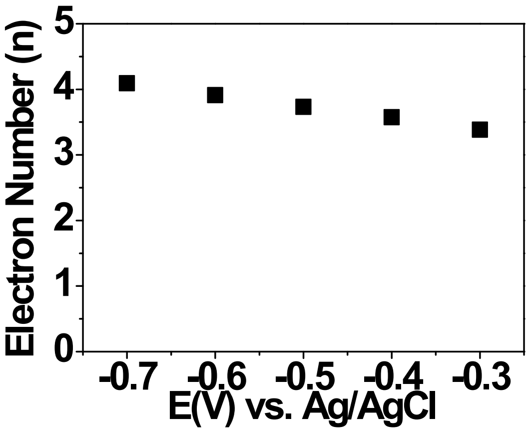

Fig. S4 The dependence of *n* on potential for the N-CDs/G electrode.

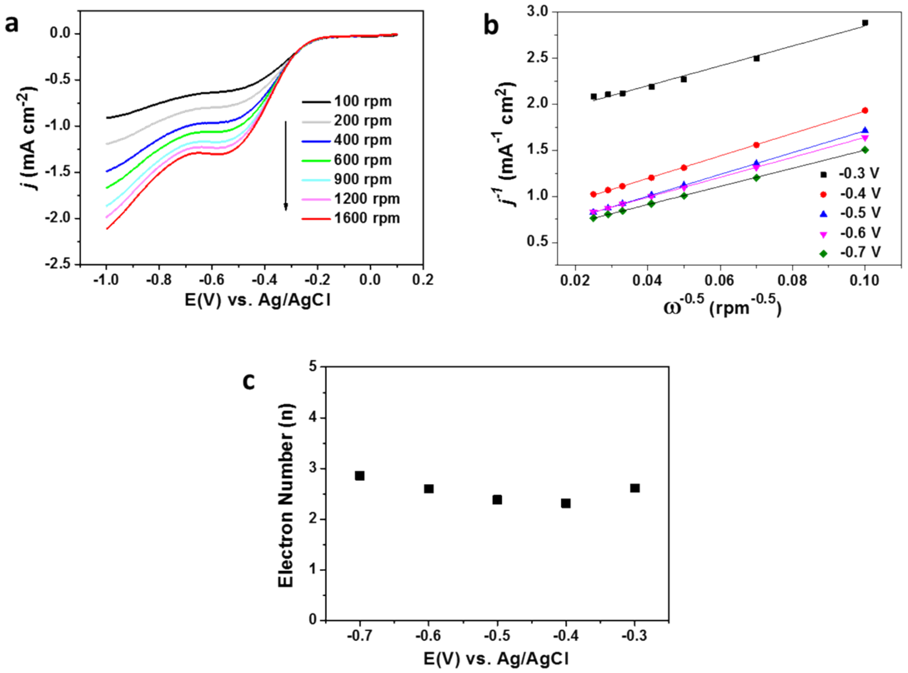

Fig. S5 Electrocatalytic performance of the rGO. (a) RDE voltammograms of the rGO electrode in O_2-saturated 0.1 M KOH with a sweep rate of 10 mV s^{-1} at different rotation rates. (b) Corresponding K-L plots of j^{-1} versus $\omega^{-0.5}$ at the electrode potentials of -0.3, -0.4, -0.5, -0.6, and -0.7 V. (c) The dependence of *n* on potential. The experimental data was obtained from (b).

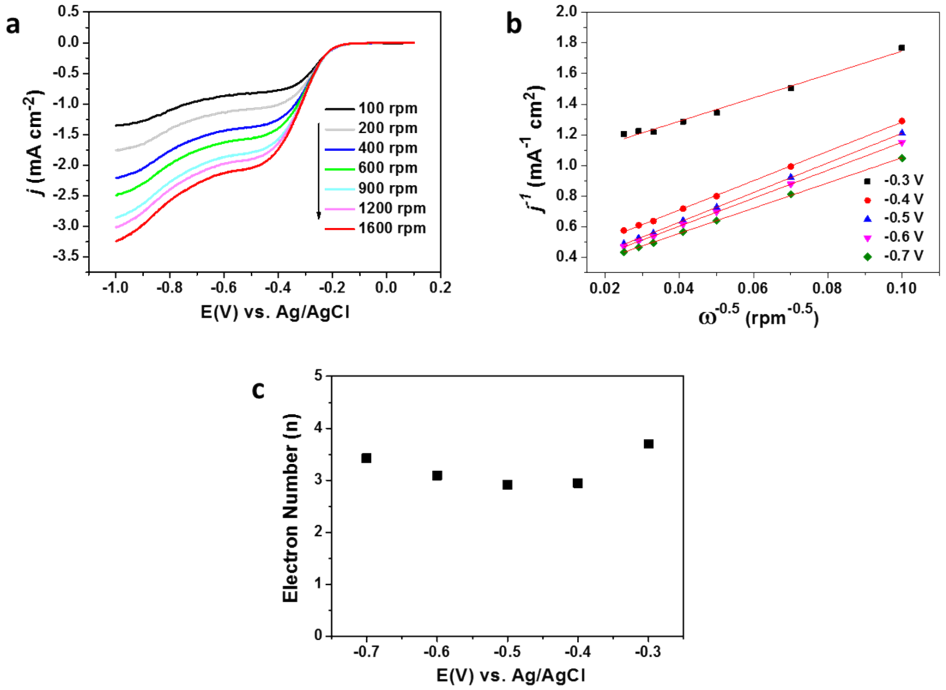

Fig. S6 Electrocatalytic performance of the CDs/G hybrid. (a) RDE voltammograms of the CDs/G electrode in O_2-saturated 0.1 M KOH with a sweep rate of 10 mV s^{-1} at different rotation rates. (b) Corresponding K-L plots of j^{-1} versus $\omega^{-0.5}$ at the electrode potentials of -0.3, -0.4, -0.5, -0.6, and -0.7 V. (c) The dependence of *n* on potential. The experimental data was obtained from (b)

Table S1 Analysis data of the coal sample

Coal	Proximate analysis (wt.%)			Ultimate analysis (daf, wt.%)				
	M_{ad}	A_d	V_{daf}	C	H	N	S	O*
Taixi	1.16	3.11	4.54	93.73	1.32	1.42	0.23	3.30

* by difference