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Electronic Supplementary Information

Graphene-based Hollow Spheres as Efficient Electrocatalyst for Oxygen Reduction

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Experimental section

Preparation of SiO_2 spheres: Monodisperse SiO_2 spheres were prepared by a modified Stöber's method.[1,2] In a typical synthesis, 10 ml aqueous ammonia (25 %) was added into 50 ml ethanol, after stirring for a few minutes, a mixture of 4 ml etraethylorthosilicate (TEOS) and 16 ml ethanol was added, the solution was stirred for 2h at room temperature. SiO_2 spheres were centrifuged and washed by ethanol for several times, and finally dried at 60 ℃, the resulting SiO_2 spheres were about 400 nm.

Preparation of graphene oxide: Graphene oxide (GO) was prepared according to the Hummer's method.[3,4] Graphite powder (1 g, Bay Carbon; SP-1 graphite) was added into 6 ml concentrated H_2SO_4, then mixed with $K_2S_2O_8$ (2.5 g), P_2O_5 (2.5 g) and reacting at 80 ℃ for 4.5 h. After cooling to room temperature, 250 ml deionized water was added under vigorous stirring (in ice-bath), the mixture was standing for night before filtered through PVDF membrane (with pore diameter of 0.2 μm). The prepared pre-oxidized graphite was dried under room temperature and then added to 50 ml H_2SO_4 (in ice-bath), afterwards, 5 g $KMnO_4$, was slowly added into the mixture. After stirring at 35 ℃ for 2 h, 83 ml deionized water was added (in ice-bath) and stirred for another 2 h. Subsequently, 230 ml deionized water and 10 ml 30% H_2O_2 were added respectively (the solution became bright yellow and generated enormous bubbles after adding H_2O_2). The solution was filtered on PVDF membrane and subsequently washed with 330 ml 1:10 hydrochloric acid and the same amount of deionized water. After dialysis for a week, the graphite oxide (GO) solution was filtered and vacuum drying at 30 ℃.

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Fabrication of rGO-sp: 5 mg GO was dispersed in 400 ml water and ultrasonic treated for 1 h and 250 mg polyethyleneimine (PEI) was dissolved in 100 ml water, both solutions were adjusted to pH 9. Specifically, 250 mg SiO_2 spheres was dispersed in 50 ml PEI solution and sonicated for 10 min and stirring for 15 min, then, excess PEI was removed by centrifuged and washed with water for two times (8000 rpm, 3 min). The resulting precipitate was redispersed in 50 ml water, then, 200 ml GO solution was added and stirring for 15 min. The mixture was centrifuged and washed with water for two times. Repeating the PEI and GO assembly process for six times, and GO encapsulated SiO_2 spheres were obtained and vacuum drying at 30 ℃. Afterwards, GO encapsulated SiO_2 spheres were dispersed in ~60 ml liquid NH_3 and stirred for 30 min, then, enough sodium was added; the reaction was proceeded in dry ice-acetone bath and finished within 2 h. Then, dry ice-acetone bath was removed and we let the ammonia volatize to remove it. The product was washed with enormous ethanol and water, and vacuum dried at 30 ℃. The powder was added to concentrated hydrofluoric acid (25 ml, 20%) and stirring for 10 h at room temperature. The obtained rGO-sp was washed with enough water and treated with freeze-drying.

Characterization: Field emission scanning electron microscopy (FE-SEM) images were obtained with JEOL JSM 7401. The graphene based hollow spheres were characterized by transmission electron microscope (TEM, H-7650B) at 80 kV. The microscopic features of the samples were observed by high-revolution transmission electron microscope (HRTEM, JEOL, JEM-2010) operated at 120 kV. X-ray diffraction (XRD) characterization was carried out on a Bruker D8-Advance using Cu-Kα radiation (λ = 1.5418 Å). Raman spectra were obtained under ambient conditions by using a RM 2000 microscope confocal Raman spectrometer (Renishaw PLC) using 488 nm laser. Fourier transform infrared spectra (FTIR) were recorded on Spectrum GX FTIR system. X-ray photoelectron spectroscopy (XPS) measurements were performed on a PHI Quantera Scanning X-ray Microprobe using a monochromic Al-Kα (λ = 1486.7 eV) (Binding energy is calibrated with C 1s - 284.8 eV).

Electrochemical experiments

CV and EIS measurements were performed by means of a CHI 1030B Instrument (CH

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Instruments, Inc., USA), and a PARSTAT 2273 advanced electrochemical system (Princeton Applied Research, USA), respectively. Electrochemical measurements were conducted in 1.0 mM $Fe(CN)_6^{3\ +/4\ +}$ in 1 M KCl with a three-electrode system connected to an electrochemical analyzer (CHI 600E, CHI Inc.). Samples were prepared by dispersing 1 mg rGO-sp in 1 ml DMF, and drop-casting of 10 μL samples over glassy carbon electrodes (with diameter of 3 mm). Ag/AgCl with saturated KCl and Pt wire were used as the reference and counter electrodes respectively.

Oxygen reduction reaction (ORR) measurement

A three-electrode system connected to an electrochemical analyzer (CHI 1030B) was adopted for ORR measurements, the working electrodes were prepared by drop-casting of samples over glassy carbon electrode (3 mm diameter), Ag/AgCl with saturated KCl and Pt wire were used as the reference and counter electrodes respectively.

The rotating disk electrode (RDE) measurements were recorded in O_2 saturated 0.1 M KOH solution at various rotating rates from 100 to 2025 rpm. The electrolyte was saturated for 20 min between each scan.

Supplementary Results

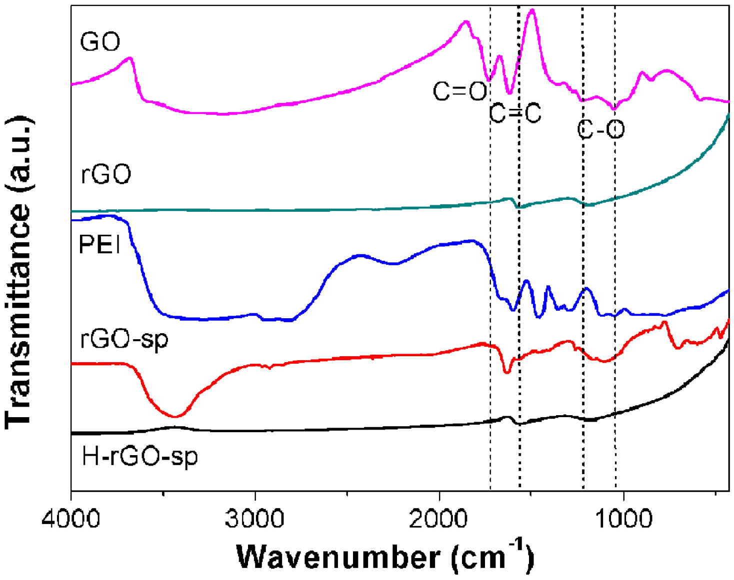

Fig. S1 FTIR spectra of GO and rGO, rGO-sp, H-rGO-sp obtained by $Na\text{-}NH_3$ reduction.

The FTIR spectrum of GO demonstrates the characteristic features of C=O stretching

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vibration peak at 1731 cm^{-1}, the C–O-C (epoxy) stretching vibration peak at 1222 cm^{-1}, the C–O (alkoxy) stretching vibration peak at 1052 cm^{-1}. The peak at 1618 cm^{-1} corresponds to the C=C sp^2 character. The characteristic peak of NH_2 bending vibration at 1631 cm^{-1} indicates the incorporation of PEI and rGO.[5-8] After thermal treatment, PEI was removed, as can be confirmed that the characteristic peak of PEI disappeared in the FTIR spectra of H-rGO-sp.

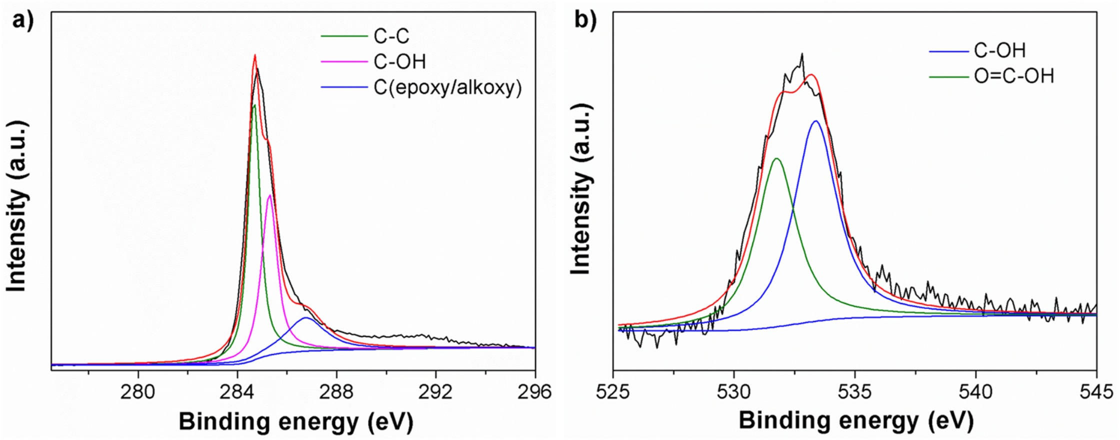

Fig. S2 High resolution XPS spectra of H-rGO-sp for C1s (a) and O1s (b).

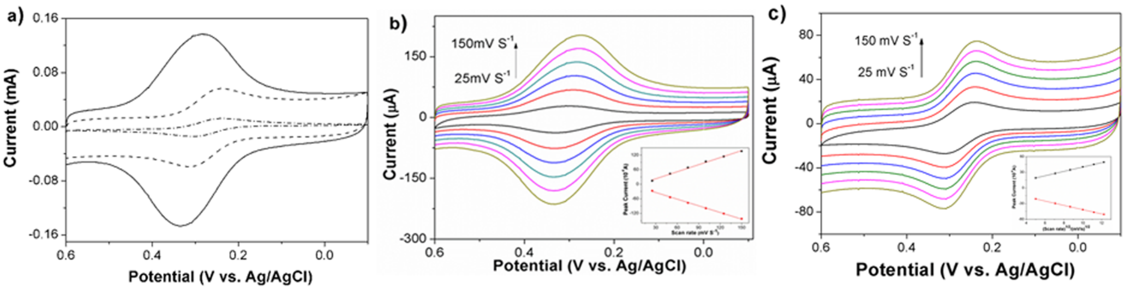

Fig. S3 a) Cyclic voltammograms for 1.0 mM $Fe(CN)_6{}^{3-/4-}$ in 1 M KCl at unmodified glassy carbon (GC) (dash-dot line) and rGO-sp (dashed line), H-rGO-sp (solid line) modified GC electrodes deoxygenated with N_2. Scan rate, 100 mV s^{-1}. Cyclic voltammograms of the rGO-sp (b), H-rGO-sp (c) modified electrodes in N_2-saturated 1 mM $Fe(CN)_6{}^{3-/4-}$containing 1 M KCl, at various scan rates: 25, 50, 75, 100, 125, 150 mV s^{-1}. The inset of (b) shows the plots of peak current vs. scan rate and the inset of (c) shows the plots of peak current vs. the square root of scan rate. The samples are dissolved in DMF by 1 mg/ml, and drop-casting of 10 μL samples over glassy carbon electrode.

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$Fe(CN)_6^{3-/4-}$ was selected as a probe to examine the electrochemical activity of materials (Fig. S3, **SI**). The peak-to-peak separation (ΔEp) value for rGO-sp was 43 mV, indicating that redox reaction at the electrode surface was adsorption control process.[9-11] This could be explained that positive PEI in rGO-sp adsorbed abundant $Fe(CN)_6^{3-/4-}$ and made the electrochemical reaction adsorption controlled. As shown in Fig. S3c in **SI**, the oxidative and reduction peak currents of H-rGO-sp electrode increase linearly with the square root of the scan rate, demonstrating that the reaction is controlled by semi-infinite linear diffusion.

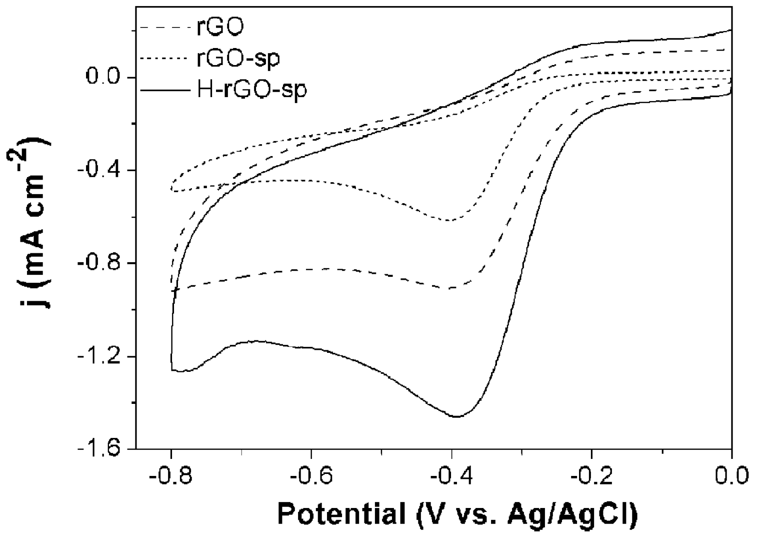
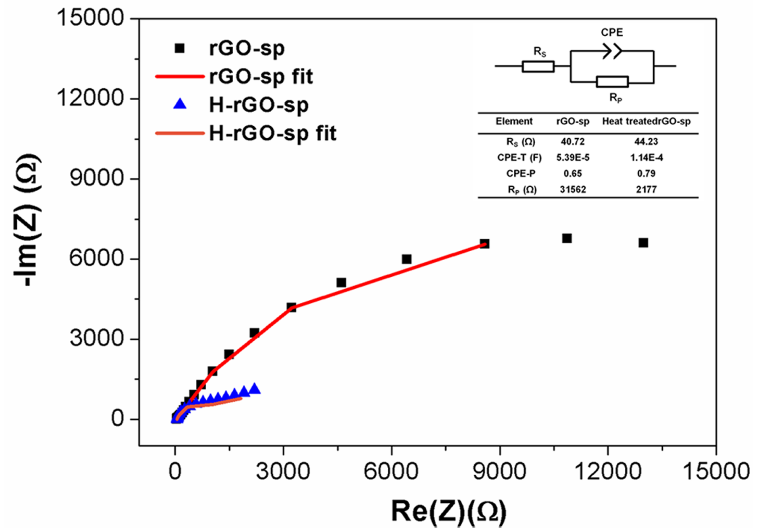


Fig. S4 Cyclic voltammograms of Glassy carbon electrodes modified with rGO, rGO-sp and H-rGO-sp in 0.1 M KOH solution saturated with O_2. Scan rate, 100 mV/s.



Element	rGO-sp	Heat treatedrGO-sp
R_S (Ω)	40.72	44.23
CPE-T (F)	5.39E-5	1.14E-4
CPE-P	0.65	0.79
R_P (Ω)	31562	2177

Fig. S5 Impedance spectra of rGO-sp (black dot), H-rGO-sp (blue dot) modified glassy carbon electrodes in 5.0 mM $Fe(CN)_6^{3\ +/4\ +}$ containing 0.5 M KCl at 25 ℃. Inset is the

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equivalent circuit used to fit the impedance spectra. The frequency range is between 0.1 and 10^5 Hz with signal amplitude of 10 mV. The samples are dissolved in 0.5% nafion solution by 1 mg/ml, and drop-casting of 6 μL samples over glassy carbon electrode.

The equivalent circuit was used to interpret electrochemical processes at the surface of the electrodes. R_s and R_p were the electrolyte resistance and the resistance of the material respectively. Constant phase element (CPE) is in place of a capacitor to compensate for non-homogeneity in the system. The CPE is defined by two values, CPE-T and CPE-P. The much smaller R_p indicated that H-rGO-sp made it easier for electron transfer took place at the electrode.[12,13]

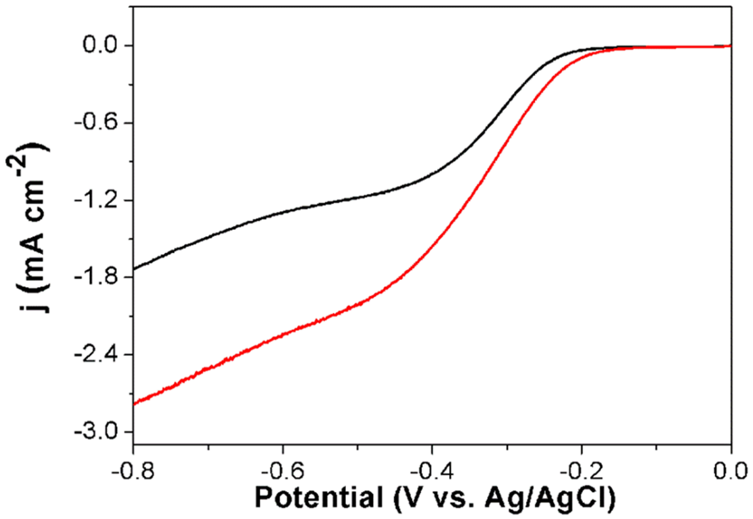

Fig. S6 Linear sweep voltammetry curves for oxygen reduction on graphene (black line), H-rGO-sp (red line) modified GCE in O_2-saturated 0.1 M KOH solution (scan rate: 5 mV s^{-1}, rotation rate: 1600 rpm).

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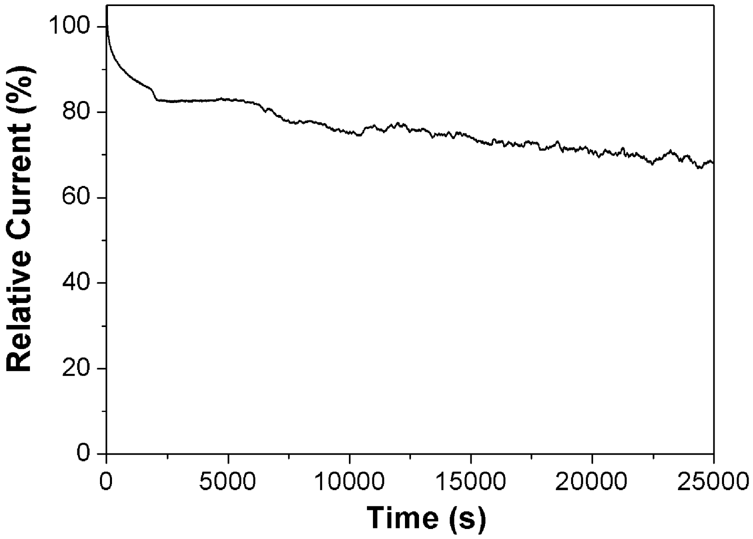

Fig. S7 Current-time (i-t) chronoamperometric response of rGO modified GC electrode at -0.4 V in O_2 saturated 0.1 M KOH at rotation rate of 1600 rpm.

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