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Supplementary Information

Cobalt Oxide-coated N- and B-doped Graphene Hollow Spheres as a Bifunctional Electrocatalyst for Oxygen Reduction and Oxygen Evolution Reactions

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Chemicals and reagents: Flake graphite (325 meshes) was purchased from Alfa Ltd. Concentrated sulphuric acid (H_2SO_4, 95.0～98.0 %), nitric acid (HNO_3, 65.0～68.0 %), methanol (CH_3OH, ≥99.7 %), sodium nitrate ($NaNO_3$, ≥99.0 %), potassium permanganate ($KMnO_4$, ≥99.5 %), hydrochloric acid (HCl, 36.0～38.0 %), hydrogen peroxide aqueous solution (H_2O_2, 30 %), *n*-hexade cyltrimethylammonium bromide (C16TMABr, ≥99.0 %), tetraethyl orthosilicate (TEOS), dimethyl sulphoxide (DMSO), and ethylene glycol (EG, ≥99.0 %) were obtained from Shanghai Chemical Reagent Co. Ltd. 3-Aminopropyltriethoxysilane (APTES, ≥ 98.0 %), and absolute ethanol (reagent grade) was obtained from aladdin Co. Ltd. The JM Pt/C with 20 wt. % Pt was purchased from the Johnson Matthey Corp. All the chemicals were used as received without further purification. Deionized (DI) water (H_2O) through Millipore system (Milli-Q®) was used in all the experiments.

Preparation of GO and GO solution: GO was synthesized from the flake graphite following the procedure reported by Hummers et al.[1] with a slight modification, as described in our previous work.[2-4] In a typical synthesis, 2.0 g of graphite and 2.5 g of $NaNO_3$ were first mixed with 150 mL of H_2SO_4 (95%) in a 500 mL flask. The obtained mixture was then stirred for 30.0 min with an ice bath. Under vigorous stirring, 15.0 g of $KMnO_4$ was added under well control to maintain the reaction temperature below 20 °C. The reaction mixture was then stirred overnight at room temperature, followed by the addition of 180 mL of H_2O also under vigorous stirring. After that, the reaction temperature was rapidly increased to 98 °C and the mixture were kept at 98 °C for 24 h, resulting in a color change from black to yellow. Followed by the addition of 80.0 mL of 30.0% H_2O_2 aqueous solution, the reaction mixture was cooled down to room temperature. The obtained graphene oxide was washed by rinsing and centrifugation with 5.0% HCl and H_2O for several times, and then filtrated and dried under vacuum.

Fabrication of amino-modified silica MCM-41 spheres (NH_2-MCM-41): The mesoporous MCM-41 spheres with sizes ranging from 450 to 800 nm were synthesized from an alkaline solution containing C16TMABr, TEOS, and $NH_3 \cdot H_2O$ according to a procedure reported in the literature.[5] For their amino-functionalization, ~1 g of MCM-41 was dispersed in 300 mL of dry toluene by ultrasonication. After the addition of 3 mL of 3-aminopropyltrimethoxysilane, the mixture was heated to 65 °C under stirring and kept at that temperature for 12 h. The obtained NH_2-MCM-41 spheres were washed through centrifugation and redispersed in water.

Fabrication of NBGHSs/NH_2-MCM-41, NGHSs/NH_2-MCM-41, BGHSs/NH_2-MCM-41, and GHSs/NH_2-MCM-41 spheres: For the fabrication of the NBGHSs/ NH_2-MCM-41, 0.3 g of NH_2-MCM-41 obtained above was dispersed in 30.0 mL of distilled water. The pH value of the solution was then adjusted to 2.5 by adding drops of 1.0 M HCl solution, which made the NH_2-MCM-41 spheres positively charged. To this solution, 20 mL of 2.0 mg mL^{-1} negatively charged GO suspension was added. The obtained mixture was stirred at room temperature for 24 h, which led to the deposition of GO onto the surface of NH_2-MCM-41 through an electrostatic interaction. 18 mmol ammonia boron trifluoride (NH_3BF_3) was then added under stirring. The resulting stable suspension was sealed in a Telfon-lined autoclave and hydrothermally treated at 180 °C for 12 h. After freeze-drying overnight and vacuum-drying at 60 °C for several hours, the obtained products were calcined in Ar atmosphere at 420 °C for 2 h and at 800 °C for 30 min, which led to the formation of NBGHSs/NH_2-MCM-41 with a core/shell structure.

The GHSs/NH_2-MCM-41 was prepared with the same synthetic procedure for the synthesis of NBGHSs/NH_2-MCM-41 without using the dopants. The same synthetic procedure was also employed for the synthesis of the NGHSs/NH_2-MCM-41 and the BGHSs/NH_2-MCM-41 with the addition of appropriate dopants as needed. For example, the synthesis of NGHSs/NH_2-MCM-41 and BGHSs/NH_2-MCM-41, urea and boric acid (H_3BO_3) were employed, respectively.

Fabrication of Co_3O_4-coated NBGHSs (Co_3O_4/NBGHSs), NGHSs (Co_3O_4/ NGHSs), BGHSs (Co_3O_4/BGHSs), and GHSs (Co_3O_4/GHSs): For the fabrication of the Co_3O_4/NBGHSs**,** the core/shell NBGHSs/NH_2-MCM-41 synthesized above was soaked in concentrated hydrochloric acid for 3 h at 150 °C and then washed by centrifugation. The obtained product was redispersed in 200 mL of 0.3 mol $Co(NO_3)_2$ solution and ultrasonicated for 15 min. The mixture was then aged for 7 days to allow the coating of NBGHSs/NH_2-MCM-41 with Co_3O_4. The coated spheres were then subjected to four cycles of centrifugation-water washing to remove impurities and unreacted cobalt precursors, followed by drying at 60 °C for 5 h in a vacuum oven. The Co_3O_4-coated NBGHSs/NH_2-MCM-41 spheres were then calcined in Ar atmosphere at 450 ^oC for 2 h to strengthen the Co_3O_4 shell and subsequently redispersed in 1.0 M NaOH to remove the NH_2-MCM-41 cores. The resulting Co_3O_4/NBGHSs were washed with deionized water and vacuum dried.

The synthesis of the Co_3O_4/NGHSs, the Co_3O_4/BGHSs, and the Co_3O_4/GHSs were carried out with a similar procedure used for the synthesis of the Co_3O_4/NBGHSs with the NBGHSs/NH_2-MCM-41 substituted by an equimolecular amount of NGHSs/NH_2-MCM-41, BGHSs/NH_2-MCM-41, GHSs/NH_2-MCM-41, respectively.

Fabrication of pure Co_3O_4 hollow microspheres: The MCM-41 spheres prepared above were redispersed in 200 mL of 0.3 mol $Co(NO_3)_2$ solution and ultrasonicated for 15 min. The mixture was aged for 7 days to allow the formation of a Co_3O_4 coating on the SiO_2 sphere surface. The coated spheres were then subjected to four cycles of centrifugation-water washing to remove impurities and unreacted cobalt precursors, followed by drying at 60 ^oC for 5 h in a vacuum oven. The Co_3O_4-coated SiO_2 spheres were then calcined in Ar atmosphere at 450 ^oC for 2 h to strengthen the Co_3O_4 shell. The formation of Co_3O_4 hollow microspheres were obtained by further treatment of the Co_3O_4/SiO_2 with 1.0 M NaOH, followed by washing with DI water and vacuum drying.

XPS analysis: For the XPS data analysis, the Shirley background was subtracted before curve fitting. The experimental spectra were fit into components of Gaussian line shape. The elemental compositions were determined by the ratios of peak areas corrected with the sensitivity factors. For N 1s, B 1s, O 1s, and C 1s peaks of the Co_3O_4/NBGHSs before and after etching, the line widths (fwhm) of the components with the same oxidation states were kept relative constant to minimize the fitting errors.

Electrical conductivity measurement: Typically, the catalysts were mixed with 1.0 wt% polytetrafluoroethylene (PTFE, solid powder, Dupont) as a binder, and homogenized in an agate mortar. The mixture was rolled into 80–100 μm thickness sheets, pressed by 20 MPa and finally cut into 3 × 1 cm^2 sheets. Then the obtained sheets were coated with silver conductive adhesives on both sides and tested using a multimeter. The conductivity of the catalysts was calculated using the formula:

$$\lambda = \frac{L}{R_x W d} \tag{S1}$$

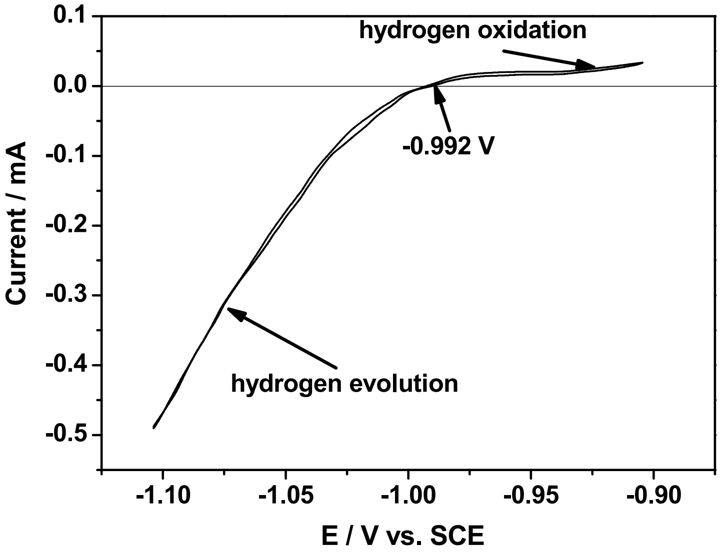
where λ is the electrical conductivity of the catalyst, L, W, d is the length, width and thickness of the sheet, respectively, and Rx is the resistance of the catalysts tested by the multimeter.

BET and Raman spectra: Brunauer−Emmet−Teller (BET) surface area was determined by using an AUTOSORB-IQ-MP instrument with nitrogen adsorption at 77 K using the Barrett−Joyner−Halenda (BJH) method. Raman spectra were recorded on a RENISHAW inVia instrument with an Ar laser source of 488 nm in a macroscopic configuration.

Electrochemical measurement: Cyclic voltammetry was performed with a computer-controlled potentiostat (CHI 760C, CH Instrument, USA) with a typical three-electrode cell, in which a saturated calomel electrode (SCE), a platinum wire, and a glassy carbon electrode/rotating disk electrode (RDE) loaded with various catalysts were employed as the reference electrode, the counter-electrode and the working electrode, respectively. For the preparation of the working electrode, 5.0 mg as-synthesized catalyst was mixed with 50 μL Nafion solution (5.0% Nafion in ethanol), 450 μL DI water, and 500 μL isopropyl alcohol. The mixture was sonicated and 5.0 μL suspensions were dropped onto an electrode (5 mm diameter) and then fully dried. For a comparison, the commercially available Johnson Matthey (JM) Pt/C with 20 wt. % Pt (Johnson Matthey Corp., Pt loading: 20 wt. % Pt on the carbon) electrode was also prepared. The Pt/C suspension was prepared by dispersing 10 mg of the Pt/C powder in 2 mL of ethanol in the presence of 50 μL of isopropyl alcohol solution with 5 wt. % Nafion. The addition of a small amount of Nafion could effectively improve the dispersion of the Pt/C catalyst suspension and prevent its dropping from the electrode during the electrochemical measurements. For the RDE measurements, catalyst inks were prepared by the same method for the CV's. 5 μL ink (containing 25 μg catalyst) was loaded onto a glassy carbon rotating disk electrode of 5 mm in diameter (Pine Instruments) giving a loading of 0.13 mg/cm^2. The working electrode was scanned cathodically at a rate of 5 mV s^{-1} with varying rotating speeds from 400 rpm to 2025 rpm. Koutecky–Levich plots were analyzed at various electrode potentials. The slopes of their best linear fit lines were used to calculate the number of electrons transferred on the basis of the Koutecky-Levich equation. The scan rate was 5 mV s^{-1} for both cyclic voltammetry and rotating disk electrode measurements. For the OER measurements, 24.5 μL of the catalyst ink suspension thus obtained was coated onto the polished glassy carbon electrode. The working electrode was scanned cathodically at a rate of 20 mV s^{-1}. All the experiments were carried out in 0.1 M KOH (pH = 13) electrolyte at room temperature (25 °C). The geometrical surface area of the glassy carbon electrode (19.6 mm^2) was used to calculate the current density. The potentials reported in this work were referenced to the reversible hydrogen electrode (RHE) through RHE calibration. In 0.1 M KOH, E (RHE) = E (SCE) + 0.992 V, as demonstrated by the calibration curve as below.

a. Calibration of SCE and Conversion to RHE

The calibration of SCE reference electrode was performed in a standard three-electrode system with polished Pt wires as the working and counter electrodes, and the SCE as the reference electrode. Electrolytes were pre-purged and saturated with high purity H_2. CVs were run at a scan rate of 1 mV s^{-1}, and the average of the two potentials at which the current crossed zero was taken to be the thermodynamic potential for the hydrogen electrode reactions.[6, 7]



In 0.1 M KOH, the zero current point is at -0.992 V, so E (RHE) = E (SCE) + 0.992 V.

b. Diffusion Corrected Tafel Plot

For the ORR Tafel plot, the kinetic current was calculated from the mass-transport correction of RDE by:

$$J_K = \frac{J \times J_L}{(J_L - J)} \tag{S2}$$

Zn-Air Battery Assembling: Primary Zn-air batteries were tested in home-built electrochemical cells. Typically, a two electrode configuration was used by pairing Co_3O_4/NBGHSs loaded on a carbon paper electrode (1.0 cm^2, catalyst loading of 1.0 mg) with a Zn foil (Alfa Aesar) in 30-40 mL of 6 M KOH. During battery measurements, oxygen was continuously fed to the cathode. It was humidified by passing through a separate liquid water container before entering the cell. The battery internal impedance was measured to be 0.95 Ω at the open circuit condition.

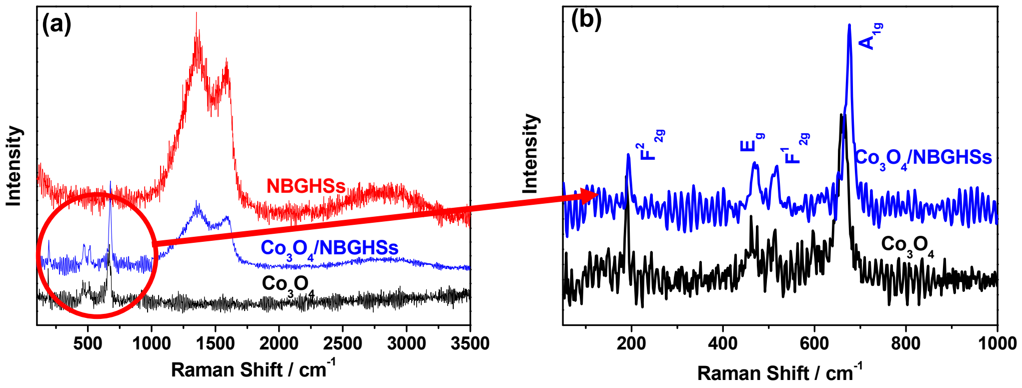


Figure S1. (a) Raman spectrum of pure Co_3O_4 hollow microspheres, Co_3O_4/NBGHSs, and NBGHSs. (b) Raman spectrum of pure Co_3O_4 hollow microspheres and Co_3O_4/NBGHSs at the low wavenumber.

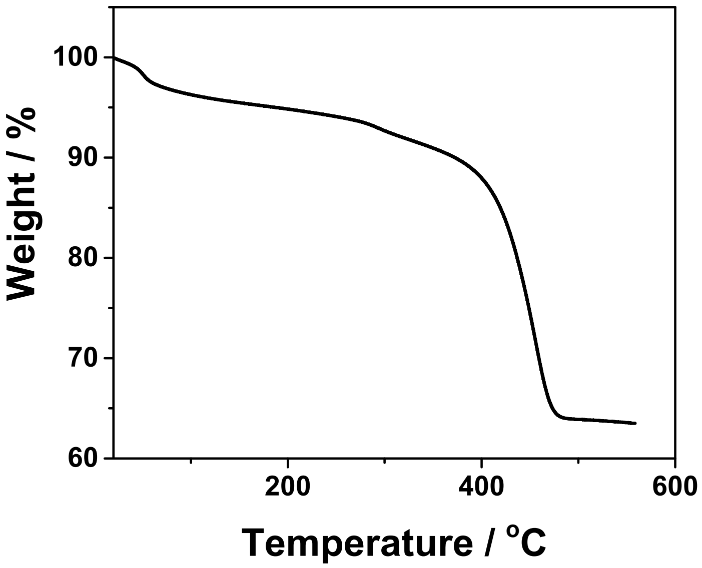


Figure S2. TGA analysis of Co_3O_4/NBGHSs.

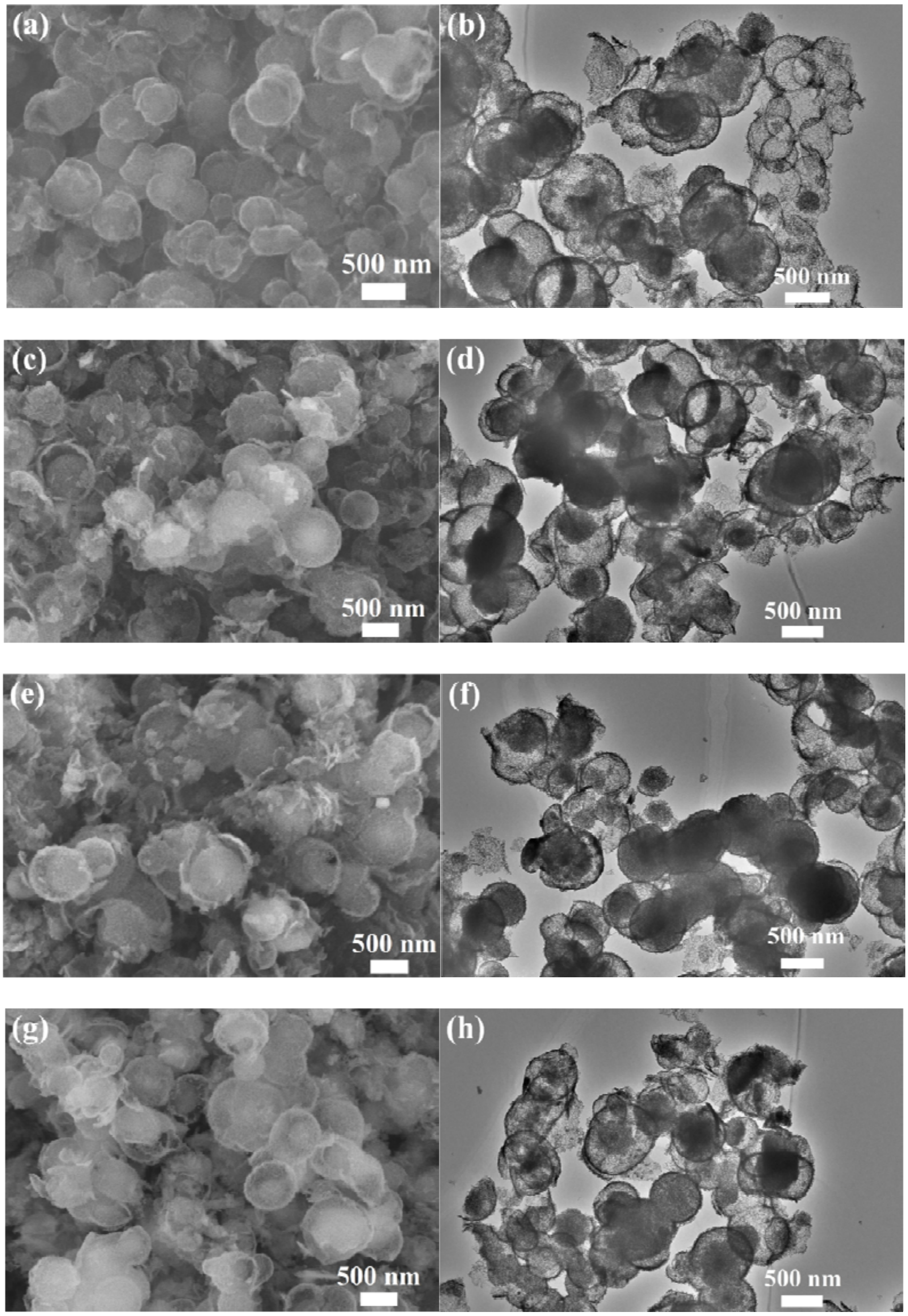


Figure S3. SEM and TEM images of (a,b) pure Co_3O_4 hollow microspheres, (c,d) Co_3O_4/GHSs, (e, f) Co_3O_4/NGHSs, and (g, h) Co_3O_4/BGHSs.

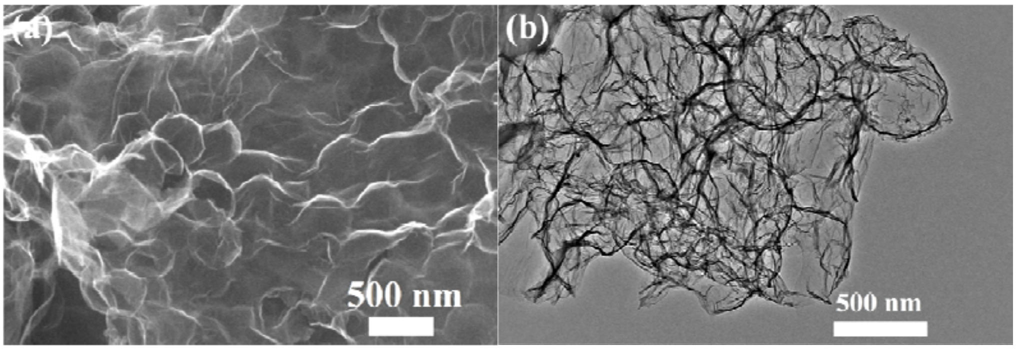


Figure S4. SEM and TEM images of NBGHSs fabricated by the removal of the Co_3O_4 hollow microspheres from Co_3O_4/NBGHSs with a 1.0 M HCl solution.

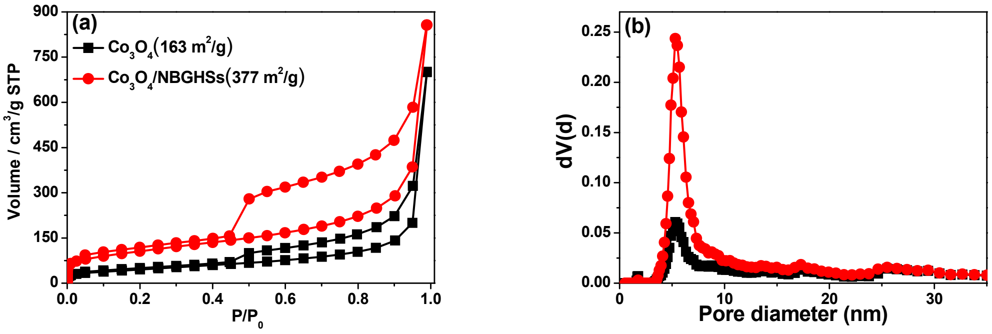


Figure S5. (a) Nitrogen adsorption/desorption isotherms of the Co_3O_4 hollow microspheres and Co_3O_4/NBGHSs. (b) The pore size distribution of the Co_3O_4 hollow microspheres and Co_3O_4/NBGHSs calculated using a slit/cylindrical NLDFT model.

Electroactive surface areas of the catalysts.

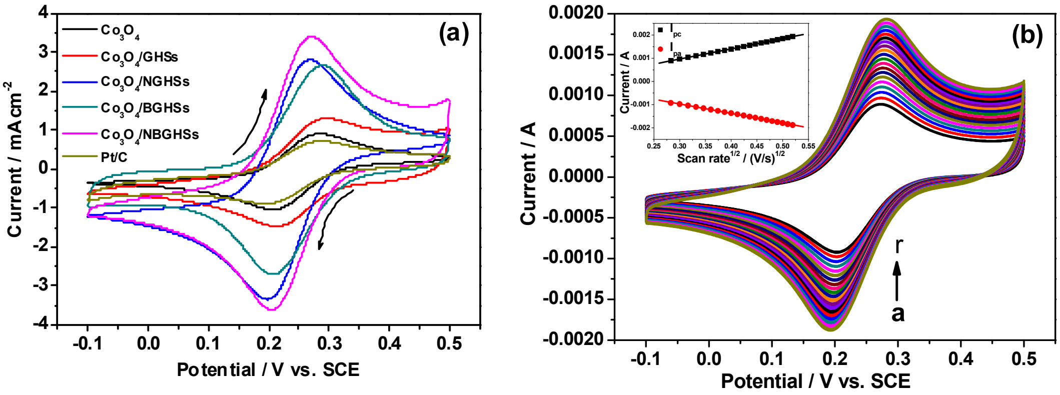


Figure S6. (a) CVs of the Co_3O_4 hollow microspheres, the Co_3O_4/GHSs, the Co_3O_4/NGHSs, the Co_3O_4/BGHSs, the Co_3O_4/NBGHSs, and the Pt/C 20 wt. % casted on the glassy carbon (GC) electrode in 10.0 mM $Fe(CN)_6^{3-/4-}$ in 1.0 M KCl. The scan rate was 50 mV/s. (b) CVs of the Co_3O_4/NBGHSs on GC electrode in 10 mM $Fe(CN)_6^{3-/4-}$/1.0 M KCl at various scan rates from 80 mV/s to 270 mV/s. Inset: plot of peak current vs. (scan rate)$^{1/2}$ of the Co_3O_4/NBGHSs casted on the GC electrode. The loadings of the catalysts on GC electrode kept the same and were ~0.2 mg/cm^2 for all the cases.

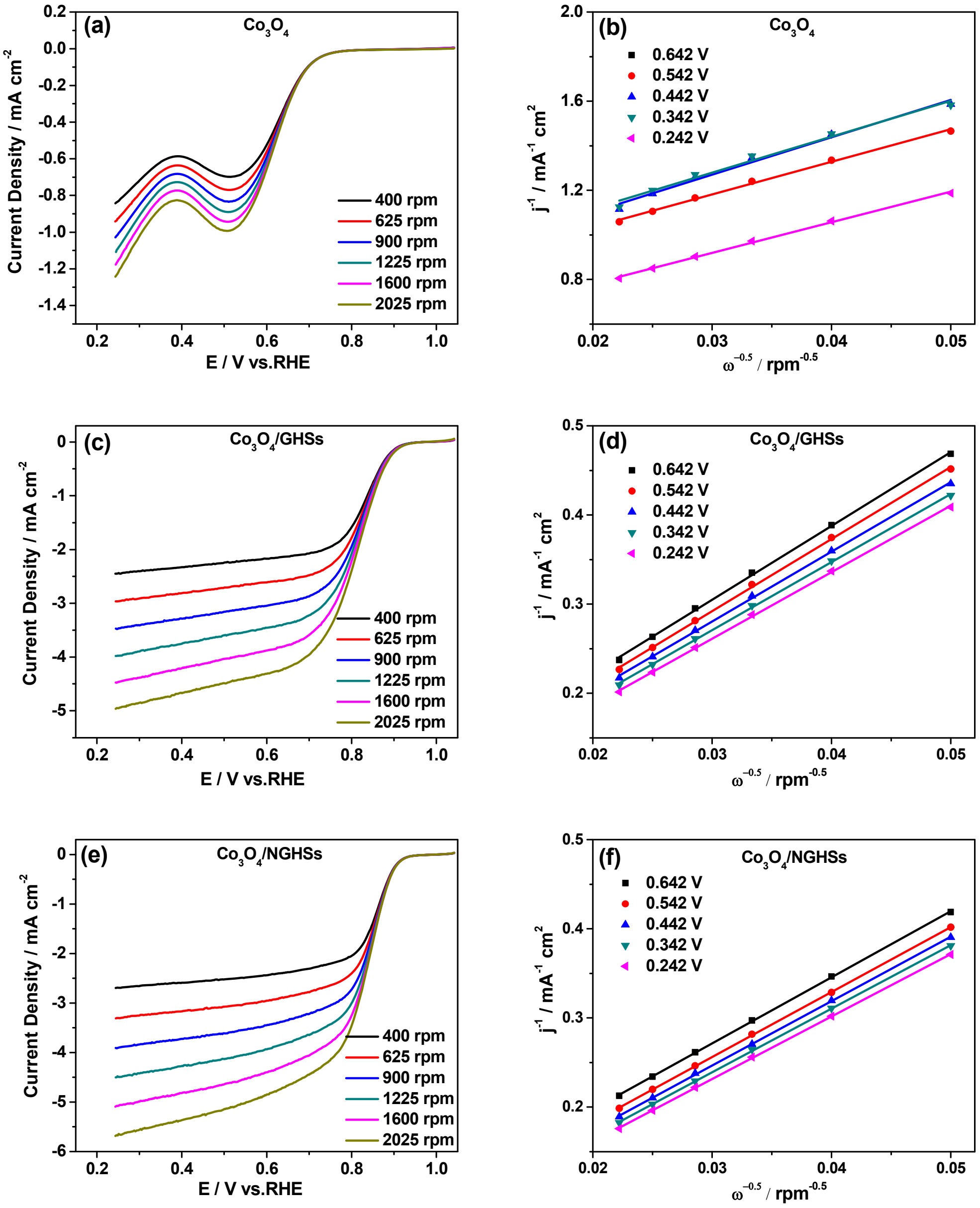
The electrocatalytic surface areas of the catalysts were determined by cyclic voltammetry using 10 mM $Fe(CN)_6^{3-/4-}$ in 1.0 M KCl, as shown in Figure S6a. Figure S6b shows that the $\Delta E_p = (E_{pa} - E_{pc})$ of the Co_3O_4/NBGHSs increases with increasing scan rate, but the formal potential ($E^{0'} = 1/2(E_{pc} + E_{pa})$) is almost constant, indicating the quasi-reversibility of the electron transfer process.[8] The electroactive surface area can then be estimated according to the Randles-Sevcik equation[9, 10]:

$$i_p = 2.99\times10^5 nACD^{1/2}\upsilon^{1/2} \quad \text{(S3)}$$

$$A = k/(2.99\times10^5 nCD^{1/2}) \quad \text{(S4)}$$

where i_p, n, A, C, D, and υ are the peak current, the number of electrons involved in the reaction, the electroactive surface area, the concentration of the reactant, the diffusion coefficient of the reactant species, and the scan rate, respectively. k is the slope of the straight line for i_p *vs.* $\upsilon^{1/2}$. The redox reaction of $Fe(CN)_6^{3-/4-}$ involves one-electron transfer (n =1), and the diffusion coefficient (D) is 6.30×10^{-6} cm^2/s.

Based on the results shown in Figure S6a, the electroactive surface areas of the Co_3O_4 hollow microspheres, Co_3O_4/GHSs, Co_3O_4/NGHSs, Co_3O_4/BGHSs, Co_3O_4/NBGHSs, and the Pt/C 20 wt.% are 3.5×10^{-2}, 6.9×10^{-2}, 31.3×10^{-2}, 23.2×10^{-2}, 58.8×10^{-2} and 2.53×10^{-2} cm^2, respectively. This indicates that the electroactive surface area of Co_3O_4/NBGHSs is higher than the the Co_3O_4 hollow microspheres, Co_3O_4/GHSs, Co_3O_4/NGHSs, Co_3O_4/BGHSs, and the Pt/C 20 wt. %.



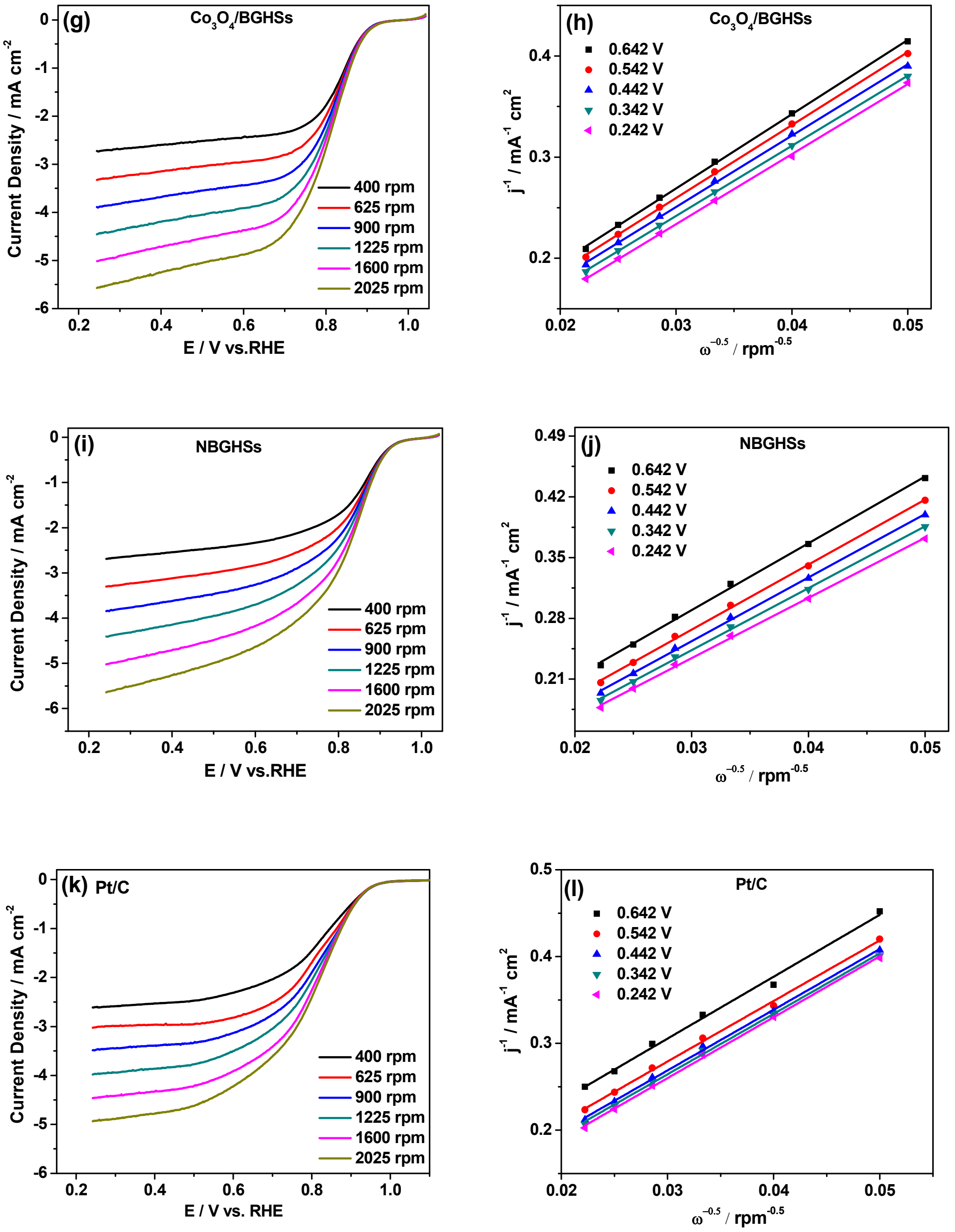


Figure S7. LSV curves at the various rotation rates for the ORR and corresponding K-L plots for the (a,b) Co_3O_4 hollow microspheres, (c,d) Co_3O_4/GHSs, (e,f) Co_3O_4/NGHSs, (g,h) Co_3O_4/BGHSs, (i,j) NBGHSs, and (k,l) Pt/C in the O_2-saturated 0.1 M KOH solution.

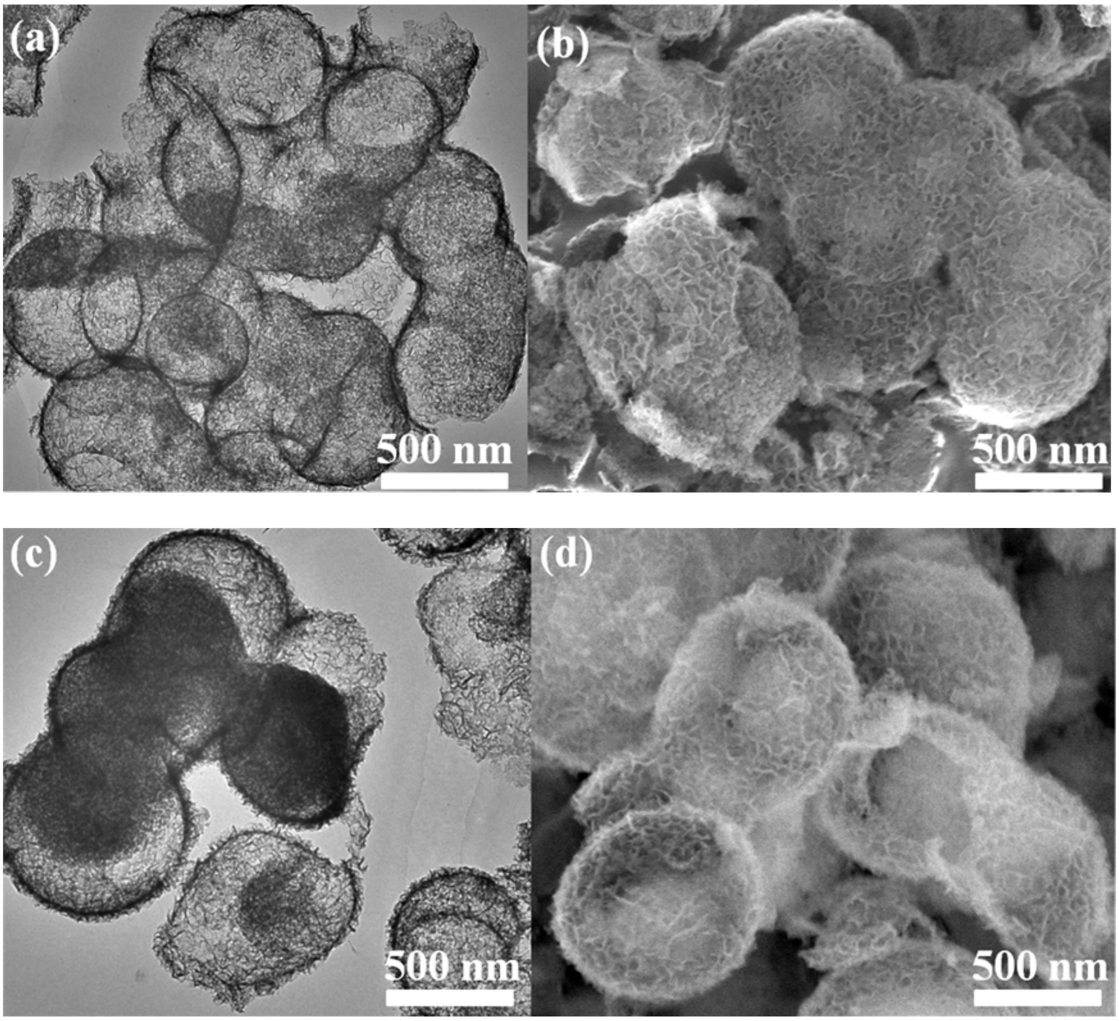
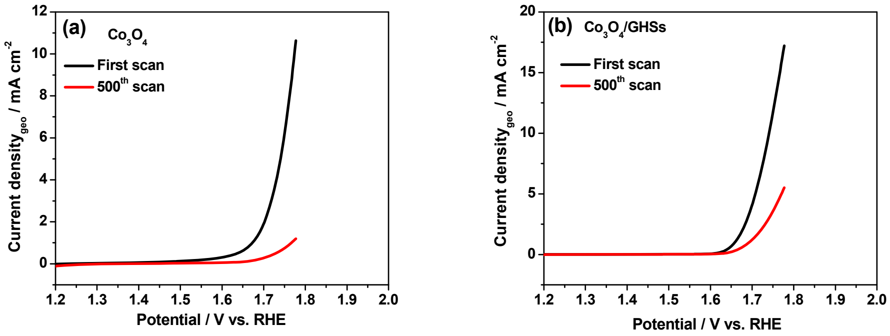


Figure S8. TEM (a) and SEM (b) images of the Co_3O_4/NBGHSs after 10 h of the ORR at 0.642 V vs. RHE and a rotation rate of 1600 rpm in an O_2-saturated 0.1 M KOH solution. TEM (a) and SEM (b) images of the Co_3O_4/NBGHSs after 10800 s of the OER at 1.7 V vs. RHE.



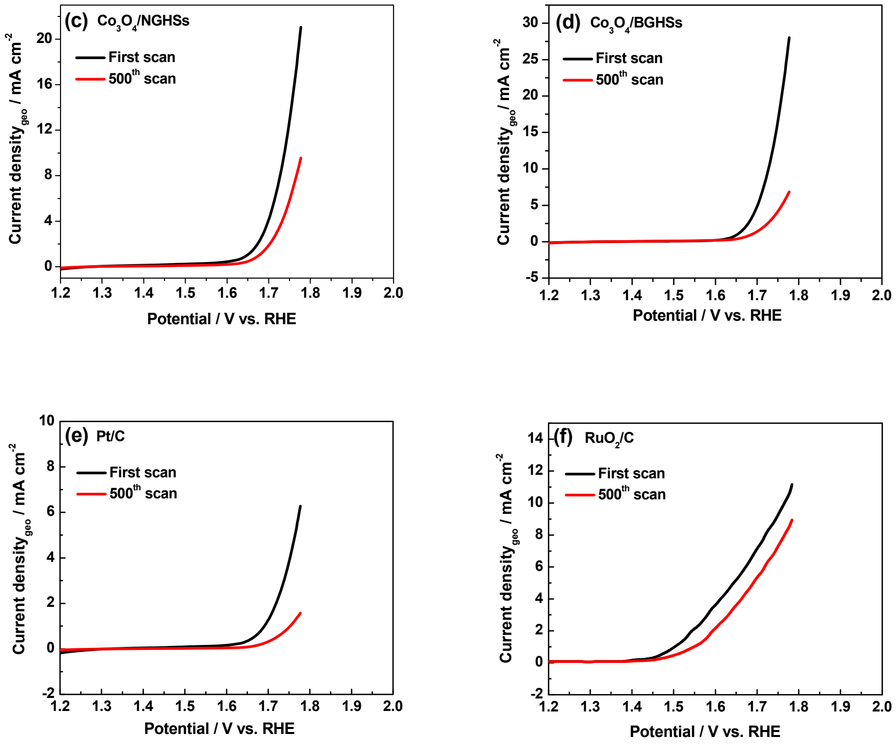


Figure S9. OER LSV curves of (a) the Co_3O_4 hollow microspheres, (b) the Co_3O_4/GHSs, (c) the Co_3O_4/NGHSs, (d) the Co_3O_4/BGHSs, (e) the Pt/C, and (f) RuO_2/C catalysts at a scan rate of 20 mV s^{-1} at 1600 rpm in 0.1 M KOH electrolyte (pH=13).

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