Electronic Supplementary Information (ESI) for Inorganic Chemistry Frontiers
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Supporting Information

Enhancing oxygen reduction reaction with three-dimensional graphene hollow nanospheres supported single-atomic cobalt catalyst

Ji-Sen Li,[a,*] Meng-Jie Huang,[a] and Xiao-Nan Chen[a]

[†]Department of Chemistry and Chemical Engineering, Jining University, Qufu 273155, P. R. China

E-mail: senjili@sina.com

S1. Figures in Supporting Information

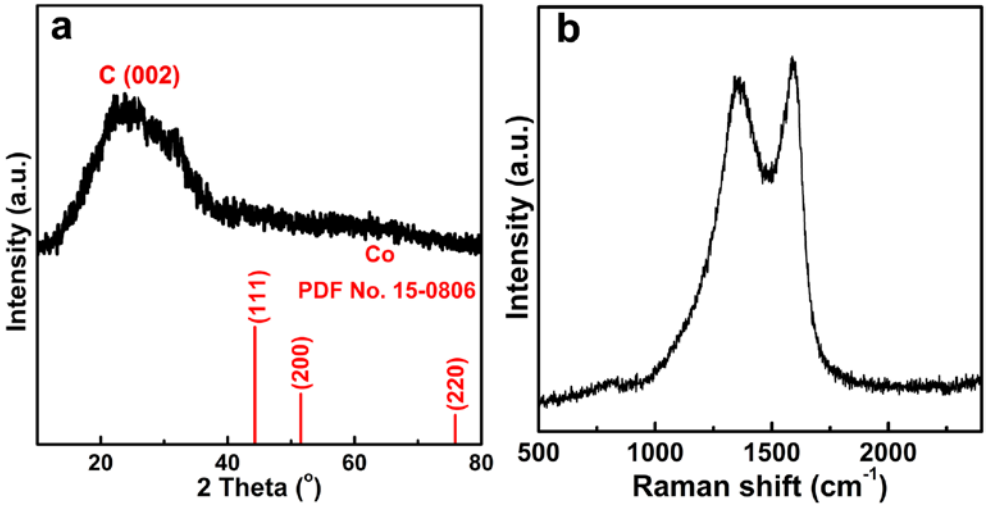

Fig. S1 (a) PXRD pattern and (b) Raman spectrum of Co ISAs/GHSs.

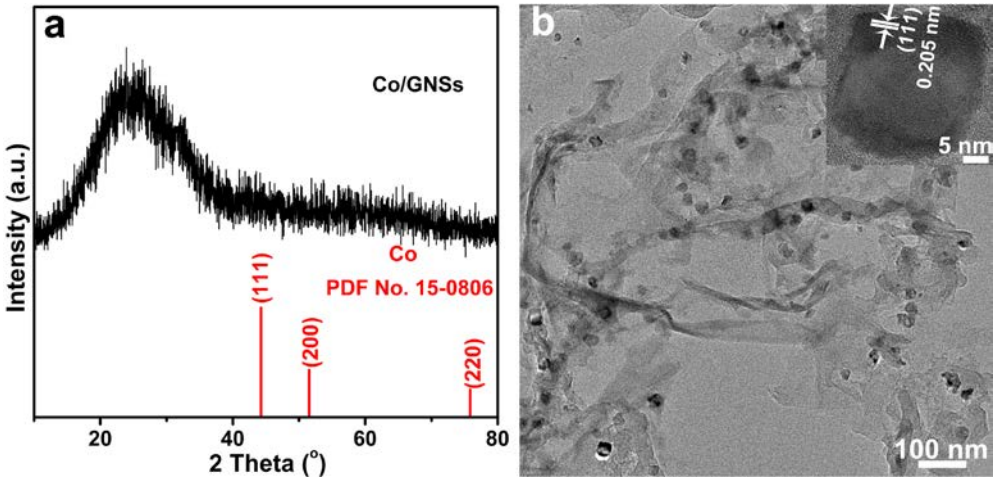

Fig. S2 (a) PXRD pattern and (b) TEM image of Co/GNSs. Inset: HRTEM image of Co/GNSs.

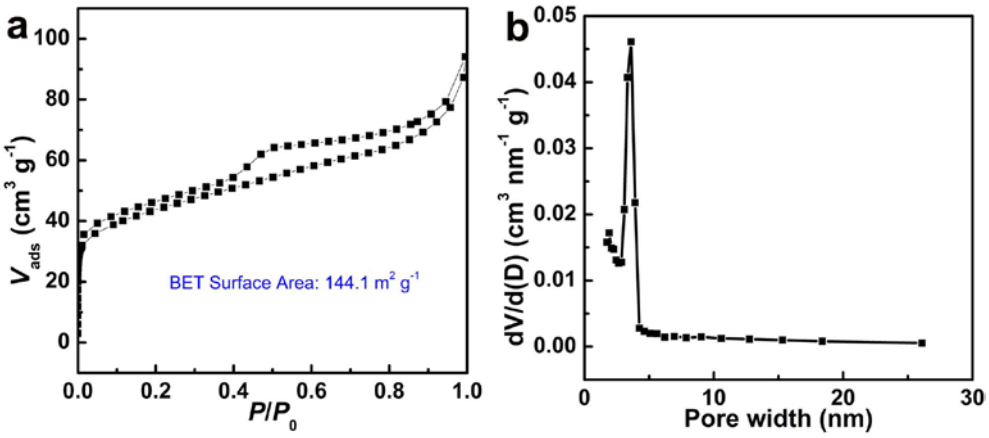

Fig. S3 (a) N_2 sorption isotherm and (b) pore size distribution of Co NPs/GNSs.

The BET surface area of Co ISAs/GHSs is 459.6 m^2 g^{-1}, which is larger than that of Co NPs/GNSs (144.1 m^2 g^{-1}). This is favorable to the wonderful ORR performance.

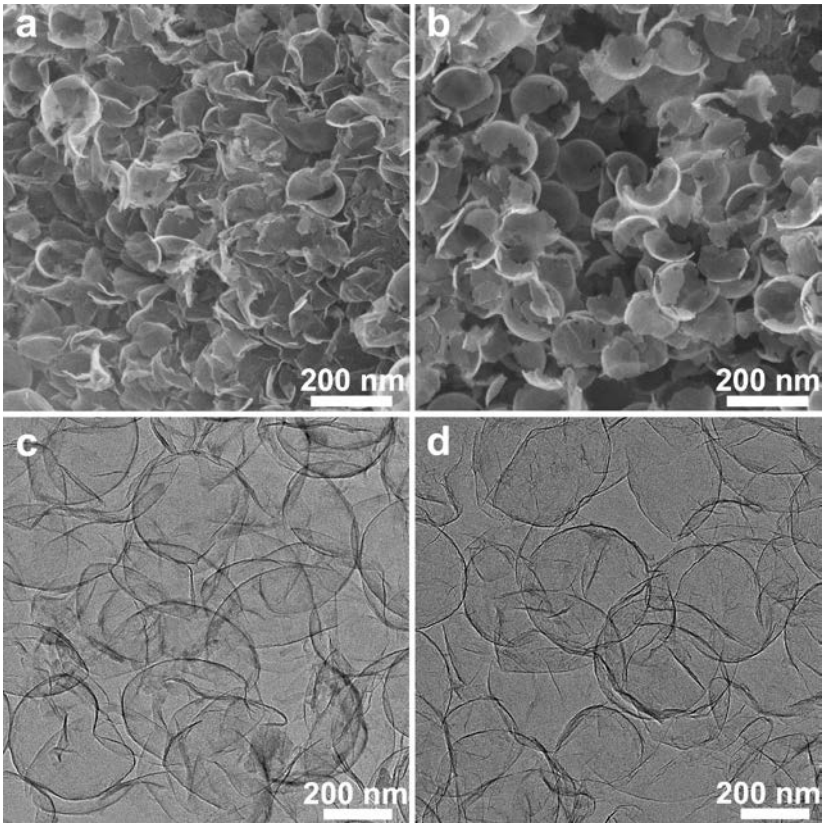

Fig. S4 (a, b) SEM and (c, d) TEM images of Co ISAs/GHSs carbonized at 600 and 800 °C.

As exhibited in **Fig. S4**, the samples achieved at different carbonization temperature present the similar hollow spherical nanostructures. Moreover, nanoparticles cannot be clearly found from the corresponding TEM images.

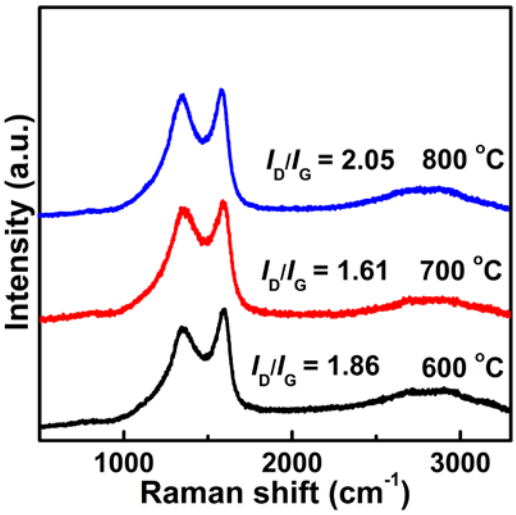

Fig. S5 Raman spectra of the products prepared at different pyrolysis temperature.

As observed from **Fig. S5**, the sample obtained at 600 °C has lower graphitization degree and poor conductivity, while the graphic structure of the composite prepared at 800 °C would be destroyed. Consequently, the optimal carbonization temperature should be 700 °C.

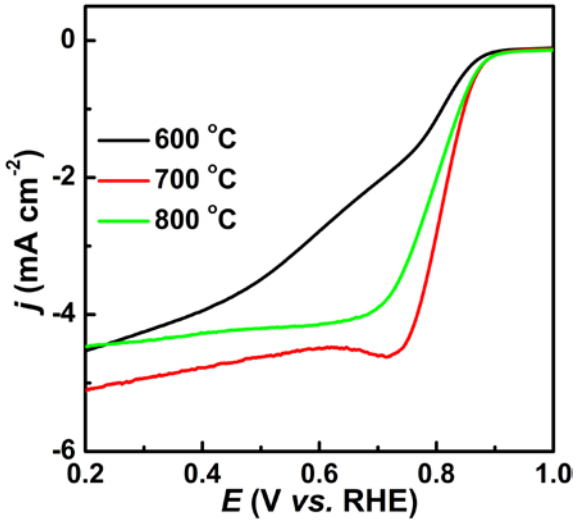

Fig. S6 (a) ORR polarization curves of the Co ISAs/GHSs synthesized at 600, 700, and 800 °C in O_2-saturated 0.1 M KOH solution at 1600 rpm.

The turn-over frequency (TOF) is estimated:

$$\mathrm{TOF} = \frac{j_k \times N_e}{\omega_{Co} \times c_{cat} \times N_A / M_{Co}}$$

Where j_k is the kinetic current density (A cm^{-2}), *Ne* is electron number per Coulomb 6.24×10^{18}, ω_{Co} is the metal content in the catalyst, c_{cat} is the catalyst loading on the electrode, N_A is Avogadro constant 6.022×10^{23}, M_{Co} is molar mass of Co 58.93 g mol^{-1}.

$$\mathrm{TOF} = \frac{j_k \times 6.23\times10^{18}}{1.1\% \times 20\times10^{-6} \times 6.022\times10^{23} / 58.93} = j_k * 2768.9$$

At 0.8 V, the TOF values follow the trend Co ISAs/GHSs-600 (3.38) < Co ISAs/GHSs-800 (6.81) < Co ISAs/GHSs-700 (9.85), strongly confirming the outstanding electrocatalytic performance of Co ISAs/GHSs-700 for the ORR.

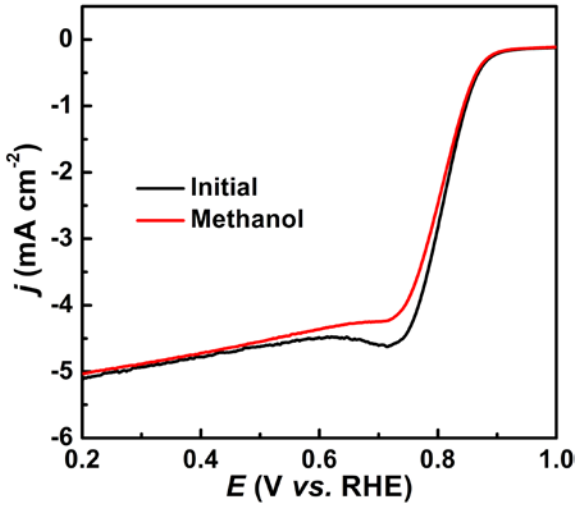

Fig. S7. LSVs for the ORR at the Co ISAs/GHSs electrode in an O_2-saturated 0.1 M KOH solution or an O_2-saturated 0.1 M KOH solution upon addition of methanol.

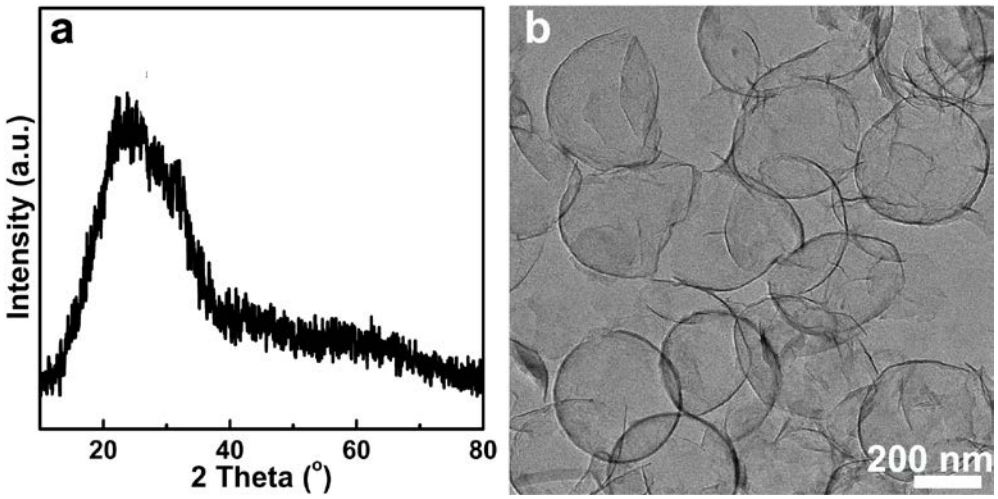

Fig. S8 (a) PXRD pattern and (b) TEM image of Co ISAs/GHSs after stability test.

S2. Table in Supporting Information

Table S1. Comparison of electrocatalytic performance of with other ORR elecrocatalysts

Catalysts	$E_{1/2}$ / V *vs.* RHE	Reference
Co ISAs/GHSs	**0.82**	**This work**
Pt-C	**0.85**	**This work**
10Co-N@DCNF	0.83	*Angew. Chem. Int. Ed.* 2**020**, *59*, 6122.
CoSA + Co_9S_8/ HCNT	0.855	*Small* **2020**, *16*, 1906735.
CHS-Co	0.65	*ChemCatChem* 2**020**, *12*, 3230.
Co@G-750	0.87	*ACS Sustainable Chem. Eng.* **2019**, *7*, 9249.
CoS_x/Co-NC-800	0.80	*Adv. Funct. Mater.* **2019**, *29*, 1904481.
NOGB-800	0.84	*Adv. Energy Mater*. **2019**, *9*, 1803867.
Hybrid nanosheets	0.79	*Adv. Mater.* **2018**, *30*, 1703657.
Co−N/CNFs	0.82	*ACS Catal.* **2017**, *7*, 6864.
NC@Co-NGC	0.82	*Adv. Mater.* **2017**, *29*, 1700874.