Electronic Supplementary Information(ESI†)

Coupled Cobalt Oxide/Hollow Carbon Sphere as an Efficient Electrocatalyst for Oxygen Reduction Reaction

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Rotating disk electrode (RDE) and Rotating-ring disk electrode (RRDE) measurement. An RRDE-3A (JAPAN) rotating ring disk electrode system was used for RDE and RRDE voltammetry experiments. A rotating GC disk-platinum ring electrode (4 mm diameter) was used as a working electrode. The oxygen reduction activities were measured by hydrodynamic voltammetry in an O_2-saturated 0.1 M KOH at room temperature. The electrolyte solution was purged with oxygen gas for 30 min before the electrochemical measurement. A flow of O_2 was maintained over the electrolyte during the measurement to ensure O_2 atmosphere inside the cell. The electron transfer number from Koutecky-Levich plots were determined by the following equation.

$$1/J=1/J_L+1/J_K=1/(B\omega^{1/2})+1/J_K$$

$$B = 0.20nFC_0D_0^{2/3}\ v^{-1/6}$$

Where, J is the experimentally measured current, J_L is the diffusion-limiting current, J_K is the kinetic current, ω is the angular velocity, F is the Faraday constant, C_0 is the saturated concentration of O_2 in 0.1M KOH (1.2×10^{-6} mol cm^{-3}), D_0 is the diffusion coefficient of O_2 in 0.1M KOH (1.9×10^{-5} cm^2 s^{-1}), and ν is the kinematic viscosity of the electrolyte.

The electron transfer number from RRDE experiment was determined by the following equation;

$$n = 4I_D/[I_D + (I_R/N)]$$

where, I_D is the disk current, I_R is the ring current, and N is the ring correction coefficient in RRDE experiment was determine to be 0.43 from the reduction of $Fe(CN)_6^{4-/3-}$ redox couple. The ring potential was held at 0.5 V vs. Ag/AgCl.

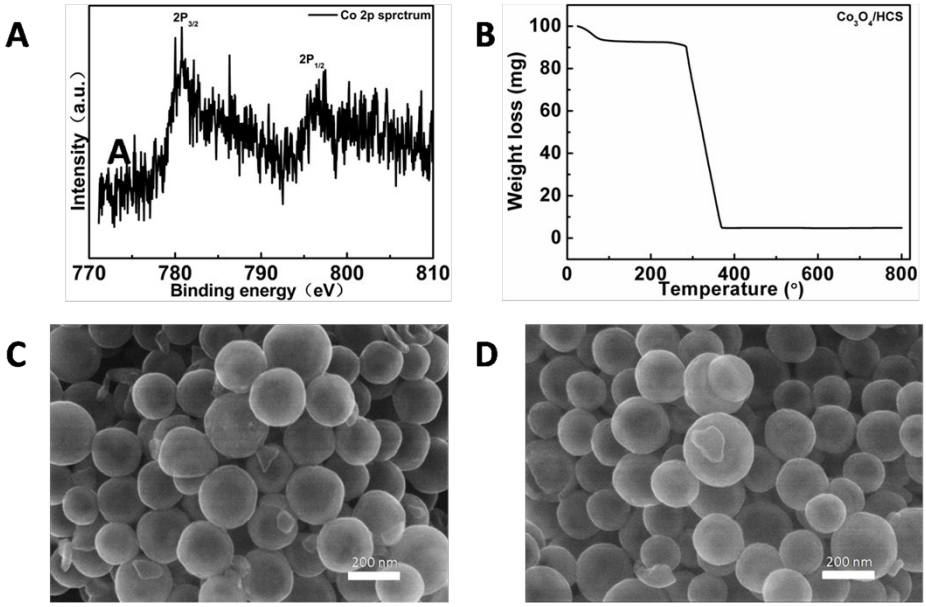

Fig. S1. (A) The high-resolution XPS spectrum of Co 2p for Co_3O_4/HCS. (B) TG curves of Co_3O_4/HCS. SEM images of HCS (C) and Co_3O_4/HCS (D).

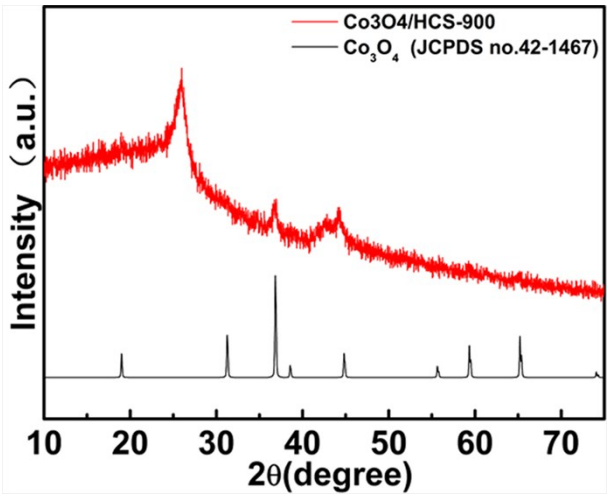

Fig. S2. XRD patterns of Co_3O_4/HCS at the calcination of 900℃.

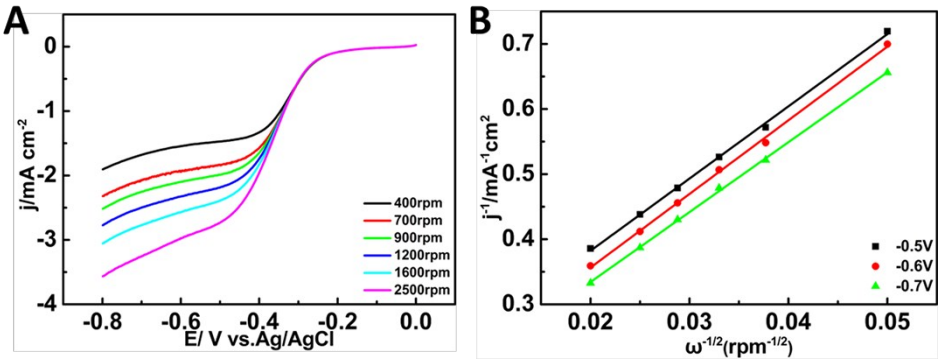

Fig. S3. (A) RDE voltammograms of HCS at different rotation rates. (B) Koutecheky–Levich plots of the ORR for Co_3O_4/HCS.

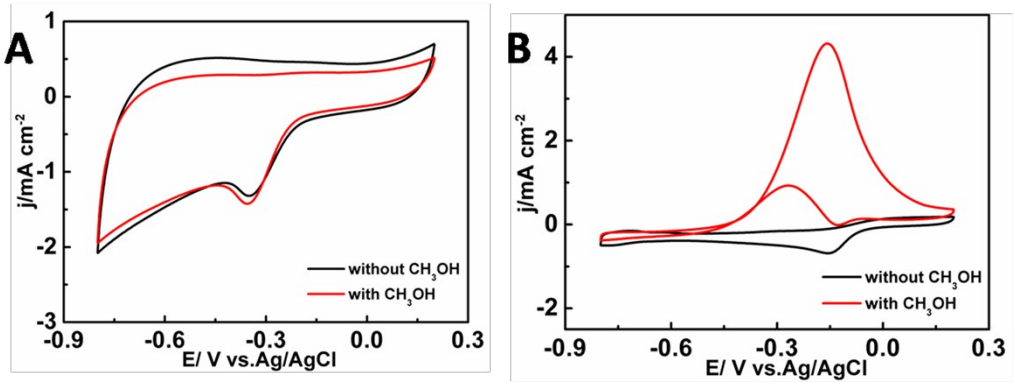

Fig. S4. CVs of Co_3O_4/HCS (A) and Pt/C (B) at 50 mV s^{-1} in O_2-saturated 0.1 M KOH solution with or without the addition of 1.0 M methanol.

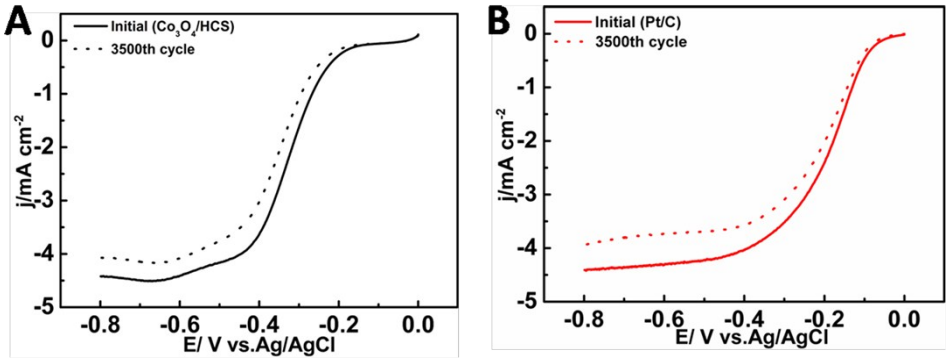

Fig. S5. Polarization curves of Co_3O_4/HCS (A) and Pt/C (B) measured during cycling durability tests at 1600 rpm in O_2-saturated 0.1 M KOH (cycling tests were carried

out in a potential window of -0.5 to -0.1 V vs. Ag/AgCl with 100 mV s^{-1}).