

## Supplementary Information

### *Experimental*

*Synthesizing carbon spheres:* The carbon spheres used in the present study were prepared by hydrothermal treatment of glucose. First, 6 grams of glucose (analytical purity, Beijing Chemical Reagent Factory) were dissolved in 90 mL DI-water to form a clear solution. The solution was placed in a teflon-sealed autoclave (100 mL) and heat-treated at 170°C for 10h for the hydrothermal reaction. The product, carbon spheres, was then separated from the solution by centrifugation. Finally, the carbon spheres were purified by repeatedly washing them in water and in alcohol for at least three times, followed by drying at 80°C for 6h in a vacuum oven. The surface modification of the resultant carbon spheres was carried out by soaking them in either NaOH solution (1M) or concentrated hydrochloric acid for 3h at 150°C.

*Preparing Co<sub>3</sub>O<sub>4</sub> hollow spheres:* The carbon spheres prepared above were redispersed in 0.05M Co(NO<sub>3</sub>)<sub>2</sub> solution, and ultrasonicated for a quarter. The mixture was aged for 1h to allow the formation of a cobalt-oxide coating on the carbon sphere surface. The coated spheres were then subjected to four cycles of centrifugation-water wash to remove impurities, followed by drying at 60°C for 5h in a vacuum oven. The cobalt oxide coated carbon spheres were then calcined in Ar atmosphere at 450°C for 2h to strengthen the Co<sub>3</sub>O<sub>4</sub> shell and subsequently calcined in air at 450°C to remove the carbon core.

*Characterization:* X-ray diffraction (XRD) patterns were taken on a Bruker D8-Advance diffractometer using Ni filtered Cu K<sub>α</sub> radiation. The applied current and voltage were 40 mA and 40 kV, respectively. During the analysis, the samples were scanned from 10 to 70° at a speed of 4°/min. Scanning electron microscopy (SEM) images were collected using a S-4800 scanning microscope; and transmission electron microscopy (TEM) images were taken using a JEOL JEM-1010/2010 system operated at 200 kV. BET-surface area was measured by N<sub>2</sub> adsorption at liquid nitrogen temperature using a NOVA4000 automated gas sorption system.

The X-ray photoelectron spectra (XPS) chemical analyzing was carried out using a PHI Quantera SXM system. Al  $K_{\alpha}$  radiation was used as the source and the  $C_{1s}$  peak was used as the reference. FTIR spectra were measured using Nicolet Magna 750 in the wave number region of 4000 to 500  $\text{cm}^{-1}$  with 64 scans at 8  $\text{cm}^{-1}$  resolution.

*Catalytic test:* The activity of the  $\text{Co}_3\text{O}_4$  hollow spheres for methane combustion was tested in a fixed-bed quartz reactor (i.d. = 8 mm) containing 0.5 g of the catalysts. The test was carried out at the temperature range of 250-400°C. The gas mixture containing 1 vol.%  $\text{CH}_4$ , 10 vol.%  $\text{O}_2$  and  $\text{N}_2$  as the balance gas was flowed into the reactor at a total flow rate of 150 mL/min, which corresponds to a WHSV about 36,000  $\text{mL h}^{-1}\text{g}^{-1}$ . The concentration of  $\text{CH}_4$  in inlet and outlet gas mixtures was measured by an on-line gas chromatograph (Shimadzu GC 17A). The activity was evaluated in term of  $\text{CH}_4$  conversion, defined as  $(C_{\text{in}}-C_{\text{out}})/C_{\text{in}} \times 100\%$ , where  $C_{\text{in}}$  and  $C_{\text{out}}$  are methane concentration at the inlet and outlet, respectively.

**Table S1:** Zeta potential of the carbon spheres treated at different conditions, measured at pH=7.

	Acidic treatment		No treatment	Alkaline treatment	
Treatment time (h)	0.5	1.5	0	0.5	1.5
Zeta potential (mV)	-20.9	-12.6	-33.5	-49.1	-61.4

**Table S2.** Surface properties of  $\text{Co}_3\text{O}_4$  hollow spheres synthesized using carbon spheres treated at different conditions as the template.

Catalyst sample	$S_{\text{BET}}$ ( $\text{m}^2\text{g}^{-1}$ )	Pore volume ( $\text{cm}^3\text{g}^{-1}$ )	Mesopore diameter (nm)
Acidic treatment	301	0.36	9.9
None treatment	223	0.29	15.3
Alkaline treatment	174	0.20	23.0

The pore volume and pore diameter are calculated by BJH method (desorption branch).

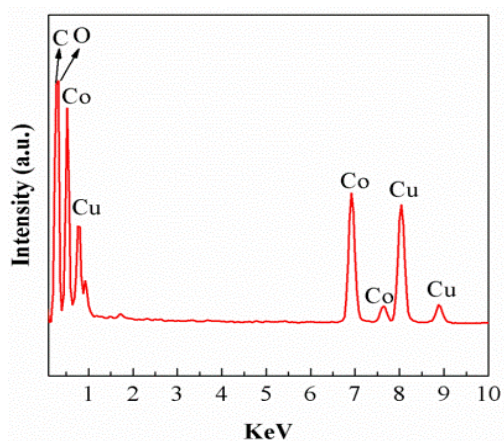


Figure S1: EDS spectrum of the surface of the coated spheres.

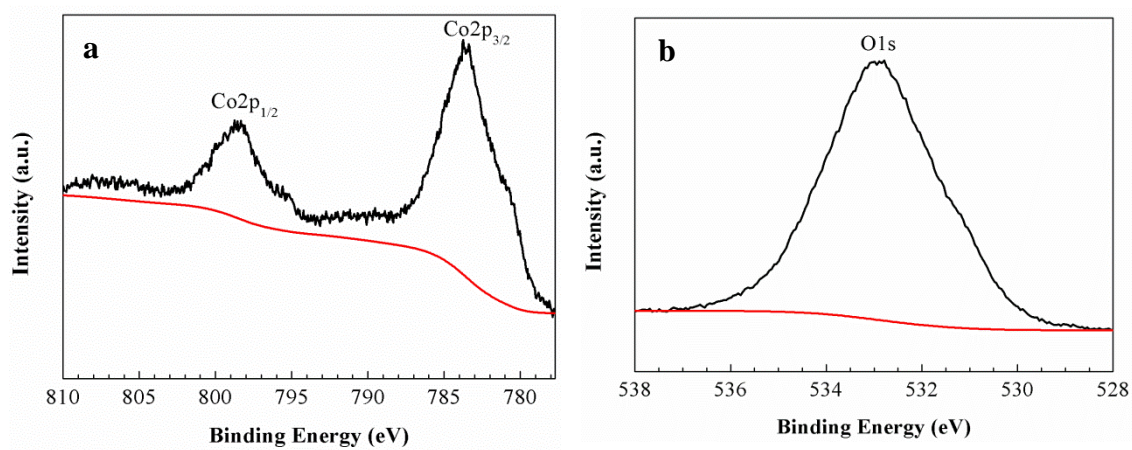


Figure S2: XPS spectra of (a) Co2p, b) O1s.

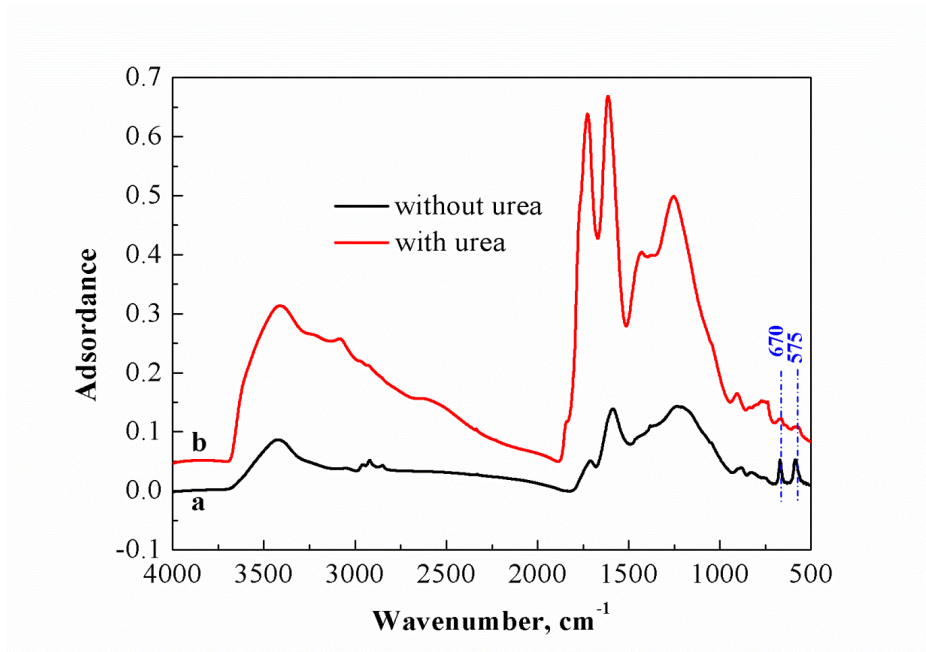


Figure S3: FTIR spectra of coated spheres synthesized using the solution with and without urea.

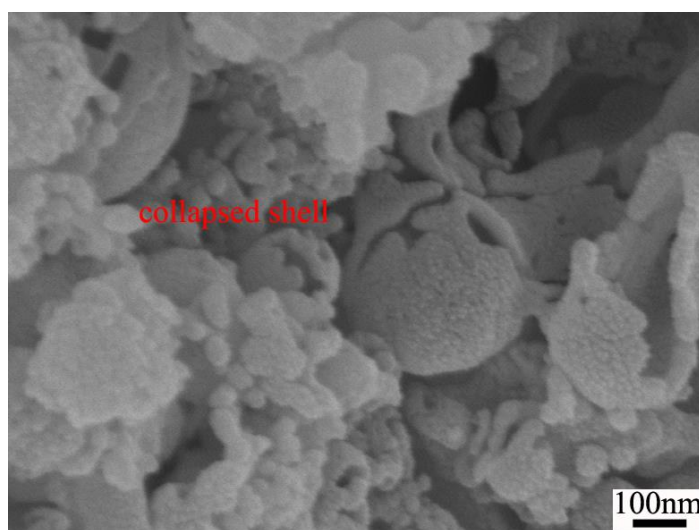


Figure S4: SEM image of  $\text{Co}_3\text{O}_4$  hollow spheres obtained from one-step calcination of the sample synthesized by using un-treated carbon spheres as the template.

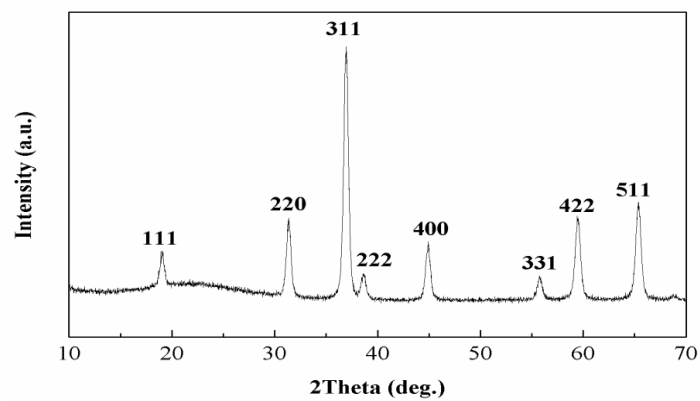


Figure S5: XRD pattern of the hollow structure after core removal. The diffraction peaks are identified as spinel  $\text{Co}_3\text{O}_4$  (JCPDS no. 43-1003).

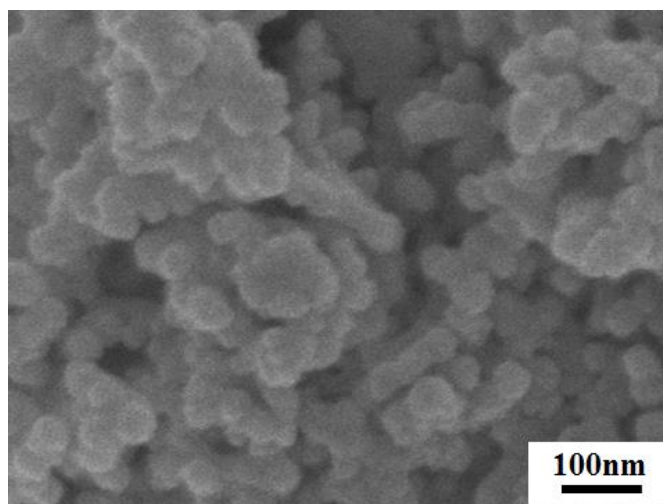


Figure S6: SEM image of commercial  $\text{Co}_3\text{O}_4$  powders.