

Double-shelled carbon nanocages grafted with carbon nanotubes embedding Co nanoparticles for enhanced hydrogen evolution electrocatalysis

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Experimental Sections

All commercially available chemical materials of analytical grade were used as received without further purification. The $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, methanol, ethanol and KOH were supplied from Tianjin Damao Chemical Reagent Co., Ltd. The 2-methylimidazole and Cetyltrimethylammonium bromide (CTAB) were supplied from Macklin Biochemical Co., Ltd. The tannin acid was purchased from Adamas Reagent Co., Ltd. The nafion ethanol solution (5 wt%) were purchased from Aldrich corporation. Deionized (DI) water was used throughout all the parallel experiment.

The synthesis of solid BMZIF-0 nanocube

$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (174 mg) and CTAB (3 mg) were dissolved in deionized water (6 mL) to obtain a pink solution A. Separately, 2-methylimidazole (2724 mg) was dissolved in deionized water (42 mL) to form another solution B. Then, the solution A was quickly added to solution B, leading to the formation of dark blue suspension immediately. After stirred vigorously for 20 min, the product of BMZIF-0 was collected by centrifugation at 10000 rpm for 10 min, and then washed with ethanol for four times and dried at the temperature of 50 °C for 12 h.

The synthesis of BMZIF-5, and BMZIF-10 cubes

The syntheses of BMZIF-5, and BMZIF-10 cubes were similar with BMZIF-0 cube, except that $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ at a $\text{Zn}^{2+}/\text{Co}^{2+}$ molar ratio of 5:1 and 10:1 were added, designated as BMZIF-5 and BMZIF-10, respectively.

The synthesis of yolk-shell BMZIF-5 nanocubes

The yolk-shell BMZIF-5 nanocubes were synthesized by following the previous procedure to achieve the partial etching of solid ZIF precursor (P. Zhang, B. Y. Guan, L. Yu and X. W. David Lou, *Angew. Chem. Int. Ed.*, 2017, **56**, 7141-7145). Solid BMZIF-5 nanocubes (10 mg) prepared above was dispersed in 20 mL methanol and mixed quickly under sonication. Tannic acid (20 mg) in methanol (20 mL) was added

dropwise to the BMZIF suspension under stirring for 30 min. The dark pink powder was collected by centrifugation at 10000 rpm for 10 min, washed with deionized water and ethanol for 5 times, respectively, and finally dried at 60 °C in a vacuum.

The synthesis of Co@CNTs@DSCNCs and Co@CNTs@PC

The above samples (BMZIF-0, BMZIF-5, BMZIF-10, yolk-shell BMZIF-5) were put in a tubular heating furnace and heated at 950 °C for 2 h under Ar gas. The heating rate is 5 °C/min. After cooling to room temperature, four kinds of black powders were obtained, designated as Co@CNTs@PC-0, 5, 10, and Co@CNTs@DSCNCs, respectively.

Characterization Methods X-ray diffraction (XRD) analyses were recorded on a SHIMADZU XRD-7000S diffractometer with Cu K α ($\lambda = 1.5406 \text{ \AA}$) as the radiation source, the 2θ range was 10°–80° with a scan speed of 5 °/min. Scanning Electron Microscopy (SEM) images were collected by using field-emission scanning electron microscope (FEI Nova NanoSEM 450) with an accelerating voltage of 18.00 kV. Transmission electron microscopy (TEM) was obtained on a FEI Tecnai-G²F30 transmission electron microscope operated at 300 kV. X-ray photoelectron spectroscopy (XPS) was tested by using a ThermoFisher ESCALABTM250Xi equipment with Al K α X-ray radiation as excitation source. All the binding energies in the XPS analysis were corrected for specimen charging by reflecting them to the C 1s peak. The Raman spectra were measured by a laser Raman spectroscopy (Renishaw inVia). The Brunauer-Emmett-Teller (BET) specific surface areas were characterized by nitrogen adsorption–desorption isotherms in a Quantachrome Instruments Autosorb-iQ-C equipment and the pore diameter distributions were calculated with the Barrett–Joyner–Halenda (BJH) model.

Electrochemical Measurement

The HER measurements were performed on a three–electrode system (CHI660E), which include a saturated calomel electrode (SCE) as a reference electrode, a Pt wire

counter electrode and a modified glassy carbon electrode with a diameter of 5 mm and a theoretical area of 0.1963 cm² as the working electrode. The electrolyte was N₂-saturated 1 mol/L KOH. The working electrode was prepared as follows: 5 mg catalyst, 0.48 mL deionized water, 0.48 mL ethanol and 0.04 mL 5%wt nafion solution were homogeneously mixed under the sonication for 30 min. Then, 7.5 μL of this ink was drop-casted onto a GCE (5 mm in diameter) and dried naturally. Linear sweep voltammetry (LSV) polarization curves were conducted at a scan rate of 5 mV·s⁻¹. The double layer capacitance (C_{dl}) was measured by using cyclic voltammetry scanning from 0.05 to 0.15 V versus RHE (Reversible Hydrogen Electrode) under different scan rates from 80 to 200 mV/s for HER. Electrochemical impedance spectroscopy (EIS) was recorded at an overpotential at a current density of 10 mA·cm² in the frequency range of 1~10⁵ Hz. All potentials reported in this study were calibrated to RHE by the following equation: $E_{RHE} = E_{Hg/HgO} + 0.05914 \times pH + 0.098$ V. Chronoamperometric measurements were implemented by applying the corresponding potential to support an initial current density of about 10 mA·cm⁻² for 12 h for HER.

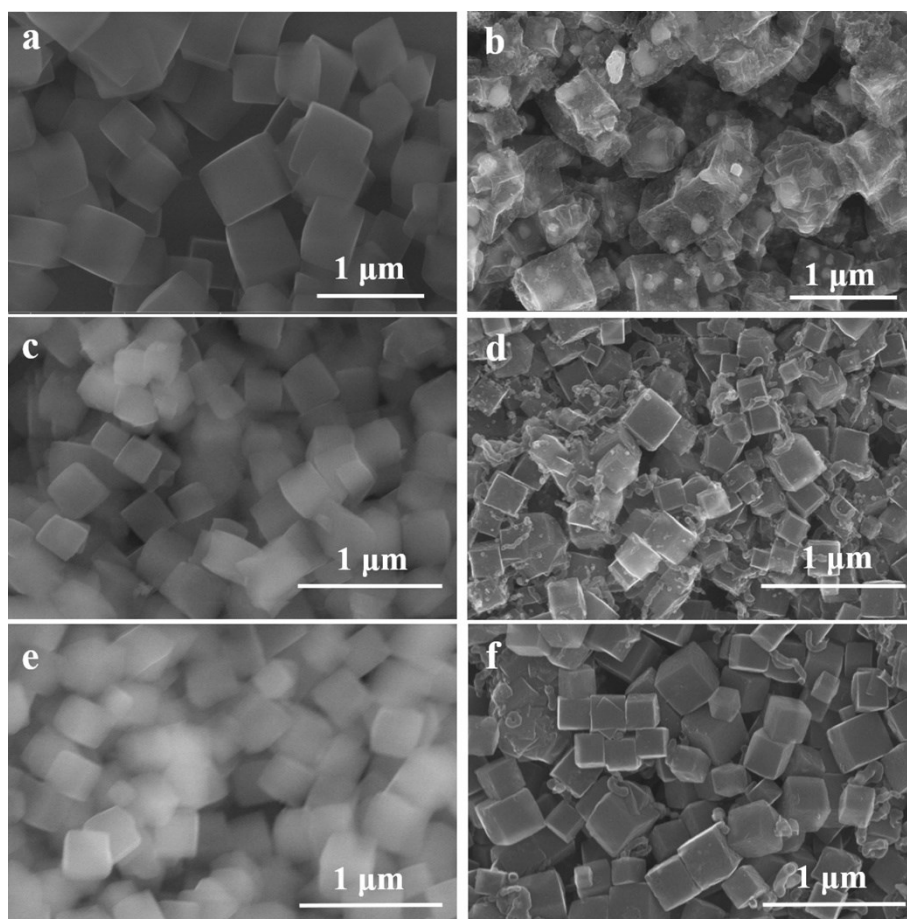


Fig. S1 SEM images of BMZIF-0 (a), BMZIF-5 (c) and BMZIF-10 (e) before and after calcination (b, d, f).

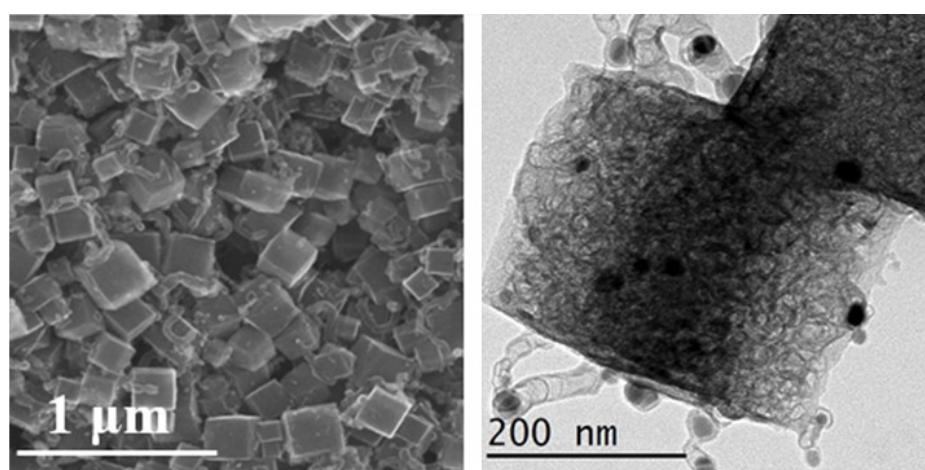


Fig. S2 SEM (left) and TEM (right) images of Co@CNTs@PC-5.

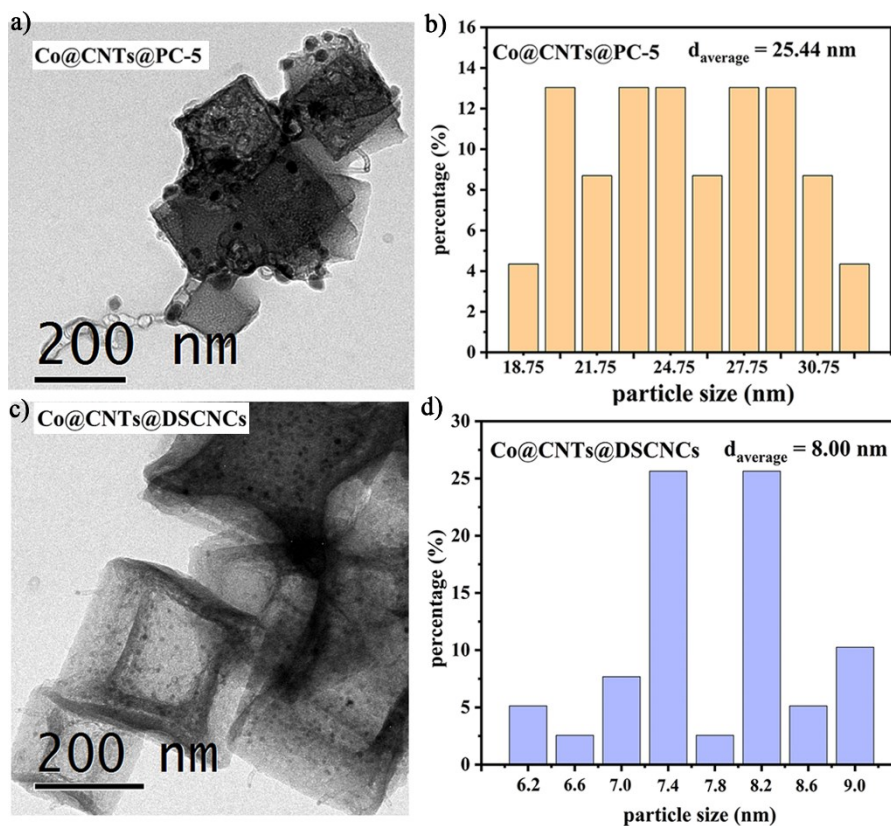


Fig. S3 The TEM images and size distribution analyses of Co nanoparticles in Co@CNTs@PC-5 (a, b) and Co@CNTs@DSCNCs (c, d).

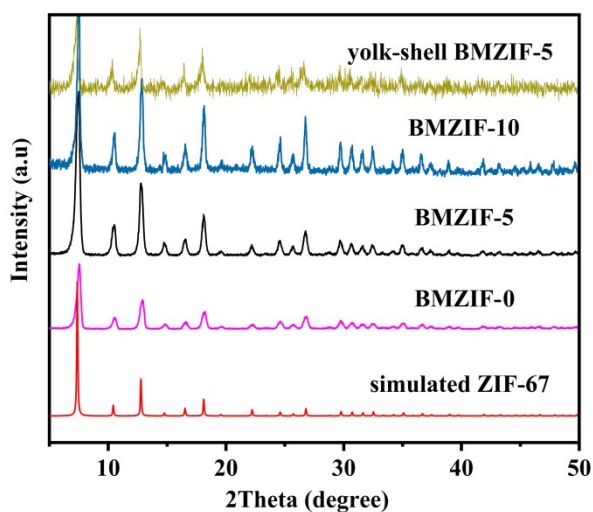


Fig. S4 The XRD patterns for all the precursors (BMZIF-0, BMZIF-5, BMZIF-10 and yolk-shell BMZIF-5).

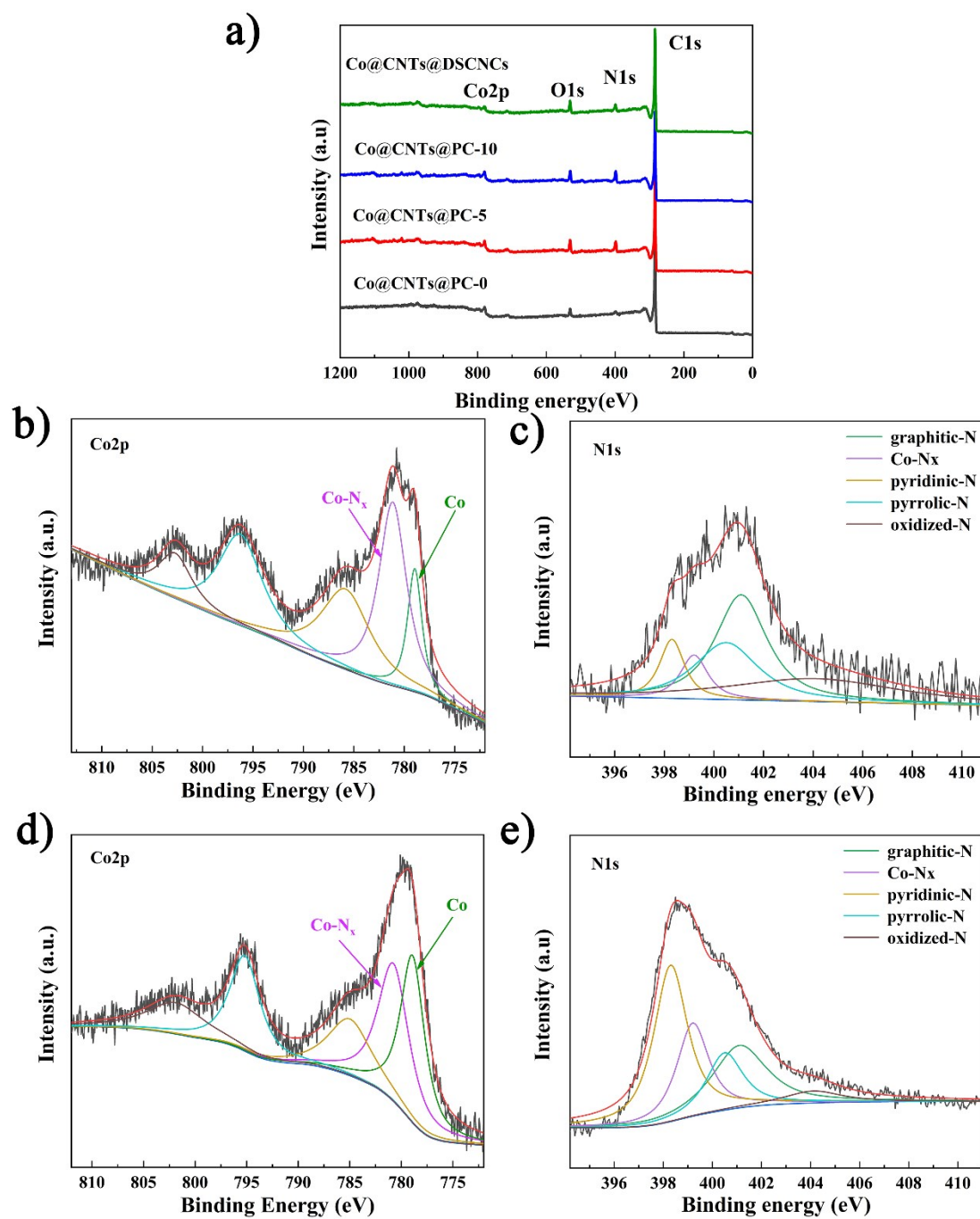


Fig. S5 The survey spectrum of the four samples (a) and the XPS spectra of Co 2p and N 1s for Co@CNTs@PC-0 (b, c) and Co@CNTs@PC-10 (d, e).

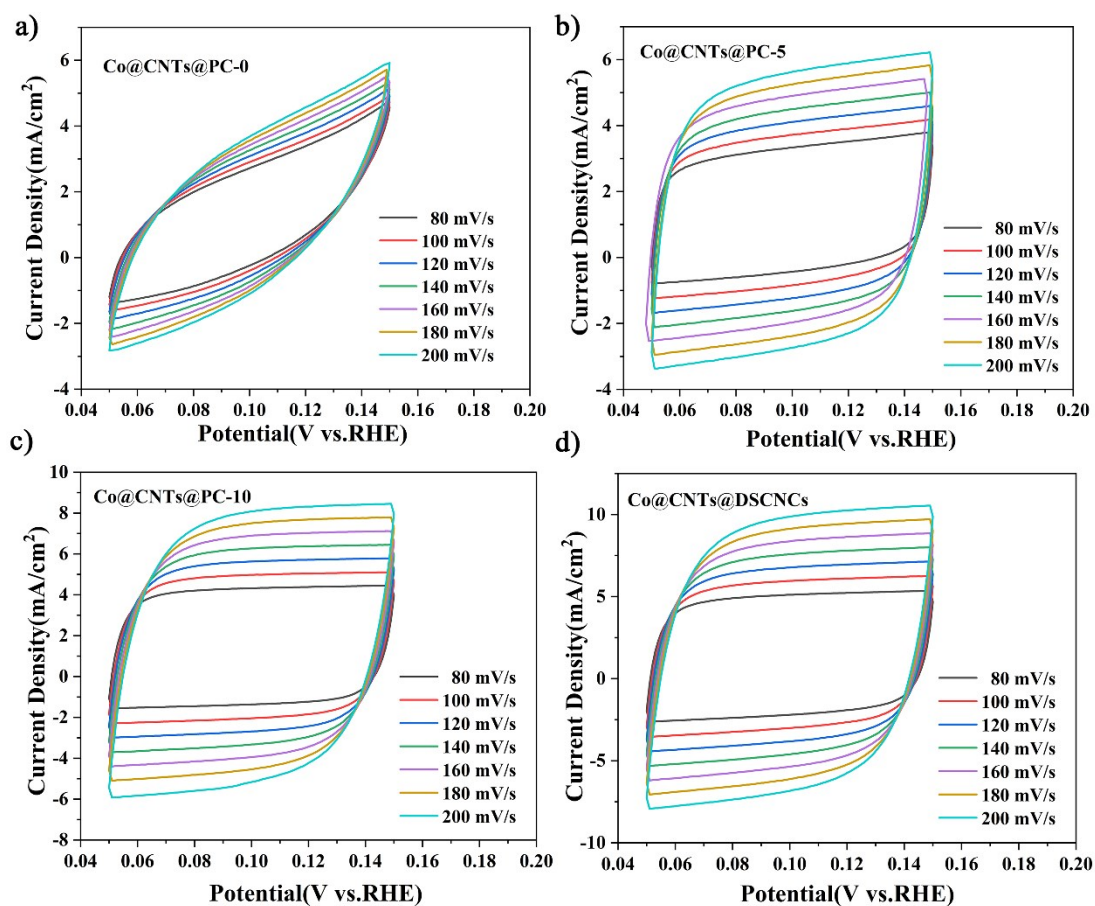


Fig. S6 Cyclic Voltammetry Curves of Co@CNTs@PC-0 (a), Co@CNTs@PC-5 (b), Co@CNTs@PC-10 (c) and Co@CNTs@DSCNCs (d) at Different Scan Rates.

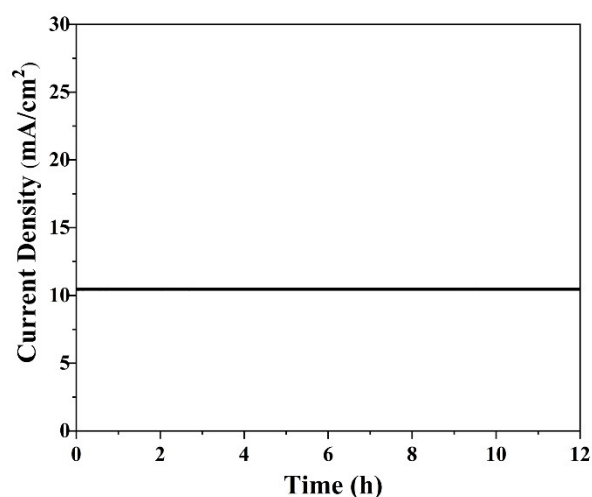


Fig. S7 Chronoamperometric measurement for Co@CNTs@DSCNCs.

Table S1 Specific surface area and aperture data for the calcinated samples.

Sample	S_{BET} (m ² /g)	V_{sp} (cm ³ /g)	D (nm)
Co@CNTs@PC-0	192.228	0.248	5.168
Co@CNTs@PC -5	527.093	0.518	3.928
Co@CNTs@PC -10	655.513	0.516	3.148
Co@CNTs@DSCNCs	375.997	0.742	7.889

Table S2 Summary of various Co-based non-noble metal catalysts for HER in 1 M KOH.

Catalysts	Overpotential (mV)	Tafel slope (mV·dec ⁻¹)	Reference
Co@CNTs@DSCNCs	214	65.9	Our work
4.55% Co-N/C	299	114	<i>ACS Appl. Energy Mater.</i> , 2020, 3, 687-694.
Co-NC-800	242	94	<i>Int. J. Hydrogen Energy</i> , 2019, 44, 11838-11847.
CoFe/NH-CNS	230	97.2	<i>ACS Sustainable Chem. Eng.</i> , 2019, 7, 15278-15288.
Co-CoO@3DHPG	402	85	<i>Electrochim. Acta</i> , 2019, 298, 163-171.
ZnCo-11-NC	200	86	<i>J. Alloys Compd.</i> , 2019, 789, 100-107.
Co ₂ B/Co/N-B-C/B ₄ C	220	105	<i>ACS Appl. Mater. Interfaces</i> , 2018, 10, 37067-37078.