

Electronic Supplementary Information

Co₃O₄ nanocrystals ink printing on carbon fiber paper as large-area electrode for electrochemical water splitting

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Experimental section

Materials.

$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{NH}_3 \cdot \text{H}_2\text{O}$ were obtained from Beijing Chemical Reagents. Ethanol and toluene were obtained from Longxi Chemical Corp. OA (99%) was obtained from Aladdin Chemistry Co. Carbon fiber papers (TGP-H-060) was obtained from Toray. All of the reagents and solvents were analytical grade and used as received without further purification.

Synthesis of $[\text{Co}(\text{NH}_3)_n]^{2+}$ -OA complexes by phase-transfer.

In a typical experimental procedure, briefly, 0.75 mmol of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dispersed in 40 mL of deionized water by ultrasonication. An equal volume of ethanol containing 3 mL of OA and 1.5 mL of $\text{NH}_3 \cdot \text{H}_2\text{O}$ were added. After stirring for 3 min, 40 mL of toluene was added and stirred for 5 min. Then, the mixture was transferred to a separatory funnel and left stationary for at least 10 minutes. The toluene layer with dark green in the upper, containing $[\text{Co}(\text{NH}_3)_n]^{2+}$ -OA complexes, was removed and used in the next step.

The Synthesize of OA-Stabilized Co_3O_4 NCs.

Typically, 38 mL of the obtained solution was transferred to 40 mL autoclave, and then kept at 170 °C for 3 h. After the autoclave cooled down to room temperature, ethanol was added to precipitate the product. To remove the byproducts and unreacted precursors, the product was washed three times, and re-dispersed in 10 mL toluene, denoted as OA- Co_3O_4 NCs. The OA- Co_3O_4 NCs colloidal was stored at room temperature as NCs ink. As a control, OA- Co_3O_4 NCs was calcinated at 300 °C in the air to remove the surface OA, denoted as calcinated Co_3O_4 NCs.

Physical characterization.

The morphology of the products was analyzed using transmission electron microscopy (TEM, JEOL JEM-3010) with an acceleration voltage of 300 kV. Carbon-coated copper grids were used as sample holders for TEM analysis. X-ray diffraction

(XRD) patterns were obtained by a Bruker D8 ADVANCE diffractometer by using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). Thermogravimetric (TG) and differential scanning calorimetry (DSC) were performed on a TA Q600 under a stream of air at a heating rate of $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet IS10 spectrometer. The concentration of Co ion were analyzed using Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Optima 700 DV, PerkinElmer).

Electrochemical measurements.

Sample Preparation for Electrochemical Characterizations: The working electrodes, OA-Co₃O₄ NCs printing on carbon fiber paper, were prepared using an airbrush (KUSING BD-130, 0.5 mm) operated at $\sim 15\text{-}20$ psig of head pressure. Briefly, 5 mL of OA-Co₃O₄ NC ink was sprayed on 8 cm² of carbon fiber paper. The carbon fiber paper with OA-Co₃O₄ NCs was cut apart into smaller pieces (about 1 cm²), and immersed in 1 M KOH solution to remove OA, denoted as Co₃O₄ NCs print carbon paper. The treated carbon fiber paper was used as working electrode, denoted as Co₃O₄ NCs. In order to ensure the amount of Co₃O₄ NCs on carbon fiber paper, 1cm² of working electrode was cut off, and immersed in 10 mL of HCl (0.01M) for 1h. The Co ion concentration in the solution is measured by ICP-OES, which is to calculate the quantity of Co₃O₄ NCs. The mass of Co₃O₄ NCs on carbon paper was about 0.35 mg cm⁻². Other three kinds of electrodes, named as calcinated Co₃O₄ NCs, and commercial Pt/C, were prepared by spray corresponding suspension ink (5 mg catalytic per 5 ml ethanol) on 8 cm² of carbon fiber paper, then 1 cm² carbon fiber paper cut as working electrode.

Electrochemical Characterizations: Electrochemical studies were carried out in a standard three electrode system controlled by a VersaSTAT 3 electrochemistry workstation. A typical three-electrode experimental cell equipped with a Pt-foil having 2 cm² of surface area as the counter electrode and Hg/HgO as the reference electrode. The reference was calibrated against and converted to reversible hydrogen electrode (RHE). Each catalyst electrode was immersed in 1 M KOH for two days to

remove OA, and cycled ~50 times by cyclic voltammetry (CV) at a scan rate of 50 mVs⁻¹, until a stable CV curve was developed before measuring. linear sweep voltammetry (LSV) was carried out at 5 mVs⁻¹ for the polarization curves. Chronopotentiometry and chronoamperometry were carried out under a serial constant current density of 10 mAcm⁻² (or -10 mAcm⁻²) for 1 h, a serial constant operating potential at 1.55 V (or -0.38V) for 1 h. Other three kinds of electrodes were also investigated in same condition. All the tests were carried out at room temperature (about 25°C).

Tafel slope calculation of the catalysts: These Tafel plots were fit to the Tafel equation ($\eta = b \log(j/j_0)$), where η is the potential, b is the Tafel slope, j is the current density, and j_0 is the exchange current density.)^[1]

Results and discussion

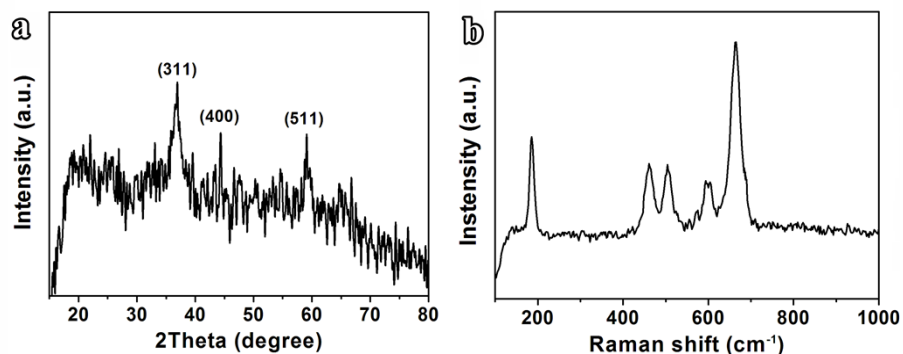


Fig. S1 (a) XRD pattern and (b) Raman spectrum of Co₃O₄ NCs.

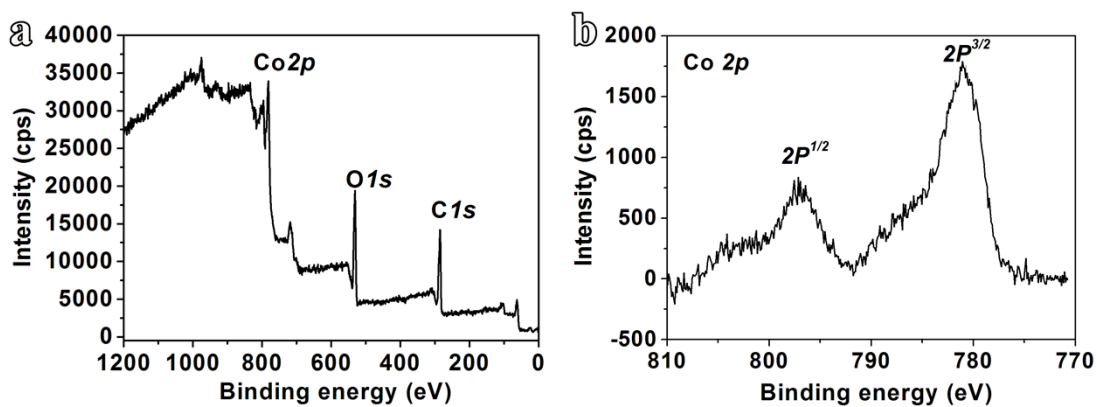


Fig. S2 XPS spectra of Co₃O₄ NCs, (a) survey spectrum, (b) high-resolution XPS spectra of Co 2p.

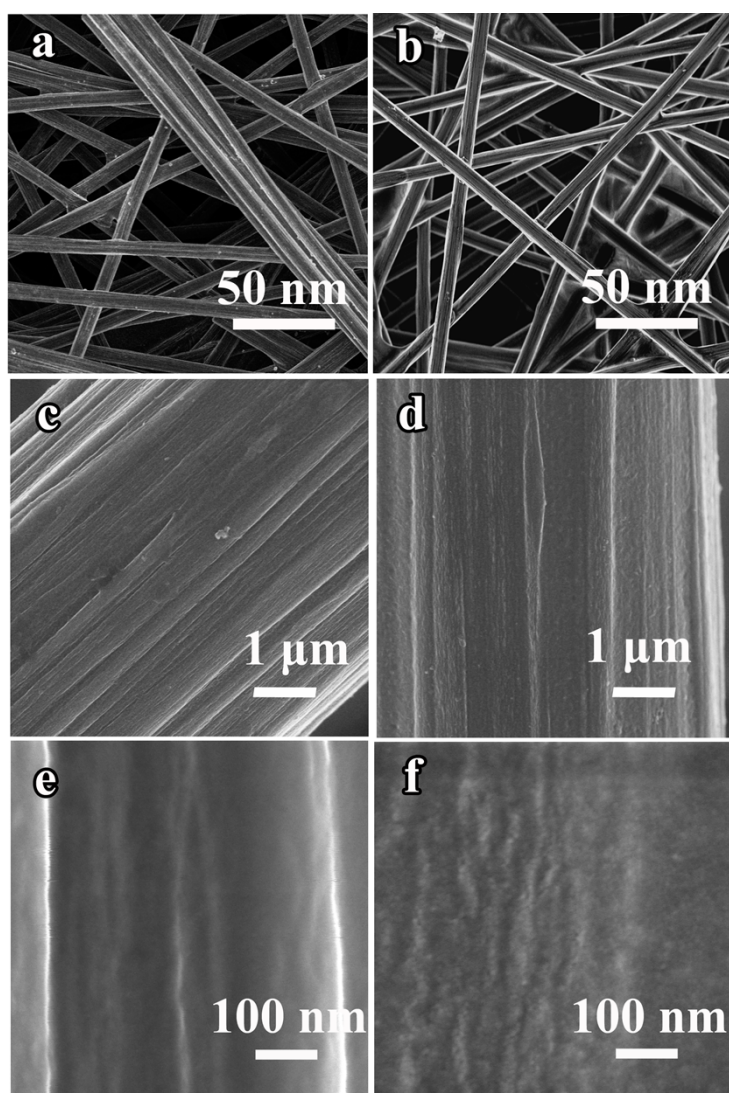


Fig. S3 The SEM and high-magnification SEM images of carbon fiber paper before (a, c, e), and after printing Co_3O_4 NCs (b, d, f).

NH_3 and OA play an important role for the formation of $[\text{Co}(\text{NH}_3)_n]^{2+}$ -OA complexes in toluene solution. Fig. S4 shows the phase-transfer photos of $[\text{Co}(\text{NH}_3)_n]^{2+}$ -OA complexes. When the system is no ammonia, the pink Co ions only exist in the water phase, indicating that Co ions cannot coordinate with OA directly (Fig. S4a). In contrast, when the system is no OA, the water phase appears green, due to the formation of coordination complexes of cobalt ions and NH_3 ($[\text{Co}(\text{NH}_3)_n]^{2+}$) (Fig. S4b). Apparently, $[\text{Co}(\text{NH}_3)_n]^{2+}$ cannot transfer to toluene phase without OA assistance.

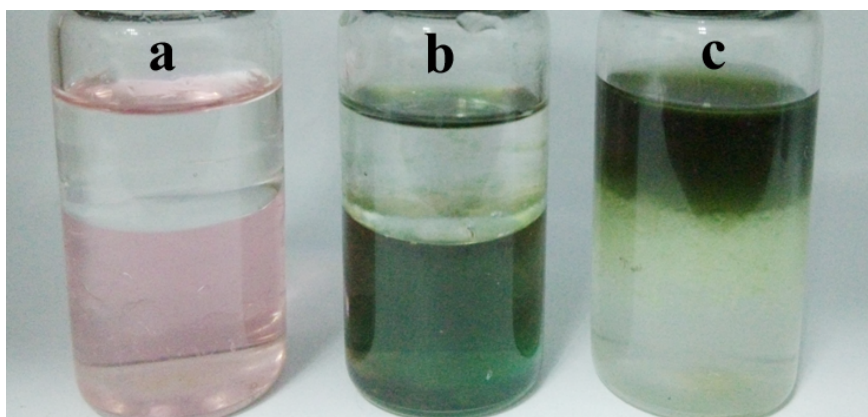


Fig. S4 The phase-transfer photos of $[\text{Co}(\text{NH}_3)_n]^{2+}$ -OA complex, (a) without NH_3 , (b) without OA, and (c) $[\text{Co}(\text{NH}_3)_n]^{2+}$ -OA complex in toluene phase (the upper phase is toluene and bottom phase is water and ethanol).

The FT-IR spectra of OA- Co_3O_4 NCs and $[\text{Co}(\text{NH}_3)_n]^{2+}$ -OA complexes are showed in Fig. S5. In the spectrum of $[\text{Co}(\text{NH}_3)_n]^{2+}$ -OA complexes, the strong stretching regions of C-N and N-H indicated Co^{2+} bounded by the NH_3 .^[2] In contrast, the peaks of C-N and N-H were disappeared in OA- Co_3O_4 NCs, indicating that NH_3 was released during the synthesis of OA- Co_3O_4 NCs.

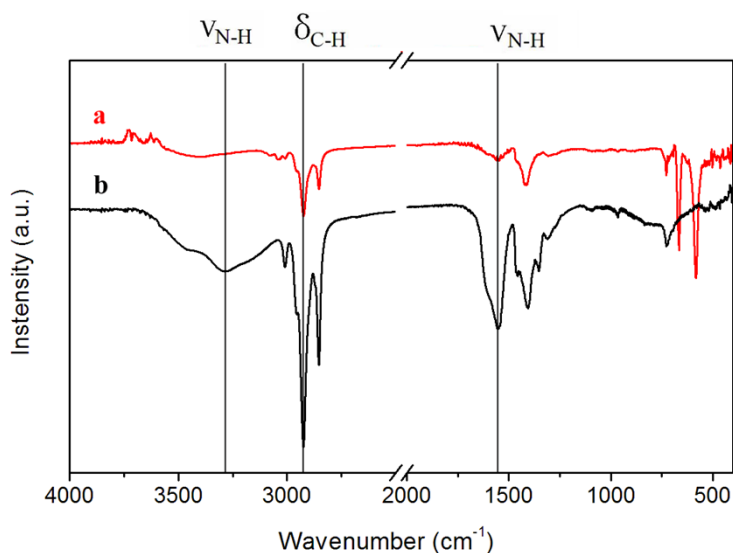


Fig. S5 The FT-IR spectra of OA- Co_3O_4 NCs (a) and $[\text{Co}(\text{NH}_3)_n]^{2+}$ -OA complex (b).

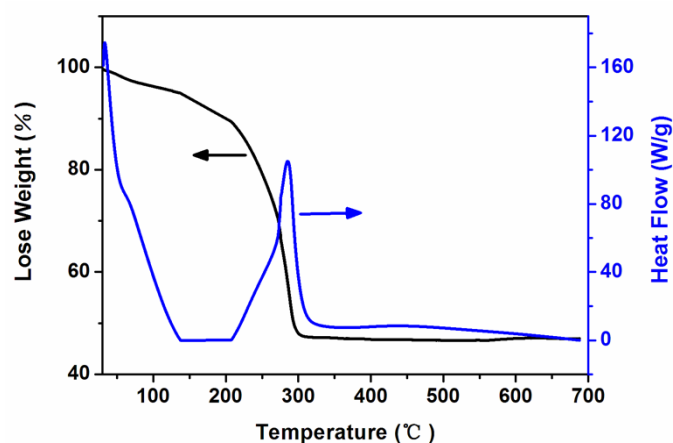


Fig. S6 TG and DSC curves of OA-Co₃O₄ NCs.

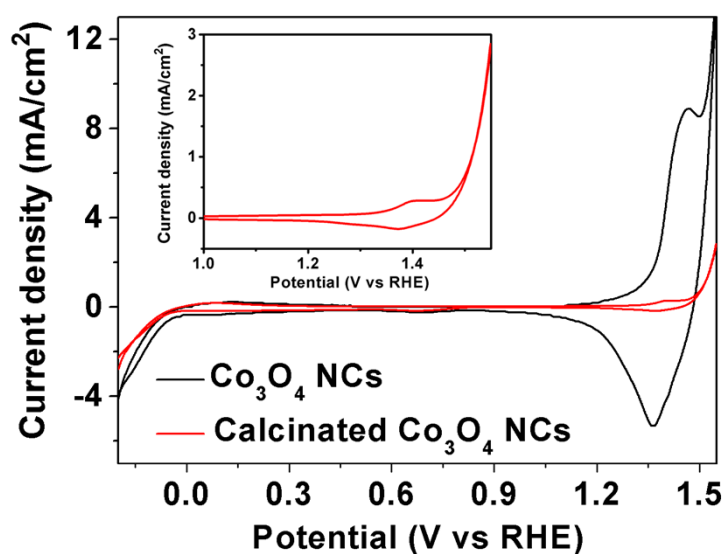


Fig. S7 *iR*-corrected CV plots of Co₃O₄ NCs and calcinated Co₃O₄ NCs on carbon fiber paper electrodes at a loading of 0.35 mg cm⁻² in 1 M KOH (The inset is the enlarged CV plot of calcinated Co₃O₄ NCs).

Table S1. Comparison of catalytic performance of Co₃O₄ NCs on carbon fiber paper to reported Co-based catalysts

Catalyst	Catalyst amount (mg cm ²)	Electrode	Over potential (mV vs.RHE)/current density (mA cm ²) (OER or HER)	Electrolyte	Ref.
Co ₃ O ₄ /N-rGO	1	GCE ^[1]	155/10 (OER)	1 M KOH	3
N-CG-CoO	0.71	GCE ^[1]	157/10 (OER)	1 M KOH	4
Zn _x Co _{3-x} O ₄	1	Ti Foil	155/10 (OER)	1 M KOH	5
CoP/CNT	0.285	GCE ^[1]	122/(-10) (HER)	1.0 M H ₂ SO ₄	6
CoS ₂ /RGO	1.15	GCF ^[2]	313/(-20) (HER)	0.5 M H ₂ SO ₄	7

CoSe ₂ NP	No	CFP ^[3]	155/(-20) (HER)	0.5 M H ₂ SO ₄	8
Co-NRCNTs	0.28	GCE ^[1]	260/(-10) (HER) 370/(-10) (HER)	0.5 M H ₂ SO ₄ 1 M KOH	9
CoO _x @CN	0.12	Ni foam	149/10 (OER) 232/(-10) (HER)	1M KOH	10
Co ₃ O ₄ NCs	0.35	CFP ^[2]	155/10 (OER) 380/(-10) (HER)	1 M KOH	This work

[1] GCE, abbreviation for glassy carbon electrode;

[2] GCF, abbreviation for Graphene/Carbon Nanotube film;

[3] CFP, abbreviation for carbon fiber paper.

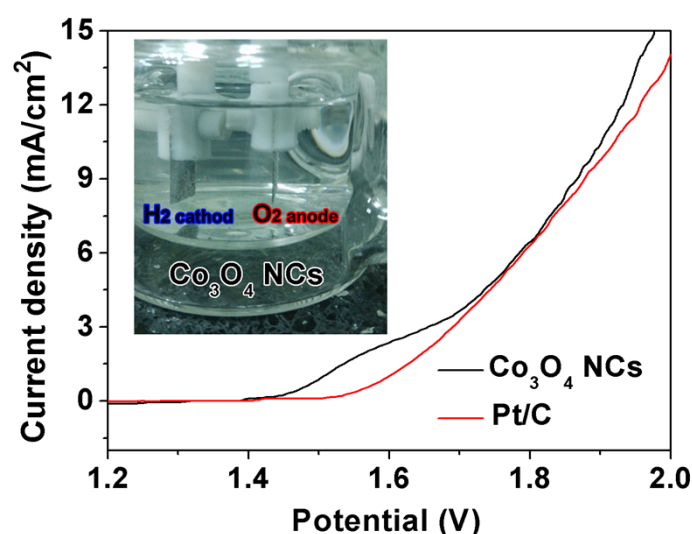


Fig. S8 LSV plots of overall water splitting using Co₃O₄ NCs, Pt/C on carbon fiber paper electrodes at a loading of 0.35 mg cm⁻² in 1 M KOH.

Additional References

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