Electronic Supplementary Information

N-doped Carbon-Coated Cobalt Nanorod Arrays Supported on a Titanium Mesh as Highly Active Electrocatalysts for Hydrogen Evolution Reaction

Weijia Zhou[a]*, Yucheng, Zhou[a], Linjing Yang[a], Jilin Huang[a], Yunting Ke[a], Kai Zhou[a], Ligui Li[a], Shaowei Chen[a,b]*

[a] New Energy Research Institute, School of Environment and Energy, South China University of Technology, Guangzhou Higher Education Mega Center, Guangzhou, Guangdong 510006, China

[b] Department of Chemistry and Biochemistry, University of California, 1156 High Street, Santa Cruz, California 95064, United States

* Address correspondence to eszhouwj@scut.edu.cn (W. J. Z.) and shaowei@ucsc.edu (S.W.C.)

Experimental Section

Materials

All reagents were of analytical grade and used without further purification. Cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$), urea ($CO(NH_2)_2$), dicyanodiamine ($C_2H_4N_4$), Ti mesh, and 20 wt% Pt/C were obtained from Sinopharm Chemical Reagents Beijing Co. and used as received. Water was supplied with a Barnstead Nanopure Water System (18.3 MΩ cm).

Synthesis of N-doped carbon-coated cobalt nanorods supported on a Ti mesh (Co@NC/Ti)

The synthesis involved two major steps. In the first step, Co_3O_4 nanorods was grown on a Ti mesh by adopting a hydrothermal method and calcination process reported in the literature.[S1] In brief, 0.582 g (2 mmol) of $Co(NO_3)_2 \cdot 6H_2O$ and 0.6 g (10 mmol) of $CO(NH_2)_2$ were dissolved in 50 mL of water under stirring, and then transferred into a Teflon-lined stainless steel autoclave, into which was immersed a piece of Ti mesh (20 mm × 20 mm) that was pretreated by hydrofluoric acid for 1 min and distilled water successively. The liner was sealed and heated at 90 °C for 8 h in an electrical oven. After cooling down naturally to room temperature, the purple-colored mesh, which was presumably $Co(OH)_2$ on Ti, was removed from the autoclave, rinsed with distilled water several times, and subject to thermal annealing at 450 °C for 4 h in air to produce Co_3O_4 nanorods supported on Ti mesh (Co_3O_4/Ti).

In the second step, the Co_3O_4/Ti prepared above was put on top of the dicyanodiamine powders (2 g) that were placed in a closed porcelain crucible. The samples were heated at 450 °C for 2 h, then at 700 °C for 2 more hours in an Ar atmosphere at a heating rate of 5 °C/min. Thermal decomposition of dicyanodiamine led to the formation of carbon that reduced Co_3O_4 into Co at high temperatures and concurrently served as an overcoating layer, affording Co@NC/Ti hybrids.

Co nanowires supported on Ti mesh without a N-doped carbon shell was synthesized by reducing the Co_3O_4 nanowires on Ti mesh by H_2 at 600 °C.

Characterization

Scanning electron microscopic (SEM) analysis was carried out with a FEI NOVA NanoSEM 430 field-emission microscope. Transmission electron microscopic (TEM) measurements were carried out with a JOEL JEM 2100F microscope. Powder X-ray diffraction (XRD) patterns were recorded on a Bruke D8 Advance powder X-ray diffractometer with Cu Kα (λ = 0.15406 nm) radiation. X-ray photoelectron spectroscopic (XPS) measurements were performed using an ESCALAB 250.

Electrochemistry

Electrochemical measurements were performed with an electrochemical workstation (CHI 760C, CH Instruments Inc.) in a 0.5 M H_2SO_4 aqueous solution. A Ag/AgCl electrode (saturated KCl) and platinum wire were used as the reference and counter electrode, respectively. The Co@NC/Ti prepared above was used directly as a binder-free working electrode. The current densities were evaluated in terms of the geometric area of Co@NC/Ti. Polarization curves were acquired by sweeping the potential from 0 to −0.8 V (vs. Ag/AgCl) at a potential sweep rate of 5 mV/s. Ohmic losses were compensated electronically. The accelerated stability tests were performed in 0.5 M H_2SO_4 at room temperature by potential cycling between 0 and −0.6 V (vs. Ag/AgCl) at a sweep rate of 100 mV/s for a given number of cycles. Current-time responses were monitored by chronoamperometric measurements for 8 h. In order to study the HER activity of Co@NC/Ti in basic media and neutral media, 1 M KOH (pH =14) and 0.1 M phosphate buffer (pH = 7) were used as the electrolytes instead of 0.5 M H_2SO_4.

In order to study the effects of the Ti mesh, the N-doped carbon-coated Co nanowires (Co@NC) powder was obtained by ultrasonic stripping of Co@NC/Ti. 4 mg of the catalyst powders was dispersed in 1 mL of 4:1 (v/v) water/ethanol mixed solvents along with 80 µL of a Nafion solution, and the mixture was sonicated for 30 min. Then, 5 µL of the above solution was dropcast onto the surface of a glassy carbon disk electrode at a catalyst loading of 0.285 mg/cm^2, which was used as the working electrode.

In all measurements, the Ag/AgCl reference electrode (in saturated KCl) was calibrated with respect to a reversible hydrogen electrode (RHE). The calibration was performed in a high-purity H_2 (99.999%) saturated electrolyte with a Pt wire as the working electrode and counter electrode. Cyclic voltammograms (CVs) were collected at a scan rate of 1 mV/s, and the average of the two potentials at which the current crossed zero was taken as the thermodynamic potential for the hydrogen electrode reactions. In 0.5 M H_2SO_4, $E_{Ag/AgCl} = E_{RHE} + 0.273$ V. In 1 M NaOH, $E_{Ag/AgCl} = E_{RHE} + 0.972$ V. In 0.1 M phosphate buffer, $E_{Ag/AgCl} = E_{RHE} + 0.538$ V.
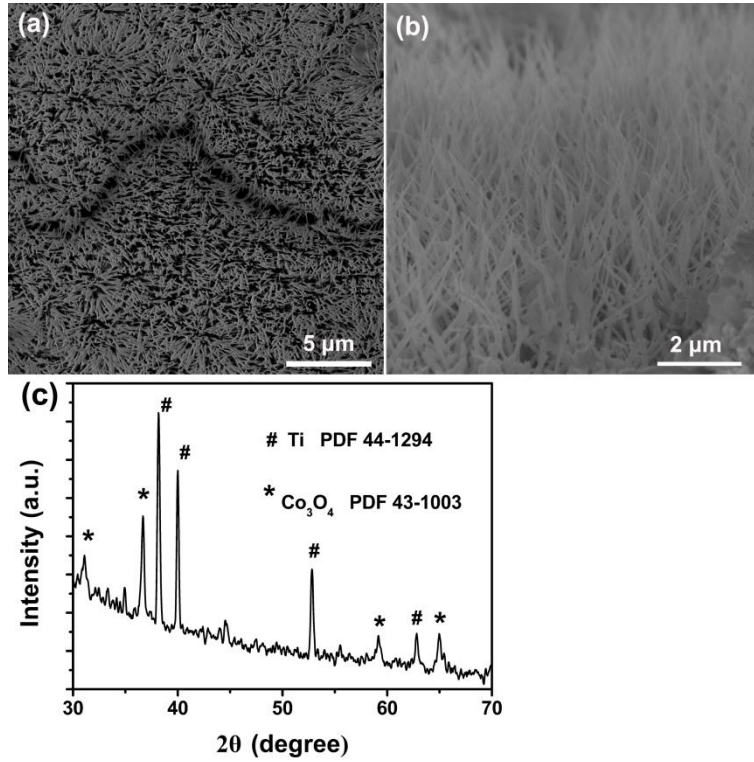
Figure S1. (a, b) SEM images and (c) XRD results of Co₃O₄ nanorod arrays on a Ti mesh.
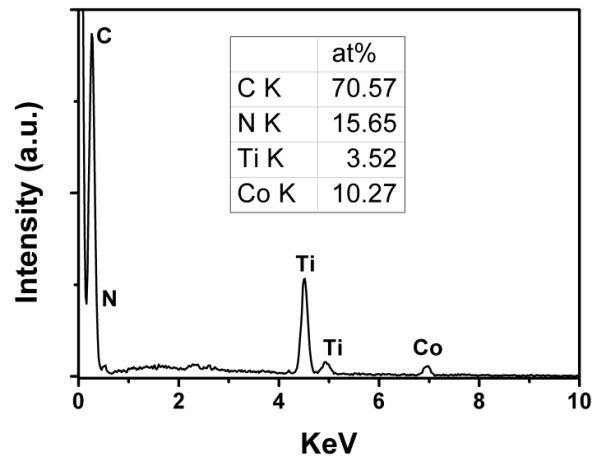

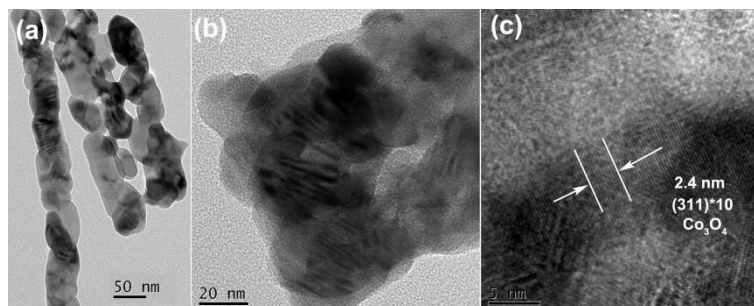**Figure S2.** Energy dispersive X-ray (EDX) spectrum of Co@NC/Ti.
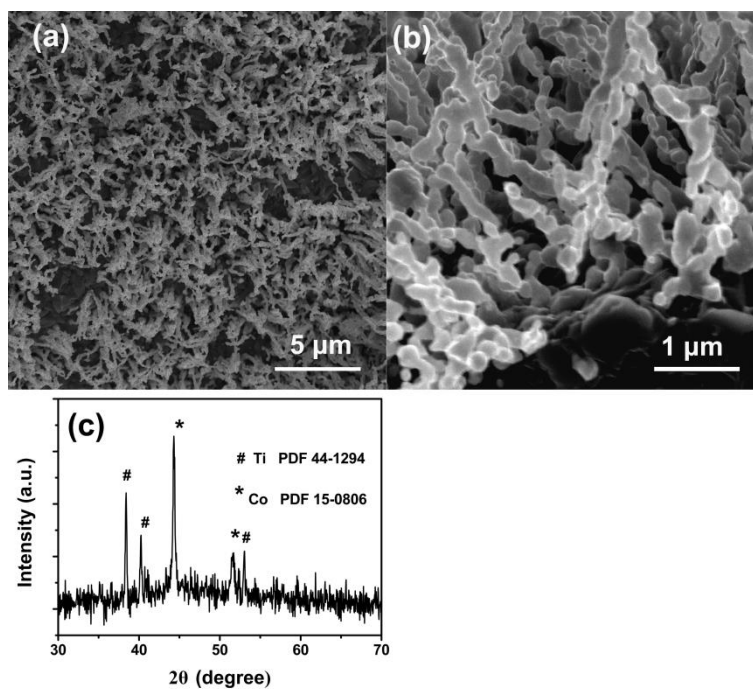

Figure S3. TEM images of Co₃O₄ nanorods.

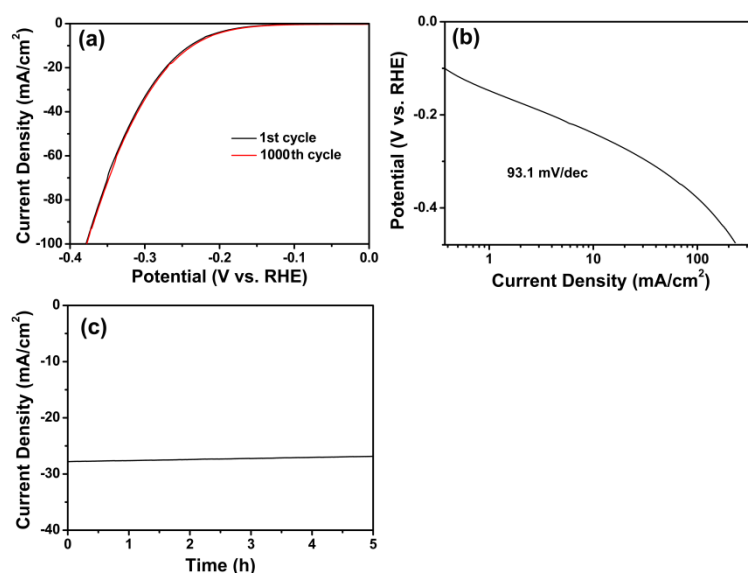**Figure S4. (a, b)** SEM images and (c) XRD patterns of Co/Ti obtained by H_2 reduction.

Figure S5. (a) HER polarization curves of Co@NC/Ti in 1 M KOH. Potential sweep rate 5 mV/s. (b) Corresponding Tafel plots (overpotential versus log current density) derived from (a). (c) Current–time plots of the Co@NC/Ti electrode at the applied potential of −0.3 V (vs RHE).
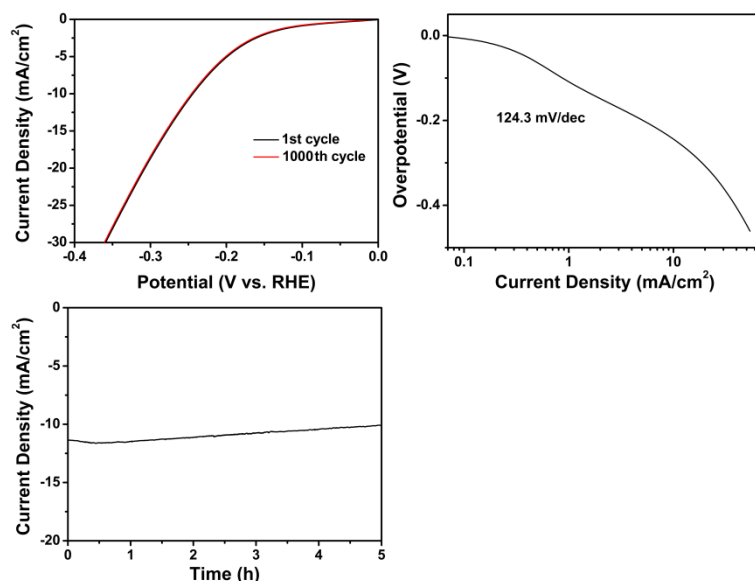
Figure S6. (a) HER polarization curves of Co@NC/Ti in 0.1 M phosphate buffer (pH = 7). Potential sweep rate 5 mV/s. (b) Corresponding Tafel plots (overpotential versus log current density) derived from (a). (c) Current–time plots of the Co@NC/Ti electrode at the applied potential of −0.3 V (vs RHE).
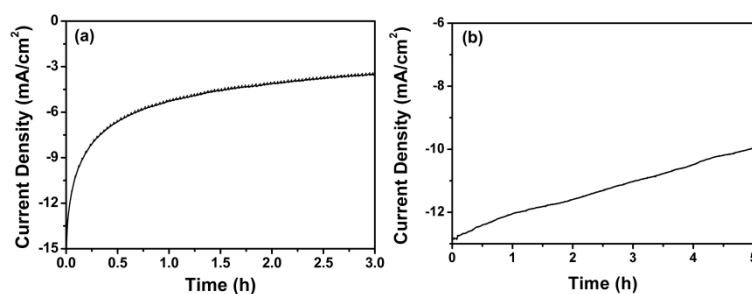

Figure S7. Current–time plots of the (a) Co/Ti and (b) Co_3O_4/Ti electrode at the applied potential of −0.35 V (vs RHE) and −0.45 V (vs RHE), respectively.
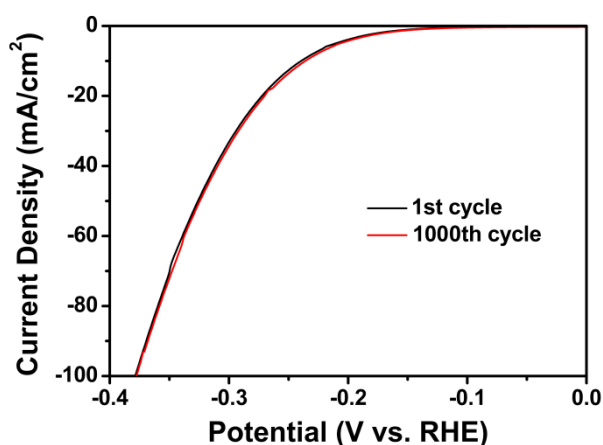

Figure S8. (a) HER polarization curves in 0.5 M H_2SO_4 with Co@NC on a glassy carbon electrode.

S1. J. Jiang, J. P. Liu, X. T. Huang, Y. Y. Li, R. M. Ding, X. X. Ji, Y. Y. Hu, Q. B. Chi and Z. H. Zhu, *Crystal Growth & Design*, 2009, 10, 70-75.