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

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Experimental Section

Materials

All reagents were of analytical grade and used without further purification. Cobalt nitrate (Co(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O), urea (CO(NH\textsubscript{2})\textsubscript{2}), dicyanodiamine (C\textsubscript{2}H\textsubscript{4}N\textsubscript{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 M\textsubscript{2}Ω 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\textsubscript{3}O\textsubscript{4} nanorods was grown on a Ti mesh by adopting a hydrothermal method and calcination process reported in the literature.\textsuperscript{S1} In brief, 0.582 g (2 mmol) of Co(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O and 0.6 g (10 mmol) of CO(NH\textsubscript{2})\textsubscript{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)\textsubscript{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\textsubscript{3}O\textsubscript{4} nanorods supported on Ti mesh (Co\textsubscript{3}O\textsubscript{4}/Ti).

In the second step, the Co\textsubscript{3}O\textsubscript{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\textsubscript{3}O\textsubscript{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\textsubscript{3}O\textsubscript{4} nanowires on Ti mesh by H\textsubscript{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 H₂SO₄ 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 H₂SO₄ 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 H₂SO₄.

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/cm², 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 H₂ (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 H₂SO₄, \( E_{Ag/AgCl} = E_{RHE} + 0.273 \) 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 Co$_3$O$_4$ nanorod arrays on a Ti mesh.

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

**Figure S3.** TEM images of Co$_3$O$_4$ nanorods.
Figure S4. (a, b) SEM images and (c) XRD patterns of Co/Ti obtained by H₂ 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) Co₃O₄/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 H₂SO₄ with Co@NC on a glassy carbon electrode.