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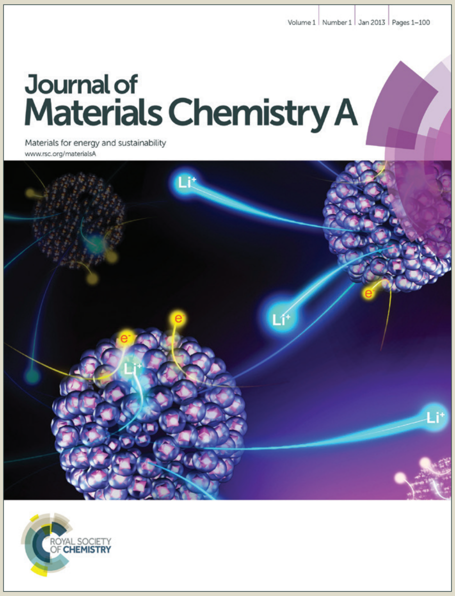

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N-doped carbon-coated cobalt nanorod arrays supported on a titanium mesh as highly active electrocatalysts for hydrogen evolution reaction

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N-doped carbon-coated cobalt nanorod arrays supported on a Ti mesh were prepared by a two-step procedure involving hydrothermal synthesis of Co_3O_4 nanorods followed by thermal reduction into metallic cobalt. The nanocomposites exhibited remarkable catalytic activity that was comparable to that of leading commercial Pt/C catalysts.

Development of effective technologies for clean and sustainable hydrogen energy has been attracting great attention lately, as hydrogen is hailed as a promising energy source to reduce our dependence on fossil fuels and benefit the environment by reducing the emissions of greenhouse and other toxic gases. Toward this end, an effective and promising approach is based on the electrolysis of water for hydrogen production.[1-3] In these studies, advanced catalysts for the electrochemical hydrogen evolution reaction (HER) are required to achieve high current density at low overpotentials.[4-6] Although platinum group metals are currently the electrocatalysts of choice that exhibit almost no overpotential,[7] the scarcity and high costs of platinum severely limit its widespread applications in HER, and it has remained a great challenge to develop highly active HER catalysts based on abundant materials (such as carbon and transition metals) with a low overpotential.[8-13]

As acidic solutions are preferred for water electrolysis to produce hydrogen, HER catalysts need to be acid-stable. Molybdenum- and tungsten-based compounds are an exciting family of HER catalysts with a high performance, including MoS_2,[14-17] $MoSe_2$,[18] Mo_2C,[19] $NiMoN_x$,[20] MoP,[21] and WS_2,[22] which exhibit excellent activity and robust stability in acidic electrolytes. Remarkable HER activity has also been observed with other transition-metal compounds, such as $CoSe_2$,[23] CoS_2,[24] CoP,[25] NiP,[26] and CuP.[27] Of these, reports have been relatively scarce where transition metals of Co, Fe and Ni are actually used for the preparation of HER catalysts largely because of their chemical instability in acidic environments, although some progress has been made recently. For instance, Zou et al.[28] recently described the synthesis of cobalt-embedded nitrogen-rich carbon nanotubes (CNTs), which were found to exhibit apparent electrocatalytic activity for HER in a wide range of pH, with a small onset potential of −50 mV and a low Tafel slope (69 mV/dec) in 0.5 M H_2SO_4. Successes like this highlight the possibility of using transition metals (e.g., Co, Ni, etc) as the active components for HER electrocatalysis in acidic electrolytes, which will significantly expand the "tool box" for the design and engineering of HER catalysts.[28-30]

Notably, to develop HER electrodes that are of high efficiency, low costs, and binder-free, active components are in general directly grown on current-collecting substrates instead of using Nafion or PTFE to immobilize catalysts on electrode surfaces. In recent years, a variety of self-supported 3D nanoarrays, such as 3D CoO@polypyrrole nanowire arrays,[31] Ni_3S_2 nanorods and FeP,[32] etc, have been constructed on current collectors that exhibit vectorial electron-transport characteristics and high electrochemical surface areas.[33-35] For instance, Sun et al.[25] reported the topotactic fabrication of self-supported nanoporous cobalt phosphide nanowire arrays on carbon cloth (CoP/CC) via low-temperature phosphidation of the corresponding Co(OH)F/CC precursor. The obtained CoP/CC, as a robust integrated 3D hydrogen-evolving cathode, showed a low onset potential of −38 mV and a small Tafel slope of 51 mV/dec, and maintained its catalytic activity for at least 80,000s in acidic media.

Herein, we described the preparation of a self-supported N-doped carbon-coated cobalt nanorod arrays supported on a Ti mesh (Co@NC/Ti), which exhibited a remarkable HER performance in acid solutions. Experimentally, Co_3O_4 nanorod arrays were first grown directly on a Ti mesh by a hydrothermal route, and subsequently reduced to Co with a carbon overcoating layer by thermal decomposition of dicyanodiamine.

The Co@NC/Ti electrode exhibited apparent HER activity in 0.5 M H_2SO_4, with an onset overpotential of –56 mV, a Tafel slope of 78.2 mV/dec, and robust stability for 8 h of continuous operation. This was ascribed to the carbon shell that protected the cobalt nanorods from dissolution in highly acidic 0.5 M H_2SO_4 as well as to the catalytic contributions from surface carbons that were mediated by the entrapped Co nanoparticles as a result of interfacial charge transfer.

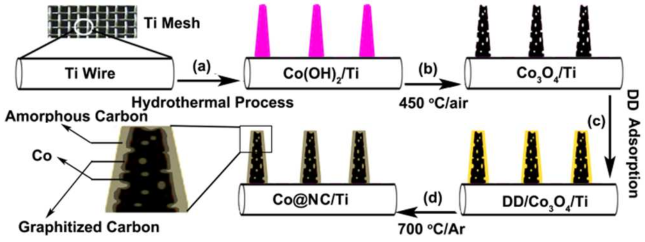


Fig. 1. Schematic of the synthesis of Co@NC/Ti. DD denotes dicyanodiamine.

The synthetic process of Co@NC/Ti is depicted in Figure 1 which entails the following major steps (details in the Electronic Supplementary Information, ESI): (a) $Co(OH)_2$ nanowires were grown on the Ti mesh surface via a hydrothermal process; (b) calcination of the $Co(OH)_2$ nanowires at 450 °C in air led to the production of porous Co_3O_4 nanorods; (c) dicyanodiamine was adsorbed onto the surface of Co_3O_4 nanorods; and (d) Co_3O_4 nanorods were reduced to Co nanorods at 700 °C in an Ar atmosphere by carbon generated from thermal decomposition of dicyanodiamine; meanwhile, the graphitic carbon formed an overcoating layer on the Co surface.[28] Of note is that the carbon layer was self-doped with nitrogen that originated from dicyanodiamine.

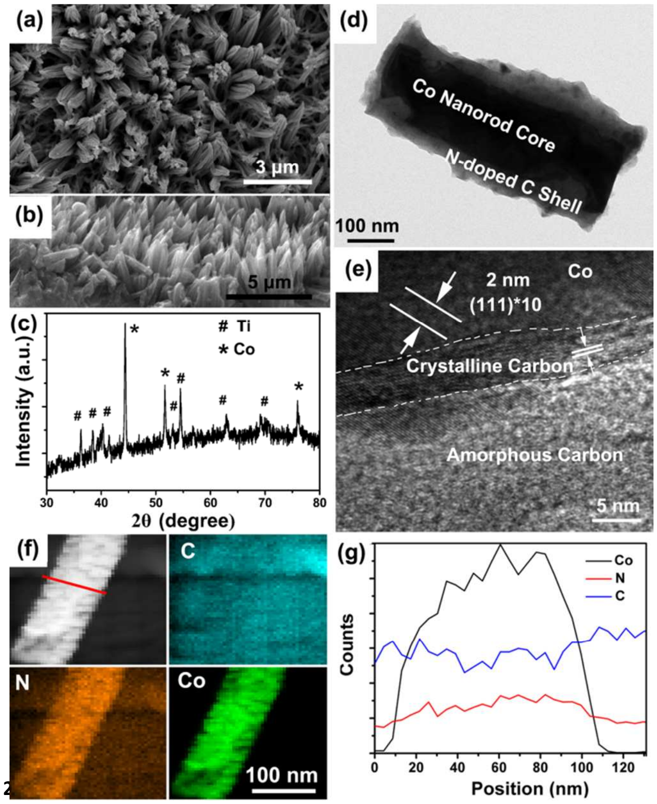
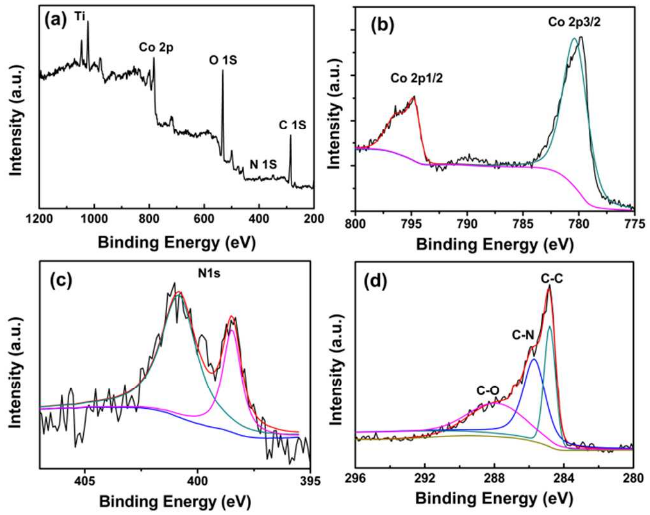


Fig. 2. (a) Top view and (b) side-view SEM images, (c) XRD patterns and (d, e) TEM images of Co@NC/Ti. (f) The corresponding EDX elemental mapping images of C, N and Co for Co@NC. (g) EDX line scan curves showing C, N, and Co element profiles across the Co@NC indicated by the red line in (f).

Further structural characterizations were carried out by TEM measurements. Figure 2 (a) and (b) show the top-view and side-view SEM micrographs of Co@NC nanorod arrays supported on a Ti mesh, respectively. It can be seen that the entire surface of the Ti mesh was covered uniformly by a densely packed Co@NC nanorod array. The size of the Co@NC nanorods was found to be about 300–400 nm in diameter, and 2 to 3 µm in length. In comparison, the Co_3O_4 nanorods before reduction were somewhat smaller at 50-150 nm in diameter (Figure S1), with the elemental composition confirmed by energy dispersive X-ray (EDX) analysis, as depicted in Figure S2. XRD measurements (Figure 2c) shows two major peaks at 44.35° and 51.64° (indicated by asterisks) that are characteristic of metallic Co (111) and (200) (JCPDS No. 15-0806), respectively. Additional diffraction peaks can be seen at 36.3°, 38.4°, 40.28°, 54.43°, 62.93°, 69.14° and 75.99° (marked by the number signs) that most likely originated from the Ti mesh substrate (JCPDS No. 44-1294). This is in marked contrast with the diffraction patterns of Co_3O_4/Ti (Figure S1c). Figure 2d shows the TEM image of a single Co@NC nanorod, where one can see a core-shell structure with different contrasts. In fact, high-resolution imaging in Figure 2e clearly shows a three-layer structure in the Co@NC nanorod. First, the core part showed well-resolved lattice fringes with an interplanar distance of 0.20 nm that was consistent with the Co(111) planes. Second, on the immediate surface of the Co nanorod, a crystalline overcoating shell can be seen which exhibited an interplanar distance of 0.34 nm that was in good agreement with the (002) planes of graphitic carbon. Third, the outermost layer appeared to consist of amorphous carbon. This carbon layer most likely originated from the thermal decomposition of cyanamide and reduced Co_3O_4 into Co at elevated temperatures. Similar results have been reported previously in the synthesis of carbon nanotubes and graphene nanosheets.[28, 36, 37] In contrast, before calcination with dicyanodiamine, the Co_3O_4 nanorods showed only a crystalline phase with the interplanar distance of 0.24 nm, corresponding to the Co_3O_4 (311) crystalline planes (Figure S3). Furthermore, in panel (f), elemental mapping analysis of a single hybrid Co@NC nanorod showed that the elements of C, N, and Co were distributed rather homogenously throughout the entire nanorod. Nevertheless, line scans across the nanorods (indicated by the red line in Figure 2f) signified the formation of a core-shell structure. From panel (g), one can see that the concentration of Co peaked at the center of the nanorord whereas those of C and N at the edges.

Fig. 3 (a) XPS survey spectra and high-resolution scans of (b) Co2p, (c) C1s and (d) N1s electrons of Co@NC/Ti.



XPS measurements were then carried out to further evaluate the chemical compositions and valence states of the nanocomposites. Figures 3a shows the survey spectrum of Co@NC/Ti, where the elements of Ti, Co, C and N can be readily identified. Figure 3b depicts the high-resolution scan of the Co2p electrons which exhibited a doublet at 795.1 eV and 780.2 eV. Deconvolution of the high-resolution scan of the N1s electrons yielded two peaks at 398.4 and 401.2 eV (Figure 3c) that are consistent with the pyridinic and pyrrolic nitrogen, respectively, indicating the successful incorporation of N into the graphitic matrix with the N-doping content of 3.36 at%.[38] In addition, the N doping was also observed in the survey spectra for C element in Figure 3b, where the C–N characteristic peak can be identified at 286.1 eV.

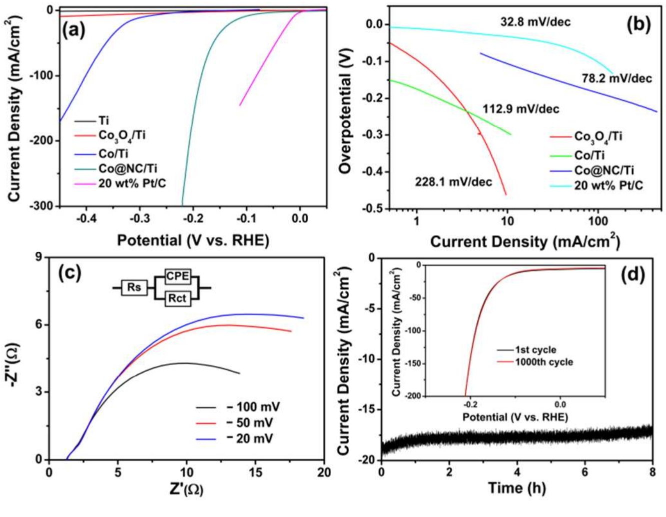


Fig. 4. (a) Polarization curves for HER in 0.5 M H_2SO_4 at a Ti mesh, Co_3O_4/Ti, Co/Ti, Co@NC/Ti and 20 wt% Pt/C on a Ti mesh. Potential sweep rate 5 mV/s. (b) Corresponding Tafel plots (overpotential versus log current density) derived from (a). (c) Nyquist plots and the equivalent circuit of Co@NC/Ti at various HER overpotentials in 0.5 M H_2SO_4. (d) Current–time plots of the Co@NC/Ti electrode at the applied potential of -0.15 V (vs RHE). Inset is that HER polarization curves for Co@NC/Ti before and after 1000 cycles in the stability test.

The HER activity of the nanocomposites prepared above was then examined by electrochemical measurements in highly acidic media. Figure 4a shows the polarization curve of Co@NC/Ti (at a loading of 11.2 mg/cm^2) in 0.5 M H_2SO_4 at a scan rate of 5 m/Vs. A blank Ti mesh, Co_3O_4/Ti (at a loading of 8.7 mg/cm^2), Co/Ti (at a loading of 7.1 mg/cm^2) and 20 wt% Pt/C on a Ti mesh (at a loading of 11.2 mg/cm^2) were also examined for comparison. The blank Ti mesh and Co_3O_4/Ti mesh showed poor HER activity with almost no reduction current until the electrode potentials were more negative than –458 mV and –245 mV, respectively. Furthermore, for Co/Ti, that was prepared by H_2 reduction of Co_3O_4/Ti at 600 °C and hence without a carbon coating layer (Figure S4), the HER activity was also low with an onset potential of –253 mV. In sharp contrast, Co@NC/Ti was significantly more active for HER with an onset potential of only –56 mV, which is close to that of commercial Pt/C (–12 mV). Increasingly negative potentials led to a rapid rise of the cathodic current. For instance, the current densities increased by 10 folds from 10 to 100 mA/cm^2 when the Co@NC/Ti electrode potential swept cathodically by less than 80 mV from –106 mV to –184 mV. This indicates the significance of the carbon coating layer in the determination of the HER activity.

Furthermore, the linear portions of the polarization curves were fitted to the Tafel equation (η = b log j + a, where j is the current density and b is the Tafel slope), yielding a Tafel slope of 78.2 mV/dec for Co@NC/Ti and 32.8 mV/dec for 20 wt% Pt/C (Figure 4b), signifying that the HER proceeded by a Volmer–Heyrovsky mechanism on Co@NC/Ti.[17, 39] Note that a much higher Tafel slope (228.1 mV/dec and 112.9 mV/dec) was observed with Co_3O_4/Ti and Co/Ti, respectively, consistent with their low HER activity. The remarkable HER catalytic performance of Co@NC/Ti (onset potential –56 mV, Tafel slope 78.2 mV/dec, current density 10 mA/cm^2 at –106 mV) is very comparable to or even better than those of leading non-platinum HER catalysts in acidic aqueous electrolytes, such as MoS_2/reduced graphene (–100 mV, 41 mV/dec),[40] nickel–molybdenum nitride nanosheets (–78 mV, 35.9 mV/dec),[20] cobalt-embedded nitrogen-rich carbon nanotubes (–50 mV, 80 mV/dec),[41] and CoS_2 nanowire array (10 mA/cm^2 at –145 mV).[24]

Interestingly, the Co@NC/Ti nanocomposites also exhibit excellent HER activity in a wide range of pH including, for instance, strongly alkaline 1 M KOH (Figure S5) and neutral 0.1 M phosphate buffer (pH = 7, Figure S6).

Electrochemical impedance measurements were also carried out to characterize the interfacial electron-transfer kinetics involved in HER. Figure 4c showed the representative Nyquist plots of the Co@NC/Ti electrode at various overpotentials, where one can see that with increasing overpotential, the diameter of the arc shrank, implying a diminishment of the charge transfer resistance (R_{ct}). More detailed analyses were carried out by fitting the impedance data to an equivalent circuit (Figure 4c inset), where a constant phase element (CPE) was employed. The charge transfer resistance Rct is related to the electrocatalysis kinetics and a lower value corresponds to a faster reaction rate. The values of Rct were found to decrease significantly with increasingly negative potentials, from 26.7 Ω at −20 mV to 9.9 Ω at −100 mV.

The durability of Co@NC/Ti for HER in 0.5 M H_2SO_4 was also examined. Figure 4d shows the time dependent current density curve for Co@NC/Ti at −150 mV. After 8 h of continuous operation, the current remained largely unchanged. As shown in the inset to Figure 4d, after 1000 cycles of potential scans in 0.5 M H_2SO_4 at a scan rate of 100 mV/s, the polarization curve shows negligible difference as compared to the initial one. In sharp contrast, both Co_3O_4/Ti and Co/Ti exhibited poor stability in 0.5 M H_2SO_4 (Figure S7), where the corresponding current density diminished by 23.4% after 5 h of continuous operation and 74.1% after 3 h of continuous operation, respectively.

The superior HER catalytic performance and stability of the Co@NC/Ti electrode might be attributed to the following factors. (1) The direct growth of Co nanorods on the Ti mesh allowed for the hybrids to possess high electrical conductivity, as confirmed in electrochemical impedance measurements (Figure 4c) in which the uncompensated resistance Rs was only 1.3 Ω, thus eliminating the use of polymer binders and conductive additives; (2) The nanorod arrays entailed a high surface area and abundant exposed active sites. In fact, when the Co@NC arrays were scratched from the Ti mesh and deposited onto a glassy carbon disk electrode, good HER activity could still be seen (Figure S8), but the performance was much lower (e.g., 10 mA/cm^2 at −239 mV) than that of Co@NC/Ti (10 mA/cm^2 at −106 mV); (3) Co likely played a crucial role in HER, where it not only decreased the local work function on the carbon surface, but also changed the electronic density of states around the carbon such that the carbon atoms served as catalytic active sites.[28, 29] (4) The overcoating shell of graphitized and amorphous carbon impeded electrochemical dissolution of cobalt in acid electrolytes, leading to improved stability of the Co@NC/Ti hybrid catalysts. In contrast, the unprotected Co_3O_4/Ti and Co/Ti hybrids exhibited only poor stability for HER in 0.5 M H_2SO_4 (Figure S7).

In summary, N-doped carbon-coated Co nanorods arrays supported on a Ti mesh (Co@NC/Ti) were prepared by a two-step procedure that entailed hydrothermal growth of Co_3O_4 nanorod arrays on a Ti mesh, followed by reduction of Co_3O_4 to Co with a carbon overcoating layer by thermal decomposition of dicyanodiamine. Electrochemical studies showed that the obtained electrocatalysts exhibited excellent HER activity with an onset potential of –56 mV (vs RHE), a large current density (10 mA/cm^2 at −106 mV), a small Tafel slope of 78.2 mV/dec and prominent electrochemical durability. The results presented herein may offer a new methodology for the design and engineering of effective HER catalysts based on earth-abundant and inexpensive components.

Notes and references

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Electronic Supplementary Information (ESI) available: Experimental details, and additional data and discussion. See DOI: 10.1039/c000000x/

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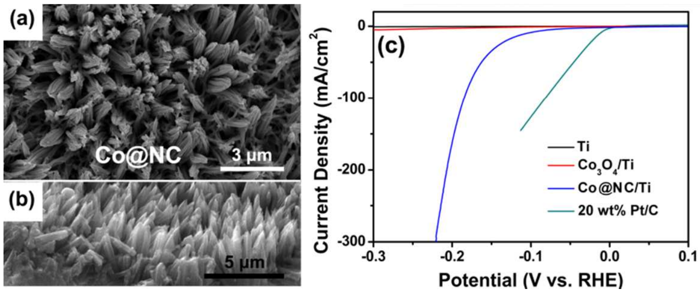

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