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Co nanoparticles embedded in 3D CoO matrix for electrocatalytic hydrogen evolution

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Earth-abundant and highly efficient electrocatalysts for hydrogen evolution reaction (HER) are desired for hydrogen production from water-splitting. Here, Co nanoparticles were embedded in the 3D CoO matrix via a template-free method, including cobalt hydroxy-carbonate nanowire arrays growth on Ni foam and the following non-contact Al-reduction process. The as-prepared 3D hierarchical structured Co/CoO nanowires possess good charge transfer and mass transport properties, and a synergistic effect at the Co/CoO interface can hugely facilitate the HER kinetics. A suitable balance between Co and CoO in the catalyst is crucial for high catalytic activity. And the optimal Co/CoO array exhibited outstanding HER activities in 1 M NaOH, achieving nearly zero onset potential, and a current density of 100 mA cm⁻² with a small overpotential of 167 mV. They also showed good long-term stabilities. This hybrid Co/CoO nanowire array is promising material for large-scale hydrogen production from water-splitting.

Introduction

Hydrogen generation from electrochemical water splitting has aroused intense attentions for the vision of clean and sustainable energy applications. Efficient electrocatalysts are required to reduce the overpotential of the hydrogen evolution reaction (HER)^{1, 2}. So far, the most active HER catalysts are Pt-based metals, which can generate large cathodic current densities for HER at low overpotentials^{3, 4}. But their scarity and high cost impede their large-scale practical application. Although many kinds of earth-abundant HER catalysts have exhibiting high activities approaching Pt in acid solutions, including transition metal chalcogenides⁵⁻⁸, phosphide⁹⁻¹², carbides¹³⁻¹⁵ and nitrides^{13, 15, 16}, all of them can not operate satisfactorily in alkaline electrolyte³. The alkaline HER electrocatalysts are more significant for the industrial water-alkali and chlor-alkali electrolyzers.

Ni, Co and their alloys are the typical alkaline electrocatalysts, but they are still far from optimization for their high HER overpotentials and large Tafel slopes^{1, 17-20}. Previous works have demonstrated that enhanced HER activity can be achieved by metal-metal oxide/carbon hybrids (Ni–NiO or

Co-CoO_x nano-particles supported on carbon nanotube or Ndoped carbon), owing to an synergistic effect that HO-H bonds are first efficiently cleaved by oxide species and the derived hydrogen intermediates (H*) are then proficiently converted to H_2 by the nearby metallic nano-particles²¹⁻²⁵. For electrochemical measurements and practical applications, these powder catalysts have to be immobilized on electrode surfaces by polymer binders. But the polymer binders usually has many disadvantages, such as increasing the series resistance, blocking active sites, inhibiting diffusion, and showing unreliable stabilities¹¹. To solve this problem, binderfree electrodes with active phases directly grown on current collectors have been developed, such as Ni/NiO and Co/Co₃O₄ core/shell nanosheet on Ni foams^{26, 27}. While these three dimensional (3D) structured binder-free electrodes have not outperformed the powder analogues, which may result from their undesirable microstructures with the nanosheets of Ni/NiO or Co/Co₃O₄ randomly stacked on the Ni foams. That leads to unefficient mass transport and charge transfer. So a 3D aligned porous metal/metal oxide array may be an optimal structure for water-alkaline HER, because it affords large metal/metal oxide interface, excellent bubble management and charge transfer properties. Our recent work has demonstrated that a well-aligned porous Ni/NiO nanosheet array can exhibit excellent HER activities approaching to the Pt/C²⁸. Compared to the nanosheet structure, the onedimensional nanowire should be more favorable considering its vectorial electron-transport property. However, it remains a challenge to fabricate such 3D metal/metal oxide nanowire arrays for HER.

Here, we demonstrated the non-contact Al reduction method can exquisitely convert the cobalt hydroxy-carbonate

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^{*}Corresponding author, Dr. Fuqiang Huang, E-mail: huangfq@pku.edu.cn Electronic Supplementary Information (ESI) available: XRD pattern and SEM image of Co₂(OH)₂CO₃·nH₂O nanowire arrays, XRD pattern of CoO powder and Co powder, TEM images of Sample IV and Sample V. See DOI: 10.1039/x0xx00000x

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precursors to desired hybrid Co/CoO nanowire arrays. Co nanoparticles were embedded in the CoO matrix to form a 3D hierarchical structure. The Co/CoO arrays exhibit enchanced HER activities compared to the metallic Co and CoO analogues. They achieved nearly zero onset potential, and a current density of 100 mA cm⁻² with a small overpotential of 167 mV, which is just 95 mV larger than Pt/C at the same current density. They also exhibited good durability.

Experimental

Synthesis of the hybrid Co/CoO nanowire array electrode

All chemicals used in this work were analytical reagent grade and commercially available, and used without further purification.

Firstly, the $Co_2(OH)_2CO_3 \cdot nH_2O$ nanowire arrays were grown on nickel foams by a facile hydrothermal method according to the previous work²⁹. Briefly, 4 mmol Co(NO₃)₂·6H₂O, 20 mmol urea and 8 mmol NH₄F were completed dissolved in 80 ml deionized water under magnetic stirring. A nickel foam substrate was vertically immersed in the solution after chemically cleaned with acetone, methanol, and deionized water. The resulting solution with nickel foams were then sealed in a 100-ml Teflon-lined stainless steel autoclave, and maintained at 120 °C for 6 h, followed by rinsing the nickel foams with deionized water and dried at 60 °C for 12 h. Powder products in the solution were collected by centrifugation. Secondly, the as-grown samples both on the nickel foams and powder from the solution were treated with a special AI reduction process to obtain the Co/CoO electrode and Co/CoO powder, according to the previous work of our group³⁰. Specifically, the as-grown samples and aluminum powder or aluminum ingot were separately placed in a two zone tube furnace and then evacuated to a base pressure ~4 Pa, then the aluminum was heated at 850 °C and samples were heated at 300 °C or 400 °C, for 2h.

Synthesis of the CoO and Co electrodes.

Firstly, the $Co_2(OH)_2CO_3 \cdot nH_2O$ nanowire arrays were grown on nickel foams and $Co_2(OH)_2CO_3 \cdot nH_2O$ powder was collected with the same method described above. Then they were annealed in Ar at 350 °C for 2h to obtain the CoO electrode and the CoO power. Similarly, the samples were annealed in H₂/Ar (H₂ 10%) at 260 °C for 2h to obtain the Co electrode and the Co power.

Preparation of the Pt/C electrode. Ethanol suspensions containing 900 μ L ethanol, 4 mg of commercial 20 wt.% Pt/C powder (Johnson Matthey Corp.) and 100 μ L 5 wt % Nafion solutions were obtained by magnetic stirring overnight. Then the 1mL catalyst ink suspension was coated onto 1 cm² Ni foam and then it was left to dry in air. So the loading mass of Pt/C is about 4mg cm².

Material characterization

The samples were characterized by powder X-ray diffraction (XRD) using a Bruck D2 X-ray diffract meter with Cu K α radiation (k = 1.5418 Å) at a scanning rate of $0.1^{\circ} \cdot \text{min}^{-1}$ in the 2ϑ range of $20^{\circ} - 85^{\circ}$. The chemical compositions, the sizes and morphologies, and the microstructures of the samples were

characterized by field-emission scanning electron microscopy (FE-SEM, JSM-6330F), transmission electron microscopy (TEM, JEM2010-HR), and X-ray photoelectron spectroscopy (XPS, ESCALab250). Nitrogen sorption isotherms were measured using a Micromeritics ASAP 2020 analyzer at -196 °C. The weight of the sample used in the measurement was 100–200 mg. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface area (SBET) using the adsorption data at p/p0 = 0.06–0.30.

Electrochemical measurements.

The electrochemical tests were carried out in a conventional three electrode electrochemical cell by using a CHI660E. A Hg/HgO (1 M NaOH) and Pt wire were used as the reference electrode and the counter electrode, respectively. The as prepared samples on Ni foams were directly used as the working electrodes. All the electrochemical measurements of catalysts were measured in 1 M NaOH solution (pH = 14) after purging the electrolyte with N₂ gas for 30 min at 25 °C. The potential, measured against a Hg/HgO (1 M NaOH) electrode, was converted to the potential versus the reversible hydrogen electrode (RHE) according to $E_{vs RHE} = E_{vs Hg/HgO} + E_{Hg/HgO}^{\theta} + 0.059$ pH - iR, and all the polarization curves were iR corrected using the data of the electrochemical impedance spectroscopy (EIS) measurements. The EIS was measured between the frequency of 0.01 Hz to 10⁵ Hz with an amplitude of 0.005V at different potentials. Linear sweep voltammetry was carried out at 1 mV s⁻¹ for the polarization curves. Chronoamperometry was measured under overpotentials of of 60 and 115 mV, respectively.

Results and discussion

Oriented Co₂(OH)₂CO₃·nH₂O nanowire arrays on nickel foams were first prepared by a hydrothermal method²⁹ confirmed by XRD and SEM results (Figure S1). Then they were treated by a non-contact Al-reduction process in a vacuum two-zone tube furnace³¹, in order to obtain the desired nanowire arrays of nanoscale Co/CoO. Figure 1a shows the scanning electron microscopy (SEM) image and the crosssection analysis of the Co/CoO prepared using Al powder at 300 °C. These results indicate the Co/CoO on Ni foam remains the aligned array structures, and each Co/CoO unit is vertically contacted on the substrate. The XRD result of the corresponding Co/CoO powder reveals the co-existing of the metallic cobalt and the cobalt oxide (Figure 1b). TEM image shows the Co/CoO nanowire consists of opaque nanodots uniformly interconnected by the light fine plates, with an uniform size of ~ 10 nm (Figure 1c). The opaque nanodots are identified to be metallic Co. seen from the interplanar spacings of 0.20 nm for Co (111) planes in their lattice-resolved HRTEM image (Figure 1d). The light plates surrounding the metals are identified to be CoO species, confirmed by the larger interplanar spacings, about 0.24 nm for CoO (111) planes (Figure 1d). The Co and CoO are well matched at their interface, where their lattice fringes are overlapped (Figure 1d). The homogeneous Co/CoO structure affords large interface area for electrocatalysis. Moreover, numerous inter-

particle mesopores with a size ranged from 2 to 5 nm in these Co/CoO units can be clearly seen (**Figure 1c**). These pores are originated from the release of water and oxygen molecules during the reduction process. It is well known that the nanoporous structures are important to facilitate the mass transport of electrolytes and gas bubbles within the electrodes, and will also provide large electroactive area for the electrochemical reaction³².



Figure 1. (a) SEM image of the porous Co/CoO nanowire array on the Ni foam, and the inset in (a) is the corresponding crosssection image. (b) The XRD pattern of Co/CoO powder. (c) TEM and (d) HRTEM images of a porous nanoscale Co/CoO nanowire. These Co/CoO samples were prepared by Al-powder reduction at 300 °C.

The pore structures of mesoporous Co/CoO were further examined by N₂ adsorption-desorption measurements. The isotherms with H3 hysteresis loops were observed for our Co/CoO (**Figure 2a**), which are commonly observed for the mesoporous transitional metal oxides³³⁻³⁵. The pore size distributions calculated from the desorption isotherms by the BJH method are shown as a plot of the relative pore filling versus pore size in **Figure 2b**. It indicates that mesopores with size of 2~50 nm are in the Co/CoO nanowires, with the main peak at 3.9 nm. This is in accordance with the TEM results. The nanoporous structures are important to facilitate the mass transport of electrolytes and gas bubbles, and will also provide large electroactive area for the electrochemical reaction²⁸.

X-ray photoelectron spectroscopy (XPS) study was performed in order to further study the chemical compositions of Co/CoO nanocomposites, shown in **Figure 2**. Both the CoO and Co/CoO nanocomposite show the main Co^{II} $2p_{3/2}$ peaks at 781.2 eV³⁶, accompanied with the broad satellites. Contrastively, the spectrum of Co/CoO nanocomposite shows an additional metallic Co peak at 778.3 eV, seen from **Figure 2c**. This result demonstrates the co-existing of CoO and metallic Co in our hybrid Co/CoO catalysts. The O 1s XPS

spectra are shown in Figure 2d. The CoO sample has two peaks, one at 529.85 eV attributed to the lattice O^{2-} and one small shoulder at 531.1 eV from the hydroxyl groups on the surface. For the Co/CoO nanocomposite, the intensity of the hydroxyl groups at 531.1 eV increased dramatically, indicating that many more hydroxyl groups were created on the CoO layers. This phenomenon is perhaps related to the oxygendefective nature in the Co/CoO sample resulting from the Alreduction process³⁷, consistent with the observations for reduced metal oxides according to previous studies^{27, 28, 38, 39}. The oxygen-defect can afford active centers to efficiently cleave water molecules^{28, 40}. And these surface hydroxyl groups could make more hydrophilic electrode surface, facilitating the electrolyte to infiltrate the nanopores in the electrode materials. Furthermore, surface hydroxyl groups could directly participate in the catalytic reactions of water cleavation^{28, 41}



Figure 2. (a) N₂ sorption isotherm of the Co/CoO powder. (b) Pore distribution calculated from the desorption branch, and the partial enlarged detail shown in the inset. The high resolution XPS spectra of (a) Co $2p_{3/2}$ and (b) O 1s peaks for the CoO and Co/CoO hybrid. These Co/CoO samples were prepared by Al-powder reduction at 300 °C.

The HER catalytic property of the hybrid Co/CoO nanowire arrays were measured in a three-electrode configuration in 1 M NaOH with a scan rate of 1 mV s⁻¹. Metallic Co electrode, CoO electrode and Pt/C electrode were also investigated under the same condition for comparison. The pure Co electrode and CoO electrode were obtained from the same precursor $Co_2(OH)_2CO_3 \cdot nH_2O/Ni$ foam annealed in H_2/Ar and Ar atmosphere, respectively. The corresponding XRD of power samples are shown in **Figure S2. Figure 3a** shows the electropolarization curves. The Co/CoO array exhibits excellent HER activity with near-zero onset overpotential as same as the Pt/C, largely better than the Co electrode (onset overpotential of 150 mV) and CoO electrode (onset overpotential of 240 mV). And Co/CoO array requires overpotentials of 60, 115 and

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167 mV to afford current densities of 20, 50 and 100 mA cm^2 , which are just 43, 77 and 95 mV larger than the Pt/C electrode,

A cm², respectively. And these overpotentials are also smaller than



Figure 3. (a) Linear sweep voltametry of the Co/CoO array, commercial Pt/C, Co and CoO electrodes at a scan rate of 1 mV s⁻¹ in 1 M NaOH; (b) Tafel plots of the Co/CoO array, Co and CoO electrodes. (c) Chronoamperometry HER measurements of the Co/CoO array at constant current densities of 20 mA cm⁻² and 50 mA cm⁻² in 1 M NaOH. These Co/CoO samples were prepared by Alpowder reduction at 300 °C.

that of other reported HER electrodes at the same current density measured in alkaline solutions, including Raney Ni¹⁹, Ni-Mo alloy¹⁷, Ni(OH)₂ modified Ni metal²³, and comparable to the CNT-Ni/NiO²². Our Co/CoO array electrode even exhibited smaller HER overpotentials than those star catalysts measured in acid electrolytes, such as NiP^{10, 42}, CoP⁴³, CuP¹², CoSe₂⁸, MoS₂⁴⁴, WS₂⁴⁵, Mo₂N¹³ and Mo₂C¹⁴. Tafel slopes of the samples were calculated from their corresponding polarization curves. Co/CoO array exhibits a Tafel slope of 90 mV/dec in the overpotential region of 0-100 mV, smaller than that of Co electrode (122 mV/dec) and CoO electrodes (132 mV/dec), shown in Figure 3b. The small Tafel slope means the fast HER kinetics and the consequent high current density at a lower overpotential. Generally, the alkaline HER follows a two-step mechanism: the first Volmer step where water is cleaved to generate the reactive intermediate H* (2H₂O + M + 2e⁻ \Leftrightarrow 2M- $H^* + 2OH^{-}$), followed by either the Heyrovsky step ($H_2O + M-H^*$ + $e^{-} \leftrightarrows H_2$ + M + OH) or the Tafel step (2M-H* $\leftrightarrows H_2$ + 2M). When Volmer reaction is the rate-determining step (r.d.s.), the Tafel slope should be above 100 mV/dec, and when the r.d.s. is Heyrovsky reaction or Tafel reaction, the Tafel slope should be about 40 mV/dec or 30 mV/dec, respectively⁴⁶. The Tafel slopes of the present Co-based electrodes lie in the range of 100 mV/dec to 140 mV/dec, evidencing the r.d.s. is the first Volmer step. Water dissociation on the pure Co surface and H* absorption on CoO surface are all kinetically difficult, which accounts for the larger Tafel slopes and higher HER onset overpotentials of the Co and CoO electrodes. For the Co/CoO electrode, the HO-H bonds can be efficiently cleaved at the interface of Co/CoO, resulting in the formation of OH* on CoO and H* on the neighboured Co site. The as-derived H* are then proficiently converted to H_2 by the Co nanoparticles²¹. Thus a faster HER kinetics can be expected on the Co/CoO hybrids. Additionally, the porous array structures and the highly conductive Co nanoparticles can further benefit the charge transfer and mass transport (inwards diffusion of electrolyte and outwards diffusion of gas bubbles). Furthermore, The specific surface areas of Co powder, CoO powder and the Co/CoO powder were calculated to be as 39.5, 90.9 and 43.4 m²/g. That is to say the surface area of Co/CoO nanocomposite is comparable to that of the metal Co nanoparticles, and even

smaller than that of CoO sample. So the enhanced HER activity of Co/CoO has little relationship with increased surface area.

The durabilities of the hybrid Co/CoO nanowire array was also examined using chronoamperometry method. **Figure 3c** shows the time-dependent current density curves under static overpotentials of 60 and 115 mV, respectively. After a long period (24 h), the current densities (20 and 50 mA cm⁻²) show barely degradations with the retention above 90%. Additionally, the nanowire-array structure of our Co/CoO is well maintained after the long-period HER measurement, seen from the corresponding SEM image (**Figure S3**). Thus, this Co/CoO electrode has superior long-term stability, which is crucial for real alkali-electrolyzer operations.



Figure 4. (a) XRD patterns and (b) Linear sweep voltametry of the investigated samples prepared with different reducing conditions. Sample I: Al ingot (AI) reduction at 300 °C, Sample II: Al ingot (AI) reduction at 400 °C, Sample III: Al powder (AP) reduction at 300 °C, Sample IV: Al powder (AP) reduction at 400 °C and Sample V: H_2/Ar reduction at 260 °C.

To study the affect of different components in Co/CoO catalyst on its HER activity, Co/CoO nanowire arrays with different ratio of Co/CoO were prepared by controlling reduction degree of the cobalt hydroxy-carbonate precursors, and they were studied by linear sweep voltametry. The annealing temperature and the surface area of the AI reductant have significant influences on the reduction degree. Al powder (AP) with a higher surface area and AI ingot (AI) with a lower one were respectively employed in our experiments. Four Co/CoO samples were prepared by AI-reduction at 300 °C (Sample I), AI-reduction at 400 °C (Sample

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II), AP-reduction at 300 °C (Sample III) and AP-reduction at 400 °C (Sample IV), respectively. Figure 4a shows the XRD results of the four Co/CoO powders. Only a weak cobalt XRD peak is observed for Sample I, indicating a slight component of metallic cobalt. With improved reduction degree, incresed raio of Co/CoO is obtained for Sample II and Sample III, and only cobalt XRD peaks are observed in Sample IV. From Sample I to Sample II to Sample III, the HER performances are more and more improved, seen from the decreasing onset overpotentials and the increasing current densities at large overpotentials, as shown in Figure 4b. The Sample III exhibits the best HER performance, indicating a higher percentage of metallic cobalt is better for HER catalysis. However, the sample IV, with a further greater reduction degree, shows a degraded HER performance. Although it displays a relatively low onset overpotential (close to Sample II), its current densities at high overpotentials are obviously lower than the Sample I-III. It is worth noting Sample IV still outperforms the H2-reduced sample (Sample V). And the corresponding TEM images (Figure S4) reveal that a ultrathin layer of CoO exists in Sample IV, but no obvious CoO species are observed for the Sample V. These results indicate that a suitable balance between Co and CoO in the catalyst is crucial for high catalytic activity, resulted from the synergistic effect as stated above. The CoO species could lower the water-dissociation energy barrier and the metallic Co acts as a relay to further convert H* to H₂ molecular. The Sample III might have the optimal balanced Co/CoO configuration that can take full advantage of this synergistic effect to achieve the best HER activity.

To further reveal the roles of Co and CoO in HER kinetics of the hybrid catalysts, the impedance spectroscopy (EIS) analyses were performed. Figure 5a and Figure 5b show the Nyquist plots of sample III at different overpotentials. Two semicircles are observed in these plots: a small one in the high frequency domain that is independent of the potential, which is attributed to the electrode porosity; and a bigger one in the middle and low frequency domain that was varied with the potential, which is related to the HER kinetics⁴⁷. The chargetransfer resistance (R_{CT}) of HER can be caculated from the diameter of the second semicircle⁴⁷. Figure 5c shows the Nyquist plots of the samples with different component ratio of Co/CoO at the same overpotential 200 mV. All the samples display similar semicircles in the high frequency domain but significantly different ones in the middle and low frequency domain, indicating the substantial correlation between the HER- R_{CT} and the Co/CoO components. The value of HER- R_{CT} of these samples are summarized in Table 1. The Sample I-IV have obviously lower HER-R_{CT} compared to the Sample V, which accounts for their lower onset overpotentials and confirms the important role of CoO in lowering the H* adsorption energy barrier. While the $HER-R_{CT}$ of pure CoO catalyst (Sample VI) is very high to 15.8 Ω from its corresponding Nyquist plot (Figure 5d), which accounts for its bad HER activity. That means fast HER kinetics also need proper metallic Co species to further produce H₂ products. Sample III has the smallest HER-R_{CT} among the Co/CoO hybrid catalysts, consistent with previous HER performances. In a

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word, the Co/CoO hybrid catalyst can enormously decrease the HER charge transfer resistance compared to the single component Co or CoO catalyst, and the lowest charge transfer resistance can be achieved by well balancing the ratio of Co/CoO components.



Figure 5. (a) Nyquist plots of the Co/CoO electrode prepared by Al powder reduction at 300 °C (Sample III) measured at different overpotentials and the enlarged detail of high frequency zone shown in (b). Nyquist plots of (c) Sample I-V and (d) pure CoO electrode (Sample VI) taken at the overpotential of 200 mV.

Table 1. HER charge transfer resistances (HER-R_{CT}) of the investigated samples (η =200 mV).

	HER- $R_{CT}(\Omega)$ at $\eta=200 \text{ mV}$
Sample I: AI reduction 300 °C	3.9
Sample II: AI reduction 400 °C	3.0
Sample III: AP reduction 300 °C	1.8
Sample IV: AP reduction 400 °C	4.5
Sample V : H_2 /Ar reduction 260 °C	6.6
Sample VI: Ar annealing 350 °C	15.8

Conclusions

In summary, we prepared Co nanoparticles embedded CoO nanowire arrays via a template-free method, including cobalt hydroxy-carbonate nanowire arrays growth on Ni foam and the following non-contact Al-reduction process. They were endowed with improved properties of charge transfer, mass transport and faster HER kinetics. A suitable balance between

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Co and CoO in the catalyst is crucial for high catalytic activity. And the optimal Co/CoO array exhibited outstanding HER activity in alkaline media, approaching to the commercial Pt/C catalyst, and they also showed good long-term stabilities. This hybrid Co/CoO nanowire array may pave ways for designing new nanomaterials for efficient hydrogen production from water-splitting.

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