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Article

Synergistic effect of metallic nickel and cobalt oxides with nitrogen-doped carbon nanospheres for highly efficient oxygen evolution

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ABSTRACT

The most energy-inefficient step in the oxygen evolution reaction (OER), which involves a complicated four-electron transfer process, limits the efficiency of the electrochemical water splitting. Here, well-defined Ni/Co₃O₄ nanoparticles coupled with N-doped carbon hybrids (Ni/Co₃O₄@NC) were synthesized via a facile impregnation-calcination method as efficient electrocatalysts for OER in alkaline media. Notably, the impregnation of the polymer with Ni and Co ions in the first step ensured the homogeneous distribution of metals, thus guaranteeing the subsequent *in situ* calcination reaction, which produced well-dispersed Ni and Co₃O₄ nanoparticles. Moreover, the N-doped carbon matrix formed at high temperatures could effectively prevent the aggregation and coalescence, and regulate the electronic configuration of active species. Benefiting from the synergistic effect between the Ni, Co₃O₄, and NC species, the obtained Ni/Co₃O₄@NC hybrids exhibited enhanced OER activities and remarkable stability in an alkaline solution with a smaller overpotential of 350 mV to afford 10 mA cm⁻², lower Tafel slope of 52.27 mV dec⁻¹, smaller charge-transfer resistance, and higher double-layer capacitance of 25.53 mF cm⁻² compared to those of unary Co₃O₄@NC or Ni@NC metal hybrids. Therefore, this paper presents a facile strategy for designing other heteroatom-doped oxides coupled with ideal carbon materials as electrocatalysts for the OER.

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1. Introduction

Water oxidation, known as the anodic oxygen evolution reaction (OER), is the essential half-reaction of water electrolysis for producing high-value hydrogen energy to replace traditional fossil fuels [1–4]. However, the OER is a sluggish multistep

reaction due to the complex four-electron transfer reaction ($2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2 + 4\text{e}^-$), which usually requires a large overpotential of more than 1.23 V (standard equilibrium potential) to drive the effective water electrolysis [5–8]. Therefore, to realize efficient H₂ generation, one should search for effective electrode materials to reduce the overpotential for the OER

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[9,10]. At present, platinum group metal oxides, such as ruthenium and iridium oxides, remain the most efficient and stable catalysts for the OER [11–14]. However, considering the scarcity and high cost of these noble metal materials, it is crucial to develop naturally abundant, non-noble metal electrocatalysts to catalyze the OER on a large scale to meet the global energy demand [15,16].

First-row transition-metal (Mn, Fe, Co, Ni, etc.) based compounds, such as oxides [17], (oxy)hydroxides [18,19], sulfides [20,21], and phosphides [22,23], are extensively investigated as efficient OER catalysts to replace noble metal catalysts. Among these catalysts, non-noble metal oxides have accumulated more attention because recent studies have demonstrated that the real active sites for the OER may be the oxides/(oxy)hydroxides, which are formed on the surface of catalysts during the electrochemical oxidation process [24,25]. Concerning this problem, designing and tuning unique metal oxides with remarkable activities and stability for an enhanced OER have gained much focus. For example, Boettcher et al. [26] reported that cobalt oxides exhibited desirable activity in alkaline media. To maximize the activity of cobalt oxides, numerous strategies have been adopted to improve the intrinsic OER activities, including doping other transition-metals, designing unique nanostructures, and improving the conductivity of catalysts using ideal conductive materials. Hu's group reported that the intentional introduction of Ni or Fe into cobalt oxides can significantly increase their intrinsic activities, because Ni or Fe dopants can increase the activity of cobalt oxides related to the anodic shift in the nominally $\text{Co}^{2+}/^{3+}$ redox wave, indicating strong synergistic metal–metal electronic interactions between Ni and Co [27]. However, it is usually challenging to synthesize well-defined Ni-doped cobalt oxides with unique structures to expose more active sites and improve the conductivity of catalysts [28]. Therefore, employing an ideal carbon substrate with high conductivity, large surface area, and strong tolerance to harsh acidic or alkaline conditions is highly desired to derive efficient Co-based hybrid catalysts. Additionally, the N heteroatoms doped into carbon materials can influence the electronic structures due to the different electronegativities of N and C, thus activating the inert carbon surface. Organic polymers, a class of N-doped carbon materials, have accumulated more interests due to their tunable shape, low density, high conductivity, and porous structures after undergoing carbonization at a high temperature [29–32]. The application of organic polymers relies on the design of homogeneously distributed nanostructures with porous structures and high conductivity. Furthermore, controlling the size of carbon nanostructures below 100 nm is essential due to the many valuable nanoscale effects [29]. Therefore, designing unique metal/nonmetal-doped oxides strongly coupled with well-defined carbon nanostructures is urgently needed, although it is still challenging.

Based on the above analysis, we have designed and synthesized well-defined $\text{Ni}/\text{Co}_3\text{O}_4@\text{NC}$ hybrids via a facile impregnation–calcination process (Fig. 1). The first step involving polymer impregnation with Ni and Co ions can ensure the homogeneous distribution of metals, thus guaranteeing the following

Fig. 1. Schematic illustration of the synthesis of $\text{Ni}/\text{Co}_3\text{O}_4@\text{NC}$ nanospheres.

in situ calcination reaction, which would produce well-dispersed Ni and Co_3O_4 nanoparticles. Moreover, the calcination process confined within the carbon matrix can effectively prevent the aggregation and excessive growth of active species. Benefiting from the synergistic effect between Ni, Co_3O_4 , and NC species, the obtained $\text{Ni}/\text{Co}_3\text{O}_4@\text{NC}$ hybrids exhibit enhanced OER activity in alkaline media, with a smaller overpotential of 350 mV to afford 10 mA cm^{-2} , lower Tafel slope of $52.27 \text{ mV dec}^{-1}$, smaller charge-transfer resistance, and higher double-layer capacitance of 25.53 mF cm^{-2} compared to those of unary $\text{Co}_3\text{O}_4@\text{NC}$ or $\text{Ni}@\text{NC}$ metal hybrids. The present strategy may be also applicable in designing other heteroatom-doped oxides coupled with the ideal carbon materials to realize high OER electrocatalytic activities.

2. Experimental

2.1. Synthesis

The well-dispersed polymer nanospheres were synthesized via the polymerization of aniline and pyrrole using Triton X-100 as a surfactant, according to the procedure employed in our previous study [33]. To synthesize $\text{Ni}^{2+}, \text{Co}^{2+}@\text{polymer}$ nanospheres, the polymer nanospheres were dispersed in 20 mL of a solution containing the same amount of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ($n_{\text{Ni}}:n_{\text{Co}} = 1:1$) with strong ultrasonication to form homogeneous ink. Subsequently, the $\text{Ni}^{2+}, \text{Co}^{2+}@\text{polymer}$ nanospheres were obtained by evaporating the residual water at 80°C .

A 0.2 g portion of the as-prepared $\text{Ni}^{2+}, \text{Co}^{2+}@\text{polymer}$ was calcined in a tube furnace at 800°C for 4 h, followed by isothermal calcination at 500°C for 2 h at a heating rate of 5°C min^{-1} in an inert atmosphere. After cooling to 25°C , the product was filtered with water and EtOH several times and subsequently dried in a vacuum. The obtained particles were denoted as $\text{NiCo}@\text{NC}$ nanospheres.

The $\text{NiCo}@\text{NC}$ nanospheres were heated in a muffle furnace to 400°C at a rate of 2°C min^{-1} , after which they were kept for 2 h to yield $\text{Ni}/\text{Co}_3\text{O}_4@\text{NC}$ nanospheres.

The NCs were synthesized using the same procedure for preparing the $\text{Ni}/\text{Co}_3\text{O}_4@\text{NC}$ nanospheres without introducing $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The $\text{Ni}@\text{NC}$ and $\text{Co}_3\text{O}_4@\text{NC}$ nanospheres were also synthesized using the synthesis procedure for the $\text{Ni}/\text{Co}_3\text{O}_4@\text{NC}$ nanospheres but without adding $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, respectively.

2.2. Characterizations

The surface morphology and size of the catalysts were observed using a Hitachi S-4800 scanning electron microscope (SEM) equipped with an energy-dispersive X-ray detector (EDX) and an FEI Tecnai G² transmission electron microscope (TEM) with an acceleration voltage of 200 kV. Powder X-ray diffraction (XRD) (Cu $K\alpha$, $\lambda = 0.154178$ nm) analysis was performed on an X'Pert PRO MPD diffractometer at a scanning rate of $3^\circ \text{C min}^{-1}$. The compositions and valence states were determined by X-ray photoelectron spectroscopy (XPS) (ThermoFisher Scientific II) with an Al $K\alpha$ (1486.6 eV) X-ray source.

2.3. Electrochemical measurements

The electrochemical measurements of all catalysts were conducted using a Gamry Reference 600 workstation in a standard three-electrode system. Hg/HgO and a platinum plate were used as the reference and counter electrodes, respectively. For the preparation of the working electrode, 5 mg portions of the catalysts were dispersed in 1 mL of a water/ethanol/Nafion aqueous solution by strong ultrasonication to form homogeneous ink. Subsequently, 5 μL of the ink was dropped onto a glassy carbon electrode (GCE) (0.1256 cm^2) and then dried in a vacuum. The OER polarization curves of all samples were obtained in an O_2 -saturated 1.0 M KOH solution at a scan rate of 2 mV s^{-1} . Electrochemical impedance spectroscopy (EIS) measurements were carried out at 1.4 V (vs. RHE) with a frequency in the range of 100000–0.1 Hz with an AC voltage of 5 mV. The estimation of the electrochemical surface area of the catalysts was carried out by cyclic voltammetry (CV) in the non-Faradaic region at various scan rates (40, 60, 80, 100, 120, and 140 mV s^{-1}). Long-term stability tests were conducted by continuous CV at a scan rate of 100 mV s^{-1} from 1.3 V to 1.6 V (vs. RHE) for 1000 cycles.

3. Results and discussion

3.1. Characterization of Ni/Co₃O₄@NC nanospheres

SEM is firstly employed to examine the morphologies and compositions of the as-synthesized products, as illustrated in Fig. 2. As shown in Figs. 2(a) and 2(b), the polymer nanospheres are composed of well-dispersed nanospheres with a diameter of ~ 100 nm, and the surface is smooth. After impregnation with Ni and Co ions, followed by calcination at high temperatures, the obtained NiCo@NC nanospheres still preserve their spherical morphology but with a shrunk size of ~ 90 nm (Figs. 2(c) and 2(d)). Despite the harsh thermal condition, the final as-synthesized Ni/Co₃O₄@NC nanospheres maintain their uniform nanospherical structures, while their surfaces become rougher, indicating the stable properties of the polymer framework (Figs. 2(e) and 2(f)). To further confirm the existence and homogeneous distribution of elements, the SEM images and elemental mappings of Ni/Co₃O₄@NC are presented. Fig. 2(g) displays the homogeneous distribution of the Ni, Co, C, N, and O elements of the Ni/Co₃O₄@NC nanospheres, which may be because Ni^{2+} and Co^{2+} , dispersed in the polymer in an atomic scale, promote the good dispersion of the

Fig. 2. SEM images of polymer (a,b), NiCo@NC (c,d), and Ni/Co₃O₄@NC (e,f); (g) SEM mapping of Ni/Co₃O₄@NC.

elements in the Ni/Co₃O₄@NC nanospheres. The EDX spectrum of Ni/Co₃O₄@NC in Fig. S1 also demonstrates the existence and contents of Ni, Co, C, N, and O. For comparison, the SEM images of NC, Ni@NC, and Co₃O₄@NC reveal that these samples also maintain the spherical morphology, implying that both Ni and Co species have no notable effect on the spherical polymer framework (Figs. S2–S4). Figs. S5 and S6 exhibit the homogeneous elemental distribution and contents of the Ni@NC and Co₃O₄@NC catalysts, respectively.

The nanostructures of the as-prepared catalysts are further examined by TEM. Figs. 3(a) and 3(b) show that the polymer nanospheres exhibit the typical spherical morphology with a diameter of ~ 100 nm, which is consistent with the SEM analysis. After the calcination of the $\text{Ni}^{2+}, \text{Co}^{2+}$ @polymer nanospheres, many nanoparticles are homogeneously dispersed throughout the nanospheres (Fig. 3(c)). Under high magnification (Fig. 3(d) and Fig. S7), numerous Ni and Co nanoparticles are embedded in several carbon layers. Benefiting from the homogeneous distribution of Ni and Co nanoparticles in NiCo@NC, the as-synthesized Ni/Co₃O₄@NC nanospheres deriving from NiCo@NC also maintain a spherical morphology with many nanoparticles well-dispersed throughout the carbon matrix, and the surface is evidently porous (Fig. 3(e) and Fig. 3(f)). It is worth noting that the carbon matrix can significantly confine the excessive growth of these nanoparticles and prevent their stacking and coalescence. Moreover, Fig. 3(g) exhibits the noticeable lattice fringes with spacings of 0.204 and 0.243 nm, which correspond to the (111) crystal plane of Ni and the (311) crystal plane of Co₃O₄, respectively. The XRD patterns of all the samples are also presented to further verify the crystallographic structures of the catalysts. As shown in Fig. S8, NC exhibits a broad peak at $\sim 24^\circ$, corresponding to the (002) facets of graphitic carbon. For NiCo@NC, the typical peaks located at

Fig. 3. TEM images of polymer (a,b), NiCo@NC (c,d), and Ni/Co₃O₄@NC (e,f); (g) HRTEM image of Ni/Co₃O₄@NC; (h) XRD patterns of NC, NiCo@NC, and Ni/Co₃O₄@NC.

44.4°, 51.7°, and 76.2° can be ascribed to the mixture of Ni (PDF No. 01-089-7128) and Co (PDF No. 01-089-4307). After annealing of NiCo@NC, the typical peaks at 44.5°, 51.7°, and 76.2° of the as-prepared Ni/Co₃O₄@NC correspond to the (111), (200), and (220) planes of Ni (PDF No. 01-089-7128), respectively. Moreover, the peaks at 37.1°, 59.2°, and 65.2° can be ascribed to the (311), (511), and (440) facets of Co₃O₄ (PDF No. 00-001-11152), respectively, which is consistent with the TEM results (Fig. 3(h)). This result indicates that the Co species are more easily oxidized during the annealing process. In addition,

the XRD patterns of the reference samples show that the Ni@NC nanospheres are composed of metallic Ni and that the Co₃O₄@NC nanospheres consist of Co₃O₄ (Fig. S9).

XPS measurements are further carried out to investigate the composition and valence states of the Ni/Co₃O₄@NC catalyst. As shown in Fig. 4(a), the XPS survey demonstrates the existence of Ni, Co, C, N, and O in the Ni/Co₃O₄@NC catalyst, which is consistent with the SEM mapping analysis. For Ni 2p in Fig. 4(b), the peaks located at 855.7 and 873.2 eV are assigned to Ni 2p_{3/2} and Ni 2p_{1/2}, respectively, which are ascribed to Ni⁰ [34,35]. Moreover, the peaks located at 856.8 eV in the Ni 2p_{3/2} region and 874.5 eV in the Ni 2p_{1/2} region correspond to Ni³⁺, whose formation is due to the surface oxidation; the Ni oxides cannot be observed in the XRD pattern due to their amorphous state [36]. The existence of the low-valence Ni⁰ in further oxidation may play a crucial role in enhancing the OER performance, while the high-valence Ni³⁺ may be inactive for the OER due to the difficulties associated with its oxidation. The other two peaks located at 861.7 and 880.1 eV are satellite peaks [37,38]. In addition, the high-resolution XPS spectra of the Co 2p region can be fitted with two different doublets (Fig. 4(c)): one doublet located at 780.6 and 795.4 eV, ascribed to Co₃O₄; and the other doublet located at 782.3 and 796.9 eV, assigned to Co³⁺ [39]. Two other peaks located at 786.4 and 803.4 eV are assigned to the satellite peaks of Co 2p [40]. The high-resolution XPS spectra of C 1s can be deconvoluted into four peaks, located at 284.6 eV for C=C, 285.0 eV for C–O, 286.0 eV for C–C, and 228.4 eV for C–N, respectively (Fig. 4(d)) [41]. This result demonstrates that the heteroatom N-doped into the carbon matrix successfully. This can also be verified in the XPS spectra of the N 1s region, which can be deconvoluted into three peaks of pyridinic-N (398.6 eV), graphitic-N (399.4 eV),

Fig. 4. Survey XPS spectrum (a) and high-resolution XPS spectrum of Ni/Co₃O₄@NC at the Ni 2p (b), Co 2p (c), C 1s (d), and N 1s (e) regions.

and pyrrolic-N (400.4 eV) (Fig. 4(e)) [42]. Notably, introducing electron-rich N dopants is beneficial for optimizing the electron configuration, and thus accomplishing intrinsic enhanced OER performance [43]. Overall, the exact composition of the Ni/Co₃O₄@NC catalyst has been confirmed as a hybrid of Ni and Co₃O₄, as verified by HRTEM, XRD, and XPS analyses.

To evaluate the electrocatalytic OER performance of Ni/Co₃O₄@NC, we utilize a three-electrode configuration with the scan rate of 2 mV s⁻¹ in 1.0 M KOH. The OER performance of bare GCE, NC, NiCo@NC, Co₃O₄@NC, and Ni@NC are also presented as a comparison (Fig. 5(a)). The linear sweep voltammetry (LSV) curves of all the samples show that Ni/Co₃O₄@NC exhibits a much higher current density (*j*) at the same overpotential (*η*) compared with other reference samples (Fig. 5(a)). To reach a current density of 10 mA cm⁻², Ni/Co₃O₄@NC only requires a small overpotential of only 350 mV compared to those of NiCo@NC (510 mV), Co₃O₄@NC (400 mV), and Ni@NC (480 mV) (Fig. 5(b)), suggesting that the synergistic effect between Ni, Co₃O₄, and NC contributes significantly to the enhanced OER performance. Bare GCE exhibits nearly no current response even with a large overpotential, excluding the effect of bare GCE on the excellent OER performance of Ni/Co₃O₄@NC. As shown in Table S1, the OER performance of the Ni/Co₃O₄@NC hybrids is superior to those of many other Co-based materials, suggesting the advantages of employing Ni/Co₃O₄@NC hybrids as efficient OER catalysts. The Tafel slope simulated from the LSV curve via the Tafel equation ($\eta = a + b \log j$, where *a* represents the intercept and *b* represents the Tafel slope) is an inherent property to elucidate the possible

reaction mechanism [1]. As observed in Figs. 5(c) and 5(d), the Tafel slope of Ni/Co₃O₄@NC is 52.27 mV dec⁻¹, which is lower than those of NC (168.05 mV dec⁻¹), NiCo@NC (143.01 mV dec⁻¹), Co₃O₄@NC (62.55 mV dec⁻¹), and Ni@NC (114.89 mV dec⁻¹), demonstrating the favorable OER kinetics of the Ni/Co₃O₄@NC electrode. Therefore, compared with NC, Co₃O₄@NC, and Ni@NC, it can be speculated that Ni, Co₃O₄, and NC can synergistically boost the OER performance.

To evaluate the electrochemical surface area (ECSA) of the interface between the catalysts and electrolyte, the double-layer capacitances (*C_{dl}*) of the catalysts were obtained by CV at different scan rates (40, 60, 80, 100, 120, and 140 mV s⁻¹) due to the proportional relationship between the ECSA and *C_{dl}* (Fig. 6(a)) [3]. The *C_{dl}* value of Ni/Co₃O₄@NC was calculated to be 25.53 mF cm⁻², which is much higher than those of NC (1.81 mF cm⁻²), NiCo@NC (1.78 mF cm⁻²), Co₃O₄@NC (15.28 mF cm⁻²), and Ni@NC (2.70 mF cm⁻²) (Fig. 6(b)). Accordingly, the calculated ECSA values of all the samples are listed in Table S2. Such a high ECSA value of Ni/Co₃O₄@NC implies the existence of additional exposed active sites, which can be ascribed to the strong coupling of Ni/Co₃O₄ with the NC matrix, thus boosting the OER performance. To further reflect the intrinsic activities of all the samples, we calculate their electrocatalytic activities, where the current density is normalized to the ECSA. As is shown in Table S2 and Fig. S10, Ni/Co₃O₄@NC exhibits a higher current density (*j*) at the same overpotential (*η*) compared with other samples, which is consistent with the current density normalized to the geometric area of the electrode, demonstrating the superior performance of the Ni/Co₃O₄@NC hy-

Fig. 5. (a) OER polarization curves of GCE, NC, NiCo@NC, Co₃O₄@NC, Ni@NC, and Ni/Co₃O₄@NC in 1.0 M KOH; (b) Overpotentials at *j* = 10 mA cm⁻² of NiCo@NC, Co₃O₄@NC, Ni@NC, and Ni/Co₃O₄@NC; (c,d) Corresponding Tafel plots.

Fig. 6. (a) CVs of Ni/Co₃O₄@NC with different rates from 40 to 140 mV s⁻¹ in 1.0 M KOH; Double-layer capacitances (b) and Nyquist plots (c) of GCE, NC, NiCo@NC, Co₃O₄@NC, Ni@NC, and Ni/Co₃O₄@NC in 1.0 M KOH; (d) Polarization curves of Ni/Co₃O₄@NC before and after 1000 CV cycles in 1.0 M KOH.

brids.

To elaborate on the intrinsic activities of the catalysts toward the OER, the charge-transfer resistances (R_{ct}) were obtained by fitting the equivalent circuit according to the EIS plots (Fig. 6(c)). Ni/Co₃O₄@NC exhibits a much smaller semicircle compared with other reference catalysts, which implies a considerably small R_{ct} value, indicating an effective electron transfer process between the catalysts and electrolyte, effective Faradic process, and favorable OER kinetics. The heterostructured Ni/Co₃O₄@NC exhibits a highly decreased R_{ct} value compared with Ni@NC or Co₃O₄@NC, which may be related to the better contact among Ni, Co₃O₄, and NC. The metallic Ni combined with Co₃O₄ induces strong synergistic metal-metal electronic interactions between Ni and Co₃O₄, thus accelerating the charge-transfer rate. The charge-transfer rate of the heterostructured Ni/Co₃O₄@NC can be further decreased when coupling Ni/Co₃O₄ with the highly conductive NC materials. Durability is also an important criterion in evaluating the performance toward the OER. Therefore, the stability of Ni/Co₃O₄@NC is tested through continuous CV for 1000 cycles in 1.0 M KOH. As shown in Fig. 6(d), the LSV curve of Ni/Co₃O₄@NC remains nearly unchanged after continuous 1000 cycles. This may be due to the intimate combination among Ni, Co₃O₄, and NC that prevents the agglomeration and corrosion of active species.

4. Conclusions

In summary, Ni/Co₃O₄@NC hybrids were synthesized via a facile impregnation-calcination process. The impregnation of Ni and Co ions ensured the homogeneous distribution of metals and guaranteed the production of well-dispersed Ni and Co₃O₄ nanoparticles by the subsequent *in situ* calcination reaction. The subsequent two-step calcination process constructed synergistic Ni and Co₃O₄ species throughout the carbon nanospheres, which prevented the aggregation and corrosion of the obtained N-doped graphitic carbon and regulated the electronic configuration of the active species. Benefiting from the intimate contact of Ni, Co₃O₄, and NC and the efficient charge transfer among these active OER species, the obtained Ni/Co₃O₄@NC hybrids demonstrated enhanced OER activity with a smaller overpotential of 350 mV to drive a current density of 10 mA cm⁻², lower Tafel slope of 52.27 mV dec⁻¹, smaller charge-transfer resistance, and higher double-layer capacitance of 25.53 mF cm⁻² compared to those of the unary Co₃O₄@NC and Ni@NC metal hybrids. This work proposes a feasible route to design other heteroatom-doped oxides supported on ideal carbon materials to realize high electrocatalytic activities for the OER.

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Graphical Abstract

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Synergistic effect of metallic nickel and cobalt oxides with nitrogen-doped carbon nanospheres for highly efficient oxygen evolution

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Well-defined Ni/Co₃O₄ nanospheres coupled with N-doped carbon hybrids (Ni/Co₃O₄@NC) have been synthesized via a facile impregnation-calcination method, and they exhibit excellent OER activity and stability in alkaline media.

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金属Ni和Co氧化物与N掺杂的碳球协同作用用于电解水析氧反应

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摘要: 电解水制氢被认为是理想的清洁制氢技术,然而,阴阳两极过电位的存在,特别是阳极析氧反应涉及复杂的四电子转移过程,阳极过电位较高,严重制约了电解水制氢效率的提高.因此,研究发现高效且成本低的析氧反应电催化剂具有重要意义.因此,本课题组利用温和的浸渍-热解策略合成了具有高效析氧活性的Ni/Co₃O₄@NC与N掺杂的碳复合电催化剂(Ni/Co₃O₄@NC).其中,第一步浸渍过程将无机Ni与Co源浸渍到聚合物纳米球结构中,可以有效地保证热解过程中产生均匀分散的极细Ni和Co₃O₄纳米颗粒;此外,高温热解过程形成的N掺杂的碳基质可以有效地阻止活性组分的团聚和交联,调控其电子结构.由于Ni, Co₃O₄和NC的协同作用,制备得到的Ni/Co₃O₄@NC电催化剂在碱性溶液中均展现了比由单一金属组成的Co₃O₄@NC和Ni@NC更优异的析氧活性和稳定性,当电流密度为10 mA cm⁻²时,所需要的过电位仅为350 mV, Tafel斜率低至52.27 mV dec⁻¹,电荷转移阻抗极小,双电层电容高达25.53 mF cm⁻².本文采用扫描电镜(SEM),高分辨透射电镜(HRTEM),X射线衍射(XRD)和X射线光电子能谱(XPS)等手段研究了Ni/Co₃O₄@NC电催化剂的微观结构、元素组成和价态,分析了复合Ni/Co₃O₄@NC电催化剂具有优异析氧性能的原因.

SEM结果表明,Ni/Co₃O₄@NC电催化剂在经历浸渍-热解过程后,完整地继承了聚合物的纳米球状形貌,只是平均粒径由100 nm缩聚为90 nm左右,SEM mapping显示各元素均匀分散在每一个纳米球结构中.HRTEM结果显示,紧密耦合的Ni和Co₃O₄超细纳米颗粒均匀分散于纳米球结构中,且碳基质有效地限制了这些颗粒的过度生长及团聚.XRD和XPS结果再次印证Ni/Co₃O₄@NC是由Ni和Co₃O₄两种晶体结构构成,此外,XPS结果显示N原子成功掺杂到碳基质中,富电子的N原子掺杂到碳基质中可以有效地调控Ni/Co₃O₄@NC的电子结构,提高本征电催化活性.相应的催化反应结果表明,Ni/Co₃O₄@NC相较于单一的Co₃O₄@NC和Ni@NC析氧活性更高,这是由于Ni与Co₃O₄协同作用,使Co₃O₄的Co^{2+/3+}氧化还原峰向阳极偏移,从而增加了Co₃O₄的本征活性;此外高导电性的Ni掺杂到Ni/Co₃O₄@NC复合物结构中,提高了催化剂的导电性,加快了电子传输能力;杂原子N的掺杂有效地调控了催化剂的电子结构,提高了催化剂的本征活性.总之,Ni、Co₃O₄和NC的协同作用使Ni/Co₃O₄@NC复合物在碱性溶液中具有高效催化析氧性能.该策略为制备杂原子掺杂的负载于高导电碳载体的氧化物基催化剂提供了有益参考.

关键词: Ni/Co₃O₄@NC; N掺杂的碳; 电催化剂; 协同效应; 析氧反应

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