Ni@RuM (M=Ni or Co) core@shell nanocrystals with high mass activity for overall water-splitting catalysis

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ABSTRACT Developing efficient water-splitting electrocatalysts with high mass activity is in urgent need for large-scale sustainable production of hydrogen but, still remains as a big challenge. Herein, we report a one-pot method to fabricate a series of core@shell Ni@RuM (M=Ni or Co) nanocrystals (NCs) with Ni as the core and tunable RuM (M=Ni or Co) as the alloy shell for efficient water-splitting catalysis. Among these core@shell NCs, the obtained Ni@RuNi NCs exhibit the highest intrinsic activity for hydrogen evolution reaction (HER) and possess an outstanding mass activity of $1590 \text{ mA mg}_{\text{Ru}}^{-1}$ at 0.07 V vs. reversible hydrogen electrode (RHE), which is 1.7 times higher than that of commercial Pt/C ($950 \text{ mA mg}_{\text{Pt}}^{-1}$). As for oxygen evolution reaction (OER), the prepared Ni@Ru_{0.4}Co_{0.6} NCs with optimized shell composition achieve more enhanced mass activity of $270 \text{ mA mg}_{\text{Ru}}^{-1}$ at 1.56 V vs. RHE, approaching three times higher than that of commercial RuO₂ ($89 \text{ mA mg}_{\text{Ru}}^{-1}$). The superb mass activity of these Ni@RuM (M=Ni or Co) NCs can be attributed to their core@shell structure and modulated electronic structure through alloying with Ni or Co metal in the shell.

Keywords: electrocatalysis, ruthenium, core-shell, oxygen evolution reaction, hydrogen evolution reaction

INTRODUCTION

Electrochemical water splitting is considered as the key technology to provide high-purity hydrogen for the next-generation of sustainable global energy system [1–3]. The key to the development of this technique is the exploitation of effective catalysts to improve the slow kinetics of both hydrogen evolution reaction (HER) and

oxygen evolution reaction (OER), thus maximizing the utilization efficiency of electricity [4–7]. Although some progress has been made in respect of non-noble metal catalysts, Pt/C and RuO₂/IrO₂ still outperform most of the reported catalysts for HER and OER, respectively [8–14]. And their wide application is severely hindered by their natural scarcity and high cost [15]. Therefore, how to further improve their catalytic activity, especially the mass activity, is an urgent task.

Compared with Pt and Ir, Ru is much cheaper [16]. Meanwhile, besides water oxidation catalysis, recently Ru-based materials have also been proved to be good candidates for HER with small overpotential and Tafel slope [17–21]. However, their mass activities are still far from satisfactory, preventing their further application [22–24]. The way to enhance the mass activity is optimization of both intrinsic activity and the number of active sites on the surface. From this point of view, the core@shell nanocatalysts with a core of cheap transition metal (such as Ni) surrounded by a thin layer of noble metal as the shell are favorable to realize the above proposals. With such core@shell structure, it can not only maximize the utilization of noble metal, but also regulate the intrinsic activity of the exposed shell by the core induced strain/electronic effect [25–27] or further modulate the shell composition [28–30]. This kind of core@shell structure design has been well developed and becomes a research hotspot in the Pt-based oxygen reduction catalysts [31–34], while few Ru-based core@shell electrocatalysts, especially with high mass activity, have been reported.

In this work, we report a new method to synthesize

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core@shell Ni@RuM (M=Ni or Co) nanocrystals (NCs) featured with Ni as a core and tunable thin Ru-based alloy layer as a class of highly efficient electrocatalysts with high mass activity for HER and OER. Specifically, the core@shell Ni@RuNi NCs display the highest HER specific activity of $12 \text{ mA cm}_{\text{ECSA}}^{-2}$ (ECSA means electrochemically active surface area) at an overpotential of 0.07 V vs. reversible hydrogen electrode (RHE), and yield a high mass activity of $1590 \text{ mA mg}_{\text{Ru}}^{-1}$, almost double the value of commercial Pt/C ($950 \text{ mA mg}_{\text{Pt}}^{-1}$). As for OER, the core@shell Ni@Ru_{0.4}Co_{0.6} NCs exhibit the current density of $2.24 \text{ mA cm}_{\text{geo}}^{-2}$ (geo represents geometric area) at 1.56 V vs. RHE with a very low mass loading of $2 \mu\text{g}_{\text{Ru}} \text{ cm}_{\text{geo}}^{-2}$, six times higher than that of commercial RuO₂ ($0.36 \text{ mA cm}_{\text{geo}}^{-2}$). The greatly enhanced mass activities for HER and OER of these core@shell Ru-based NCs are due to the shell-induced electronic effect through alloying Ru with Ni or Co on the surface, which enhances the Ru atom exposure and meantime boosts the intrinsic activity.

EXPERIMENTAL SECTION

Reagents

Ruthenium(III) acetylacetonate (Ru(acac)₃) was obtained from Alfa Aesar. Nickel(II) acetylacetonate (Ni(acac)₂) and cobalt(II) acetylacetonate (Co(acac)₂) were purchased from Sinopharm Chemical Regent Co., Ltd. Oleylamine (OAm) was bought from Sigma-Aldrich. Hexadecylammonium chloride (CTAC) was taken from Beijing Bai Ling Wei Technology Co., Ltd. The commercial Pt/C (20 wt%) was obtained from Johnson-Matthey company. The ruthenium(IV) oxide (RuO₂) was bought from Sigma-Aldrich. All chemicals were used as received and water was purified by a Millipore system.

Synthesis of Ni@RuNi NCs

In a typical process, Ru(acac)₃ (8 mg), Ni(acac)₂ (5 mg) and CTAC (20 mg) were mixed with 5 mL OAm into a vial and then ultrasonicated for 30 min. The homogeneous solution was heated to 250°C and kept for 3 h in oil bath. Thereafter, the mixture was cooled down to room temperature naturally and the products were centrifuged by cyclohexane. Finally, the resultants were washed three times by cyclohexane, then dispersed in cyclohexane for further use. Ni@Ru_xCo_y NCs with different feeding ratios were prepared by similar procedure.

Characterizations

Transmission electron microscopy (TEM) and high-re-

solution TEM (HRTEM) measurements were conducted on a Tecani-G2 T20 and F20 operated at 200 kV. Powder X-ray diffraction (XRD) spectra were collected on a X'Pert-Pro MPD diffractometer (Netherlands PAN analytical) with Cu K α X-ray radiation. The X-ray photoelectron spectroscopy (XPS) profiles were taken on an ESCALAB-MKII 250 photoelectron spectrometer (VG Co. UK) with Al K α radiation. The concentrations of catalysts ink were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES).

Electrochemical measurements

Electrochemical tests were carried out on an electrochemical workstation (CHI660E, Shanghai, China) based on a classical three-electrode system. The Ag/AgCl electrode and a graphite rod were used as the reference electrode and the counter electrode, respectively. The glassy carbon (GC, 5 mm) disk electrode loaded with the catalysts ink was applied as the working electrode. The catalysts ink (1 mg mL^{-1}) was prepared by sonicating the mixture of catalyst, H₂O, isopropanol and 5 wt% Nafion (volume ratio=3:1:0.08) until a homogeneous dispersion was obtained. Then, 10 μL of the ink was dropped on the GC electrode and dried at room temperature naturally. The loading amount was about $0.4 \mu\text{g}_{\text{Ru}}$ for each catalyst, which was determined by ICP-AES. The commercial Pt/C and RuO₂ with similar loadings as Ni@RuNi NCs and Ni@Ru_{0.4}Co_{0.6} NCs were also measured for better comparison, respectively. HER and OER of various catalysts were conducted in nitrogen and oxygen-saturated 0.1 mol L^{-1} KOH electrolyte with the scan rate of 5 mV s^{-1} , respectively. For stability test, the catalysts ink was deposited on the carbon fiber paper, and then dried naturally to carry out the chronopotentiometry measurement. To determine the ECSA of catalysts, the copper underpotential deposition (Cu_{upd}) method was utilized, which has been widely applied to measure the ECSA of Ru-based catalysts. Specifically, cyclic voltammetry (CV) was performed in nitrogen-saturated 0.25 mol L^{-1} H₂SO₄ and 0.25 mol L^{-1} H₂SO₄ + 10 mmol L^{-1} CuSO₄ with potential range between 0.3 and 0.7 V vs. RHE. Therefore, the Cu_{upd} stripping charge (Q_{Cu}) associated with active Ru sites could be obtained by integrating the close part of two curves. Provided that $420 \mu\text{C cm}^{-2}$ was needed to form saturated Cu_{upd} monolayer on active sites, then the ECSA could be calculated as follow:

$$\text{ECSA}_{(\text{cm}^2)} = \frac{Q_{\text{Cu}}}{M_{\text{metal}} \times 420 \mu\text{C cm}^{-2}},$$

where M_{metal} was mass of metal loaded on the working electrode.

RESULTS AND DISCUSSION

The core@shell Ni@RuNi NCs were prepared by a simple colloidal-chemical approach, using $\text{Ru}(\text{acac})_3$ and $\text{Ni}(\text{acac})_2$ as the metal precursors, OAm and CTAC as the solvent and surfactant, respectively (details in the experimental section). The morphology of the Ni@RuNi NCs was firstly characterized by TEM, in which they were relatively regular polyhedron with an average size of 20 nm (Fig. 1a and Fig. S1). Powder XRD (PXRD) measurement verifies the co-existence of Ru and Ni crystal-line phase in the Ni@RuNi NCs (Fig. 1b).

The strong peaks of 44.6° and 51.9° match well with the (111) and (200) plane of Ni phase (JCPDS No. 70-0989), respectively, while the weak peak of 41.5° is located between the aforementioned Ni phase and Ru phase (JCPDS No. 88-2333), indicating the existence of RuNi alloy. TEM energy dispersive X-ray spectroscopy (EDS) element mapping (Fig. 1c) and line-scanning (Fig. 1d) show that the prepared Ni@RuNi NCs have a Ni core and Ru-rich shell with obviously disparate element distribution, further indicating the core@shell structure of Ni@RuNi NCs. Two enlarged HRTEM images (Fig. 1e) display clear

Figure 1 (a) TEM image and (b) XRD pattern of the obtained Ni@RuNi NCs. (c) The high-angle annular dark field-scanning TEM (HAADF-STEM) element mapping and (d) the corresponding EDS line scan profile of the prepared Ni@RuNi NCs. (e) HRTEM image and (f) EDS profile of the synthesized Ni@RuNi NCs.

lattice distance of 2.1 Å in the center and edge region of the obtained Ni@RuNi NCs, respectively. This lattice distance is between that of the (111) plane of Ru phase (2.2 Å) and Ni phase (2.0 Å), another evidence of the formation of RuNi alloy on the surface. Additionally, the atomic ratio of Ru:Ni is about 2:8 according to the result of EDS spectrum (Fig. 1f).

Furthermore, the resultant shell composition of the synthesized Ni@RuNi NCs above can be altered from RuNi to RuCo alloys simply by adding a specific amount of Co(acac)₃ as Co source into the reaction system. A class of core@shell Ni@Ru_xCo_y NCs was prepared through a similar procedure with various molar ratios (Figs S2 and S3). When the feeding molar ratio of Co and Ni source was 3:1, the core@shell Ni@Ru_{0.4}Co_{0.6} NCs were obtained. The typical morphology of Ni@Ru_{0.4}Co_{0.6} NCs is shown in Fig. 2a and Fig. S4. The corresponding HRTEM image (Fig. 2b) reveals the clear crystal lattice with *d*-spacing of 2.1 Å, which is between those of the

(111) plane of Ru phase (2.2 Å), Ni phase (2.0 Å) and Co phase (2.0 Å, JCPDS No. 88-2325). This explains the Ru alloy structure on the surface of Ni@Ru_{0.4}Co_{0.6} NCs. The formation of Ni@Ru_{0.4}Co_{0.6} NCs was also verified by the PXRD pattern (Fig. 2c, up), in which the peak of 44.6° is indexed to (111) plane of the Ni phase (JCPDS No. 70-0989), and the shoulder peak around 43° lies between the (111) planes of the Ru phase (JCPDS No. 88-2333) and Ni/Co phase. These imply that Ru-based alloy was formed during the reaction process. By the way, the real atomic ratio of Ru:Ni:Co is 2:7:3 based on the EDS profile (Fig. 2c, down). To further analyze the composition of the alloy shell, the EDS element line-scanning (Fig. 2d) was carried out. It reveals that the shell consists of RuCo alloy with Ni as a core, re-confirming the core@shell Ni@Ru_{0.4}Co_{0.6} structure. In order to further confirm the formation of the alloy shell, the etching of Ni core was carried out by Fe³⁺, as illustrated by the TEM image (Fig. S5a, S5c), and then characterized by XRD. The peak

Figure 2 (a) TEM and (b) HRTEM images of Ni@Ru_{0.4}Co_{0.6} NCs. (c) XRD pattern (up) and EDS profile (down) of the obtained Ni@Ru_{0.4}Co_{0.6} NCs. (d) The EDS line scan profile of Ni@Ru_{0.4}Co_{0.6} NCs.

of Ni core disappears, and only one diffraction peak assigned to alloy can be observed in the XRD pattern, which is a strong evidence for the formation of the alloy shell (Fig. S5b, S5d).

Moreover, the surface chemical states of the Ni@Ru_{0.4}Co_{0.6} NCs and Ni@RuNi NCs were studied by XPS (Fig. 3). In Ru 3p spectrum (Fig. 3a), two pairs of adjacent peaks centered at 462 and 484 eV are attributed to Ru 3p_{3/2} and 3p_{1/2} of metallic Ru(0) and Ru⁴⁺, respectively [22,35]. Compared with the commercial Ru/C (as reference), the Ru(0) peak of Ni@RuNi NCs and Ni@Ru_{0.4}Co_{0.6} NCs all exhibit positive shifts, which is attributed to modified electron structure of Ru in these core-shell alloy NCs owing to the ligand or strain effect [19,36]. In this way, the hydrogen binding energy on Ru sites might be weakened because of the presence of higher valence states for Ru sites in Ni@RuNi NCs, which is beneficial to its HER activity [37]. In addition, we also observe that the ratio of Ru⁴⁺/Ru(0) in Ni@Ru_{0.4}Co_{0.6} NCs (0.57) is much larger than in Ni@RuNi NCs (0.48), and the higher ratio of Ru⁴⁺/Ru(0) is favorable for OER process. By the way, the XPS spectra of both Ni 2p (Fig. 3b) and Co 2p (Fig. 3c) also confirm their existence in the corresponding products.

Before the electrochemical measurement, in order to ensure the cleanness of our synthesized Ru-based NCs' surface, the resulting NCs were first deposited onto carbon black by sonication, and then treated with acetic acid to remove the residual OAm. Thereafter, the ECSA of these Ni@RuM (M=Ni or Co) catalysts were firstly tested by a well-established Cu_{upd} method, which had been applied for Ru-based catalysts successfully before [32]. The prepared catalyst ink was dropped onto the GC electrode (0.196 cm²) and dried naturally to conduct the CV test (Fig. S6). The anodic peak near 0.4 V vs. RHE was associated with the strip of deposited Cu, which matched well

with previous reports [33,34]. According to the Cu stripping charge (Q_{Cu}) and the charge needed for the formation of saturated Cu_{upd} monolayer (420 $\mu\text{C cm}^{-2}$), the ECSAs of Ru-based catalysts that we prepared were obtained and summarized in Table S1. Then the HER specific activity normalized by ECSA of the as-prepared core@shell Ni@RuM (M=Ni or Co) catalysts in 0.1 mol L⁻¹ KOH was examined. As shown in Fig. 4a, the specific activity of the various Ru-based catalysts follows the order of Ni@RuNi NCs > Ni@Ru_{0.6}Co_{0.4} NCs $\approx$ Ni@Ru_{0.4}Co_{0.6} NCs > Ni@Ru_{0.8}Co_{0.2} NCs. Besides, the best-performing Ni@RuNi NCs exhibit better specific activity than commercial Pt/C (Fig. S7). To provide more intuitive comparison, the histogram of specific activity of various catalysts at the overpotential of 70 mV vs. RHE is given in Fig. 4b. Obviously, the core@shell Ni@RuNi NCs display the outstanding specific activity of 11.96 mA cm⁻², which is higher than those of other core@shell Ru-based NCs catalysts under the same condition. In order to further reflect the advantage of Ni@RuNi NCs as HER catalysts in basic media. We compare the polarization curves of the core@shell Ni@RuNi NCs and the commercial Pt/C normalized by the geometric area with a very low loading mass (2 $\mu\text{g}_{\text{Ru or Pt cm}^{-2}}$). The obtained Ni@RuNi NCs exhibit better performance than the commercial Pt/C in such case (Fig. 4c). As shown in Fig. 4d, the mass activity of Ni@RuNi NCs is 1590 mA mg_{Ru}⁻¹, which is 1.7 times as much as that of commercial Pt/C (950 mA mg_{Pt}⁻¹) at the overpotential of 70 mV vs. RHE, representing the best level of other Ru-based catalysts reported yet (Table S2). The mass activity of the Ni@RuNi NCs for HER is ascribed to the favorable core@shell structure. The thin RuNi alloy layer not only reduces the usage of Ru, but also modulates the electronic structure, which is beneficial to the HER electrocatalysis [19,38,39].

Figure 3 XPS spectra of (a) Ru of the obtained Ni@RuNi NCs, Ni@Ru_{0.4}Co_{0.6} NCs and commercial Ru/C. (b) The XPS spectra of Ni of the resulting Ni@RuNi NCs and Ni@Ru_{0.4}Co_{0.6} NCs. (c) The XPS spectra of Co of the as-prepared Ni@Ru_{0.4}Co_{0.6} NCs.

Figure 4 (a) The specific activity for HER normalized by ECSA in 0.1 mol L⁻¹ KOH. (b) The current density of various catalysts normalized by ECSA at the overpotential of 70 mV vs. RHE. (c) Polarization curves of Ni@RuNi NCs and commercial Pt/C normalized by geometric area at low loading mass. (d) The corresponding mass activity of Ni@RuNi NCs and commercial Pt/C at the overpotential of 70 mV vs. RHE. (e) Polarization curves of Ni@RuNi NCs before and after 500 CV cycles. (f) Chronoamperometric measurement of the obtained Ni@RuNi NCs.

Furthermore, the stability of the Ni@RuNi NCs was checked by accelerated durability test (ADT) and chronoamperometry measurement. Fig. 4e displays the polarization curves of the Ni@RuNi NCs before and after 500 CV cycles. The ADTs only lead to an increase of 8 mV in η_{10} , implying the excellent durability of the Ni@RuNi NCs. In chronoamperometry measurement, the Ni@RuNi NCs can maintain constant current density for 12 h (Fig. 4f). In addition, no aggregation is observed for Ni@RuNi NCs (Fig. S8), revealing they are still dispersible after the stability test. The faradaic efficiency of Ni@RuNi NCs for HER is calculated to be 96% (Fig. S9), reflecting that H₂ production plays a dominant role in the electron transfer process.

Besides the excellent HER catalytic performance, the Ni@RuM (M=Ni or Co) NCs also display high specific activity and stability for OER in 0.1 mol L⁻¹ KOH. Fig. 5a shows the specific activity of our Ru-based NCs catalysts for OER, in which Ni@Ru_{0.4}Co_{0.6} NCs exhibit the highest specific activity. At the overpotential of 330 mV vs. RHE, the specific activity of the Ni@Ru_{0.4}Co_{0.6} NCs can reach 4.3 mA cm⁻² ECSA, which is two or three times larger than other samples (Fig. 5b). Fig. 5c presents the polarization curves of the Ni@Ru_{0.4}Co_{0.6} NCs and commercial RuO₂ normalized by the geometric area. The obtained Ni@Ru_{0.4}Co_{0.6} NCs exceed the commercial RuO₂ with the

same low loading mass of 4 μg_{Ru} cm⁻². Furthermore, their mass activity was calculated (Fig. 5d) based on the results of ICP-AES and the polarization curves. As is shown, the mass activity of the Ni@Ru_{0.4}Co_{0.6} NCs (270 mA mg_{Ru}⁻¹) is three times as much as that of commercial RuO₂ (89 mA mg_{Ru}⁻¹). The unique Ni@Ru_{0.4}Co_{0.6} structure may be responsible for the high mass activity and the oxidation of Ru can be promoted by alloying with Co, as confirmed by XPS, thus boosting the OER performance. Table S3 in the Supplementary information summarizes the mass activity of some reported Ru-based catalysts for OER for better comparison. To evaluate the stability of the Ni@Ru_{0.4}Co_{0.6} NCs, the ADTs were carried out over the potential window from 1.3 to 1.5 V vs. RHE for 500 cycles. The catalytic performance does not show obvious decay after ADTs (Fig. 5e), suggesting the superior durability of the Ni@Ru_{0.4}Co_{0.6} NCs, which is also verified by the chronoamperometry measurement (Fig. 5f). Similarly, the morphology of the Ni@Ru_{0.4}Co_{0.6} NCs catalysts after the OER stability test was characterized by TEM (Fig. S10). They keep good dispersibility during the measurement. Moreover, the Ni@Ru_{0.4}Co_{0.6} NCs exhibit Faradaic efficiency of 92% (Fig. S11), which means O₂ is the main product during the electrocatalysis. In addition, the stability of the other three kinds of Ru-based catalysts including Ni@RuNi NCs, Ni@Ru_{0.6}Co_{0.4} NCs and

Figure 5 (a) The specific activity for OER normalized by ECSA in 0.1 mol L⁻¹ KOH. (b) The current density of various catalysts normalized by ECSA at the overpotential of 330 mV vs. RHE. (c) Polarization curves of Ni@Ru_{0.4}Co_{0.6} NCs and commercial RuO₂ normalized by geometric area at low loading mass. (d) The corresponding mass activity of Ni@Ru_{0.4}Co_{0.6} NCs and commercial RuO₂ at the overpotential of 330 mV vs. RHE. (e) Polarization curves of Ni@Ru_{0.4}Co_{0.6} NCs before and after 500 CV cycles. (f) Chronoamperometric measurement of the obtained Ni@Ru_{0.4}Co_{0.6} NCs.

Ni@Ru_{0.8}Co_{0.2} NCs for OER was also tested (Fig. S12). The current density can remain constant with slight fluctuation in the same operating environment. Similarly, the morphologies of the aforementioned catalysts after the OER stability test were characterized by TEM (Fig. S13), and they were able to keep the good dispersibility. Based on the experimental results above, we fabricated an alkaline water electrolyzer using Ni@Ru_{0.4}Co_{0.6} NCs as anode and Ni@RuNi NCs as cathode, respectively. Fig. S14a exhibits the polarization curve of water splitting in aqueous 0.1 mol L⁻¹ KOH, which can afford a current density of 10 mA cm⁻² at voltage of 1.69 V. Moreover, the electrolyzer is able to maintain constant current density for more than 15 h without detectable decline (Fig. S14b), showing its promise for alkaline overall water splitting.

CONCLUSIONS

To summarize, we demonstrate a facile wet-chemical strategy to prepare a new class of Ni@RuM electrocatalysts for effective HER and OER in alkaline condition. They feature with high Ru atom utilization and the modulated electronic structure *via* adjusting thin Ru alloy shell, making them exhibit much enhanced specific and mass activities for HER and OER catalysis. At the over-

potential of 70 mV vs. RHE, the core@shell Ni@RuNi NCs show a remarkable HER specific activity of 12 mA cm⁻² and mass activity of 1590 mA mg⁻¹ (twice higher than that of the commercial Pt/C). Meanwhile, the mass activity of the core-shell Ni@Ru_{0.4}Co_{0.6} NCs for OER is about 270 mA mg⁻¹ at the overpotential of 330 mV vs. RHE, almost three times higher than the commercial RuO₂. This work highlights the high mass activity of Ru-based electrocatalysts achieved by introducing core@shell nanostructure with regulable shell construction.

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高质量活性的Ni@RuM (M=Ni or Co)核壳@纳米晶用于催化水分解

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摘要 发展一种高质量活性的高效水分解催化剂对于实现大规模制氢来说至关重要,但目前这仍是一个巨大的挑战. 我们报道了简便的一锅法来合成一系列核壳Ni@RuM (M=Ni or Co)纳米晶(NCs),并将其用于高效催化水分解,该系列催化剂均以金属Ni为核,壳层则是组分可调控的RuM (M=Ni or Co)合金. 在这些催化剂中, Ni@RuNi NCs对催化产氢表现出优异的性能,在过电位为0.7 V(vs. RHE)时,其质量活性高达1590 mA mg_{Ru}⁻¹,是同等条件下商业Pt/C的1.7倍(950 mA mg_{Pt}⁻¹). 而对于产氧反应来说,质量活性最高的则是Ni@Ru_{0.4}Co_{0.6} NCs,在电位为1.56 V vs. RHE时,其质量活性达270 mA mg_{Ru}⁻¹,远远超过了商业RuO₂(89 mA mg_{Ru}⁻¹). 这些催化剂优异的质量活性归因于它们的核壳结构,壳层中金属Ru通过与金属Ni或者Co形成合金来调控自身的电子结构,使其更有利于产氢/氧反应的进行.