Electronic Communication between Co and Ru Sites Decorated on Nitrogen-doped Carbon Nanotubes Boost the Alkaline Hydrogen Evolution Reaction

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Abstract: Designing highly efficient Pt-free electrocatalysts with low overpotential for the alkaline hydrogen evolution reaction (HER) remains a significant challenge. Here, a novel and efficient Co, Ru bimetallic electrocatalyst composed by CoRu nanoalloy decorated on the N-doped carbon nanotubes (N-CNTs), deriving from the fullerenol and melamine via hydrothermal treatment followed by pyrolysis. Benefiting from the electronic communication between Co and Ru sites, the as-obtained CoRu@N-CNTs exhibited superior electrocatalytic HER activity. To deliver a current density of 10 mA cm⁻², it required an overpotential of merely 19 mV along with a Tafel slope of 26.19 mV dec⁻¹ in 1 M KOH, outperforming the benchmark Pt/C catalyst. The present work would pave a new way for the design and construction of efficient electrocatalyst for energy storage and conversion.

1. Introduction

A viable approach to addressing both the direct energy deficit and the greenhouse effect is electrocatalytic water splitting, which is a significant way to manufacture hydrogen (H₂) on a big scale and at a low cost [1-6]. In the overall water splitting process, the electrochemical hydrogen evolution reaction (HER) presents an alluring approach to producing H₂ as one of the most promising substitutes for traditional fossil fuels [7-9].

Currently, noble metal Pt and/or Pt-based catalysts are extensively utilized as electrocatalysts for HER. Nevertheless, their exorbitant expense and restricted accessibility impede their widespread practical application [10-13]. Therefore, a formidable task is to find effective Pt-free electrocatalysts for HER.

Ru, the most inexpensive noble metal, has emerged as the preferred substitute for Pt due to its medium-strength bond with hydrogen (about 65 kcal mol⁻¹) and its cost, which is only one-third of Pt. The inherent activity of Ru for alkaline HER is, however, greatly diminished by its restricted capacity to adsorb and dissociate H₂O [14-17]. There are two primary factors that contribute to the enhancement of catalytic activity for Ru: (1) increasing the number of attainable active sites, which can be achieved by enlarging the specific surface area of the catalyst materials [18-22]. Generally, dispersing noble-metals on supports with high surface areas is an attractive approach to increase the number of active sites and then improve the catalytic activity [23]. (2) Improving the intrinsic activity, which is commonly accomplished by complicated structure/composition hybridization and electronic property tuning [13, 24-26]. The chemical and electrical characteristics of Ru can be readily changed by heteroatom bond formation, improving its suitability for electrocatalytic HER [27-29]. Recently, a great deal of research has been done on diatomic catalysts (DAC), which combine to increase intrinsic activity by controlling the adsorption and desorption capacities of various metals [30-33]. The adsorption capability of the catalyst on active sites can be greatly enhanced by the action of neighboring metal atoms in DAC on the surrounding electronic environment [34, 35].

Herein, a novel and efficient Co, Ru bimetallic electrocatalyst composed by CoRu nanoalloy decorated on the N-doped carbon nanotubes (N-CNTs), deriving from the fullerenol (C₆₀(OH)₃) and melamine via hydrothermal treatment followed by pyrolysis. The presence of Co catalyzed fullerenol and melamine into N-CNTs, which could serve as electron collector. Benefiting from the strong electronic communication between Co and Ru moiety, the as-obtained CoRu@N-CNTs exhibited outperforming electrocatalytic HER activity. To deliver a current density of 10 mA cm⁻², it required an overpotential of merely 19 mV along with a Tafel slope of 26.19 mV dec⁻¹ in 1 M KOH. The present work provided a new clue for design and construction of efficient HER electrocatalyst.

2. Experimental Section

2.1. Materials
Cobalt(II) chloride (CoCl₂), ethanol (EtOH, CH₃CH₂OH) isopropyl alcohol (IPA, C₃H₇OH) were purchased from Sinopharm Chemical Reagent Co., Ltd. Ruthenium (III) chloride anhydrous (RuCl₃), platinum on activated carbon (20 wt% Pt/C), Nafion solution (5%) and potassium hydroxide (KOH, 1.0 M) were purchased from Sigma-Aldrich, deionized (DI) water (resistivity: ≥18.25 MΩ cm) was provided by an ultrapure water system (ULUPURE, UPDR-I-10 T). All the chemicals are analytical grade and used directly without further treatment.

2.2. Synthesis of CoRu@N-CNTs

The preparation procedure of CoRu@N-CNTs was schematically illustrated in Scheme 1. Briefly, 1.2 g of melamine, 150 mg of Co₃(BOH)₃, 0.5 mmol of CoCl₂ and 0.5 mmol of RuCl₃ were dissolved into 70 ml of deionized water. The mixture solution was then transferred to a stainless-steel capped Teflon autoclave. After hydrothermal treatment at 150 °C for 24 h, the solid precursor of CoRu@N-CNTs was obtained by extraction filtration. Then the obtained powder was carbonized in a tube furnace under Ar/H₂ (5%) flow for 3 h at 600 °C with a raising rate of 5 °C min⁻¹. After cooling naturally to the room temperature, the CoRu@N-CNTs was successfully prepared.

For comparison, CoRu@NC, Co@N-CNTs and Ru@NC were also prepared following a similar procedure to CoRu@N-CNTs except in the absence of Co₃(BOH)₃, RuCl₃ and CoCl₂ respectively. For detail, please see in the Supporting Information.

3. Results and Discussion

3.1. Structural characterization of CoRu@N-CNTs

The synthesis route of CoRu@N-CNTs is schematically illustrated in Scheme 1. During the hydrothermal process, the as-formed CoRu nanoparticles were grafted on the surface of fullerol, which was subsequently cracked into pieces of bowl-like carbon fragments and emerged to N-doped CNTs in the presence of melamine in the following annealing step [39]. From the SEM and TEM images shown in Fig. 1a and 1b, it can be found a plenty of CNTs decorated with metal nanoparticles. To further clarify the structure of CoRu@N-CNTs, high-resolution TEM (HRTEM) images were collected as displayed in Fig. 1c. Clearly, the CoRu nanoparticles were distributed both on the surface and inner wall of CNTs. The crystal lattice fringe of 0.223 nm (Fig. 1d) and 0.207 nm (Fig. 1e) could be assigned to the (100) and (111) facets of CoRu alloy, respectively [40]. While in the absence of Co₃(BOH)₃, the CoRu nanoparticles were embedded on the planar N-doped carbon matrix in CoRu@NC (Fig. S1). As for Co@N-CNTs, the Co nanoparticles were mainly entrapped inside the CNTs (Fig. S2). Whereas in the absence of Co precursor, Co₃(BOH)₃, and melamine were difficult to transform to CNTs [23], resulting in a N-doped carbon substrate decorated with Ru nanoparticles in Ru@NC (Fig. S3). Therefore, it was Co that catalytically promote the Co₃(BOH)₃ together with melamine to generate N-doped CNTs in CoRu@N-CNTs. In this case, Co nanoparticles were in a large proportion encapsulated inside the CNTs while Ru was decorated on the surface of CNTs, as demonstrated by the energy dispersive X-ray spectroscopy (EDS) mapping of CoRu@N-CNTs (Fig. 1f).

As a result, CNTs served as electron collector that accelerate the charge communication between the inner Co and outer Ru to boost the HER activity.
The crystal phase structure of CoRu@N-CNTs was then investigated by XRD. As can be seen from Fig. 2a, the diffraction peaks at 44.2°, 51.5° and 75.8° for Co@N-CNTs can be well indexed to the (111), (200) and (220) facets of Co with a face-centered cubic crystal structure (PDF #15-0806) [40], respectively. And the peaks at 38.4°, 42.2° and 44.0° in Ru@NC were attributed to the (110), (002) and (101) crystal lattices of hexagonal Ru (PDF#06-0663) [36], respectively. Fascinatingly, only a broadened peak around 44.0° assigned to the CoRu alloy (PDF#65-8975) with a slight upshift relative to Co@N-CNTs and Ru@NC was observed for CoRu@N-CNTs, probably owing to the strong electronic communication between Co and Ru within the catalyst. Similar situation was also presented in CoRu@NC. Besides, the broad signal around 26° could be assigned to the graphitic carbon. Raman spectroscopy was also conducted to further explore the microstructure of CoRu@N-CNTs. As displayed in Fig. 2b, the D band (1345 cm⁻¹) and G band (1586 cm⁻¹) can be observed apparently [41], indicating the coexistence of disordered and graphitic carbon in the substrate. The integrated intensity ratio (I_D/I_G) were determined to be 1.08, 0.85, 0.98, 0.87 for CoRu@N-CNTs, CoRu@NC, Co@N-CNTs and Ru@NC respectively, indicative of a higher degree of defects in CoRu@N-CNTs.
XPS was employed to examine the chemical states and surface element distribution of the samples. In line with the EDS results, the survey spectra demonstrated the existence of C, N, O, Co, and Ru elements in CoRu@N-CNTs (Fig. S4 and Table S1). The lack of Cl element excluded the contribution to electrochemical process (Fig. S5). The high-resolution spectra of Co 2p was displayed in Fig. 3a. Two peaks, corresponding to Co 2p$_{3/2}$ and Co 2p$_{1/2}$ of metallic Co (Co$^0$), at 778.67 eV and 793.79 eV were observed in the spectrum of CoRu@N-CNTs. While the Co$^{2+}$ is responsible for the peaks at 781.21 eV (Co 2p$_{3/2}$) and 796.73 eV (Co 2p$_{1/2}$), and the set of peaks at 802.6 eV and 785.55 eV are satellite peaks [42, 43]. Fig. 3b displayed the high-resolution spectrum of Ru 3p. Two distinct peak groups were visible for CoRu@N-CNTs. The peaks located at 461.87 eV and 484.27 eV could be assigned to the 3p$_{3/2}$ and 3p$_{1/2}$ of Ru, corresponding to metallic Ru. While another set of peaks at 464.81 eV and 487.21 eV were responsible for oxidized Ru species [44, 45]. It is worth noting that the Co 2p peaks in CoRu@N-CNTs upsifted to the high binding energy meanwhile the Ru 3p downshifted compared with those of the Co@N-CNTs and Ru@NC counterparts, indicating a charge transfer occurred between Co and Ru in CoRu@N-CNTs, which was beneficial for the electrochemical reactions. The high-resolution N 1s spectrum of CoRu@N-CNTs could be deconvoluted into five parts (Fig. 3c), including the pyridinic N (398.56 eV), metallic N (399.3 eV), pyrrolic N (400.00 eV), graphitic N (401.14 eV) and oxidized N (402.5 eV) [38, 46]. The presence of M-N (M = Co, Ru) species suggested that N doped in the carbon nanotubes could anchor metal atoms, favoring the formation of diatomic sites. Notably, the pyridinic N can serve as active sites to promote the electrocatalytic HER process [47, 48].

3.2. Electrocatalytic performance for CoRu@N-CNTs

To evaluate the electrocatalytic performance of CoRu@N-CNTs, HER measurements were conducted in Ar-saturated 1 M KOH with a typical three-electrode system. For comparison, CoRu@NC, Co@N-CNTs, Ru@NC and commercial Pt/C were selected as references. To be accurate, the reference electrode was calibrated against RHE in H$_2$-saturated 1 M KOH media before all the tests (Fig. S6). Firstly, the HER activity was assessed using linear sweep voltammetry (LSV) with 85% iR-corrections. As shown in Fig. 4a, the CoRu@N-CNTs exhibited an outstanding electrocatalytic activity among all the samples. To achieve a current density of 10 mA cm$^{-2}$, the CoRu@N-CNTs merely required an overpotential ($\eta_{10}$) of 19 mV, much superior to CoRu@NC (45 mV), Ru@NC (39 mV), Co@N-CNTs (219 mV) and even the commercial benchmark 20% Pt/C (55 mV). The HER kinetics was then assessed by Tafel plot shown in Fig. 4b. Particularly, the CoRu@N-CNTs displayed a Tafel slope of 26.19 mV dec$^{-1}$, much smaller than that of CoRu@NC (65.84 mV dec$^{-1}$), Ru@NC (62.41 mV dec$^{-1}$), Co@N-CNTs (174.08 mV dec$^{-1}$), and the commercial benchmark 20% Pt/C (94.16 mV dec$^{-1}$), indicating a favorable electrochemical reaction kinetics of CoRu@N-CNTs [40, 46]. The small Tafel slope of CoRu@N-CNTs suggested that the rate-limiting step is the recombination of chemical adsorbed hydrogen and the HER over the catalysts follow the Volmer-Tafel mechanism [49, 50]. The histograms depicted in Fig. 4c demonstrated the superior catalytic activity of CoRu@N-CNTs and its faster reaction kinetics for the HER. In addition, the charge transfer kinetics of CoRu@N-CNTs, CoRu@NC, Ru@NC, Co@N-CNTs and the commercial benchmark 20% Pt/C were investigated by EIS measurement (Fig. 4d). The charge transfer resistance ($R_{ct}$) obtained from the semicircle in the low-frequency region of the Nyquist plot is related to the electrocatalytic kinetics at the interface between the electrocatalyst and electrolyte, and a smaller value corresponds to a faster electron transfer. Compared to CoRu@NC ($R_{ct} = 12.51$ $\Omega$), Co@N-CNTs ($R_{ct} = 28.22$ $\Omega$), Ru@NC ($R_{ct} = 11.15$) and Pt/C ($R_{ct} = 25.18$), CoRu@N-CNTs possessed the smallest $R_{ct}$ value of 7.24 $\Omega$, indicative of the fastest reaction rate. To unravel the intrinsic activity of CoRu@N-CNTs, the $C_{dl}$ were obtained by scanning CV curves in the non-faradic region (Fig. S7), which is positively proportional to ECSA [21, 27]. As shown in Fig. 4e, CoRu@N-CNTs delivers a significantly larger $C_{dl}$ value (103.9 mF cm$^{-2}$).
than that of CoRu@NC (49.8 mF cm$^{-2}$), Ru@NC (94.2 mF cm$^{-2}$), Co@N-CNTs (75.1 mF cm$^{-2}$) and Pt/C (10.2 mF cm$^{-2}$). Moreover, the ECSA-normalized LSV further confirmed the excellent intrinsic activity of CoRu@N-CNTs (Fig. S8). To further evaluate the long-term stability of the CoRu@N-CNTs, the chronopotentiometry were also conducted as shown in Fig. 4f. It can be seen that the current density remains almost unchanged after 50 h at the current density of 15 mA cm$^{-2}$. In addition, the LSV curve after continuously scanning by CV for 2000 cycles displayed negligible decay (inset of Fig. 4f). Besides, the HER performance of CoRu@N-CNTs surpassed most of the recently reported Co/Ru-based HER electrocatalysts (Fig. 4g and Table S2).

**Figure 4.** Electrochemical HER performance in 1.0 M KOH. (a) The LSV curves, (b) Tafel plots, (c) the histograms of overpotential and Tafel slopes, (d) Nyquist plot and (e) current density difference against scan rate of CoRu@N-CNTs, CoRu@NC, Ru@NC, Co@N-CNTs and the commercial benchmark 20% Pt/C. (f) Long-term chronopotentiometric test of CoRu@N-CNTs, inset showing the LSV curves of CoRu@N-CNTs before (solid) and after (dashed) 2000 CV cycles. (g) Performance comparison of CoRu@N-CNTs with recently-reported Co/Ru-based HER electrocatalysts in 1.0 M KOH.

**4. Conclusion**

In summary, a Co and Ru bimetallic electrocatalyst consisting of CoRu nanoalloy uniformly distributed on N-CNTs, were successfully prepared through hydrothermal reaction of Ru$^3+$, Cu(OH)$_2$ and melamine in the presence of Co$^2+$. The as-obtained CoRu@N-CNTs exhibited superior electrocatalytic HER activity in alkaline condition, i.e., it only needed an overpotential 19 mV to reach a current density of 10 mA cm$^{-2}$, with a Tafel slope of 26.19 mV dec$^{-1}$ in 1 M KOH and long-term durability. The enhanced electrocatalytic HER performance of CoRu@N-CNTs could be attributed to the following aspects: (1) The electronic communication between Ru and Co sites induced a synergistically electrocatalytic effect, and thus improving the charge distribution of CoRu@N-CNTs, which in turn facilitates the electrocatalytic HER process; (2) The N-CNTs not only served as electron collector, accelerating the charge transfer between the catalyst and electrolyte, but also provide a tubular channel, which is beneficial to the mass and charge transportation; (3) The synergistic electronic metal-support interaction (EMSI) between the pyridinic N and CoRu bimetallic sites improved the electronic structure of CoRu@N-CNTs, thus boosting the electrocatalyst HER performance. This work provides a new idea for the design and construction of novel and efficient electrocatalysts in the field of energy storage and conversion.

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References


氮掺杂碳纳米管上 Co 和 Ru 位点之间的电子通信促进碱性析氢反应

高梦婷 a#, 卫莹 a#, 霍雪萌 a, 朱文洁 a, 刘菁菁 a, 强晋源 a, 刘婉婉 a, 王颖 a, 李旭 a, 黄剑锋 a, 冯永强 a*

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摘要：碱性电解水析氢反应(HER)作为获取绿色氢能源的重要途径具有广泛的研究意义和应用价值，但其缓慢的电极反应动力学及较高的过电位需要高效稳定的催化剂来加速反应过程。目前商用的铂(Pt)基催化剂因高昂的成本限制了其规模化应用。设计高效、低过电位的非 Pt 电催化剂仍然是一个重大挑战。钌(Ru)基催化剂因具有类似 Pt 的活性氢结合能而受到广泛关注。本文以富勒醇和三聚氰胺为基体原料，与 CoCl 2 和 RuCl 3 在 150 °C 水热反应 24 h，随后在 Ar/H 2 (5%) 混合气氛下 600 °C 热解处理，成功在氮掺杂碳纳米管(N-CNTs)上修饰了 CoRu 纳米合金，制备了一种新型高效的 Co、Ru 双金属电催化剂。得益于 Co 和 Ru 位点之间的电子通信，所得 CoRu@N-CNTs 具有优异的电催化 HER 活性。在 1 M KOH 水溶液中达到 10 mA cm -2 的电流密度，所需过电位仅为 19 mV，塔菲尔斜率为 26.19 mV/dec -1，优于基准 Pt/C 催化剂。本研究将为高效析氢电催化剂的设计与制造开辟一条新的道路，有力推动电解水制氢技术在能源存储与转化领域的应用推广，为我国“碳达峰与碳中和”战略目标的实施蓄势赋能。

关键词：钴钌合金；电催化剂；水裂解；析氢反应；碳纳米管