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Constructing nanoneedle arrays of heterostructured RuO₂–Co₃O₄ with tip-effect-induced enrichment of reactants for enhanced water oxidation†

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Nanoneedle arrays of heterostructured RuO₂–Co₃O₄ electrocatalysts were constructed, showing improved water oxidation activity and durable stability. The synergy of tip-effect-induced OH[−] enrichment, superior hydrophilicity, and heterojunction-enhanced electron transfer promotes water oxidation activity.

Hydrogen is widely regarded as the most environmentally friendly alternative to fossil fuels. Electrocatalytic water splitting is one of the most promising strategies for sustainable hydrogen production to meet future energy demands.¹ However, the sluggish kinetics of the oxygen evolution reaction (OER) severely hinder the overall efficiency of water splitting.² Although Ru-based and Ir-based materials are currently the state-of-the-art OER catalysts, their high cost and natural scarcity present significant barriers to industrial-scale implementation.^{3,4} This challenge highlights the urgent need to develop OER catalysts that combine high efficiency, long-term stability, and economic viability.

Notably, heterointerface engineering enables precise tuning of catalyst electronic configurations, optimal modulation of intermediate adsorption strength, and consequent activity enhancement.⁵ For example, Mu *et al.* reported that defective RuO₂/TiO₂ nanoheterostructures provide 10 mA cm^{−2} at an overpotential of 296 mV for the alkaline OER.⁶ Sun *et al.* reported a rutile-structured Ru–Sn solid-solution oxide (Ru_{0.6}Sn_{0.4}O₂) displaying a low overpotential of 245 mV to reach 10 mA cm^{−2} in 1.0 M KOH electrolyte.⁷ Additionally, the construction of nanoneedle arrays provides dual functional benefits: (1) improving hydrophilicity to accelerate mass transport

processes,⁸ and (2) obtaining high-curvature nanostructures with tip-enhanced local electric fields that concentrate electrolyte ions and reactants at active sites. This combined effect simultaneously reduces reaction barriers and facilitates rapid mass transfer to active sites, ultimately boosting catalytic activity.⁹ Thus, it is expected that high-performance RuO₂-based electrocatalysts could be prepared by integrating heterojunction and morphology engineering. In addition, spinel Co₃O₄ with low cost and abundant active sites is considered to be a promising catalyst for the OER, which can improve the activity by adjusting the electronic structure and local structure. Bo and coworkers constructed Co₃S₄@Co₃O₄/NSC core@shell nanostructures as bifunctional ORR/OER electrocatalysts for rechargeable Zn–air batteries. The interfaces between Co₃S₄@Co₃O₄ and Co₃O₄/NSC could improve conductivity, and accelerate charge transfer.¹⁰ Jin *et al.* developed a heterogeneous Co₃O₄/CeO₂ nanocomposite to modify the electronic structure of Co₃O₄ and establish an improved local bonding environment by introducing CeO₂, consequently modifying the redox characteristics of Co and enhancing the acidic OER performance.¹¹ Therefore, simply constructing heterojunction structures and focusing on the surface reconstruction between multiple metal oxide surfaces could improve the OER activity for hydrogen economy.

Herein, we synthesized RuO₂ nanoparticle-decorated Co₃O₄ nanoneedle arrays on nickel foam (NF) through a sequential process involving Co₃O₄ growth, Ru³⁺ ion exchange, and subsequent annealing. The resulting RuO₂/Co₃O₄ heterostructure exhibits outstanding OER electrocatalytic performance in alkaline media, achieving a low overpotential of 223 mV at 100 mA cm^{−2} with remarkable stability exceeding 100 hours of continuous operation. XPS analysis shows that electrons transfer from RuO₂ to Co₃O₄ at the heterogeneous interface, resulting in electron redistribution, which can optimize OER energetics. The nanoneedle architecture simultaneously enhances surface hydrophilicity, accelerating mass transport. Furthermore, the densely arranged Co₃O₄ nanoneedles bind to enhance the local electric field effect induced by the tip, promoting OH[−] enrichment at active sites while exposing additional catalytic centers.

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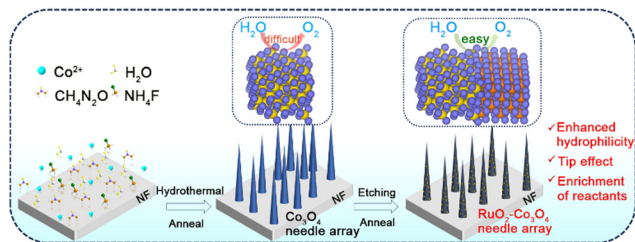


Fig. 1 Schematic drawing of heterostructured RuO₂/Co₃O₄ needle-array electrocatalysts for efficient OER.

This dual mechanism facilitates efficient O₂ evolution and significantly enhances alkaline OER kinetics. Our findings provide fundamental insights into the electronic structure modulation of heterostructured catalysts and contribute to the development of cost-effective catalytic systems for practical water electrolysis.

Fig. 1 shows the decoration of Co₃O₄ nanoneedle arrays with RuO₂ nanoparticles. The synthesis begins with the thermal conversion of cobalt carbonate hydroxide (CoCH) into a Co₃O₄ scaffold structure. Subsequently, the obtained Co₃O₄ substrates undergo controlled ion exchange reactions in an aqueous RuCl₃ solution for varying durations, followed by calcination under ambient conditions to produce the final RuO₂/Co₃O₄ electrocatalyst. Dynamic contact angle measurements (Fig. S1, ESI[†]) reveal the superior hydrophilicity of the RuO₂/Co₃O₄ electrocatalyst compared to bare NF. Upon water droplet contact ($t = 0$ s), complete surface wetting occurred within 0.073 seconds for the composite catalyst, demonstrating rapid electrolyte penetration, which facilitates optimal electrode–electrolyte interfacial contact. In addition, the rough nanoneedles formed by loaded nanoparticles can cause sharp tip enhancement and proximity effects, and generate stronger electric fields, which are conducive to the enrichment of OH[−] around the active site, optimizing the reaction energy barrier, and promoting the release of O₂ bubbles, thereby improving the OER process.¹²

The surface morphology of the catalysts was examined using field-emission scanning electron microscopy (FESEM). The as-prepared CoCH precursor exhibited smooth nanoneedle-like structures with a diameter of approximately 3–4 μm (Fig. S2, ESI[†]). After calcination to form Co₃O₄, the nanoneedle architecture remained largely intact (Fig. S3, ESI[†]). Subsequent Ru³⁺ ion exchange followed by calcination produced RuO₂/Co₃O₄ heterostructures, which preserved the nanoneedle morphology while exhibiting uniformly anchored RuO₂ nanoparticles on the surface, resulting in a roughened nanostructure (Fig. 2a–c). This well-defined nanoneedle configuration maximizes the exposure of active sites, enhances electrolyte infiltration, facilitates bubble release, and ensures structural stability during prolonged oxygen evolution reaction (OER).¹³

Transmission electron microscopy (TEM) further confirmed the unique nanowire-like structure of RuO₂/Co₃O₄ (Fig. 2d). High-resolution TEM (HRTEM) analysis revealed lattice spacings of 0.28 nm and 0.31 nm (Fig. 2e), corresponding to the (220) plane of Co₃O₄ and the (110) plane of RuO₂, respectively. High-angle annular dark-field TEM (HAADF-TEM) imaging, coupled with

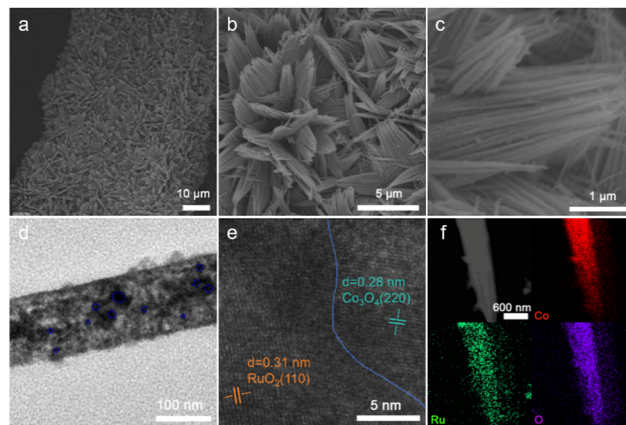


Fig. 2 (a)–(c) SEM, (d) TEM, (e) HRTEM, and (f) EDX mapping images of RuO₂/Co₃O₄ needle-arrays.

elemental mapping (Fig. 2f), demonstrated the homogeneous spatial distribution of Ru, Co, and O throughout the whole needle, conclusively verifying the formation of RuO₂/Co₃O₄ heterogeneous nanoneedles.

The heterostructure of RuO₂/Co₃O₄ was analyzed using X-ray diffraction (XRD, Fig. 3a). It shows distinct diffraction peaks at 31.2°, 36.8°, 44.8°, 59.3°, and 65.2°, corresponding to the (220), (311), (400), (511), and (440) planes of cubic Co₃O₄ (JCPDS no. 09-0418). Additional peaks at 28.0°, 35.0°, and 54.3° align with the (110), (101), and (211) planes of tetragonal RuO₂ (JCPDS no. 43-1027), confirming the successful formation of the heterostructure.

The electronic structure of RuO₂/Co₃O₄ was investigated by X-ray photoelectron spectroscopy (XPS, Fig. 3b). In the Co 2p XPS spectra (Fig. 3c), two significant peaks of pristine Co₃O₄ located at 779.3 and 794.3 eV belong to Co³⁺, while another two peaks positioned at 780.5 and 795.5 eV are attributed to Co²⁺. In the spinel structure of Co₃O₄, Co²⁺ is located at a tetrahedral position, while Co³⁺ cations are located in octahedral sites.¹⁴ Compared to Co₃O₄, the binding energies of RuO₂/Co₃O₄ exhibit a negative shift of *ca.* 0.5 eV. As displayed in Fig. 3d,

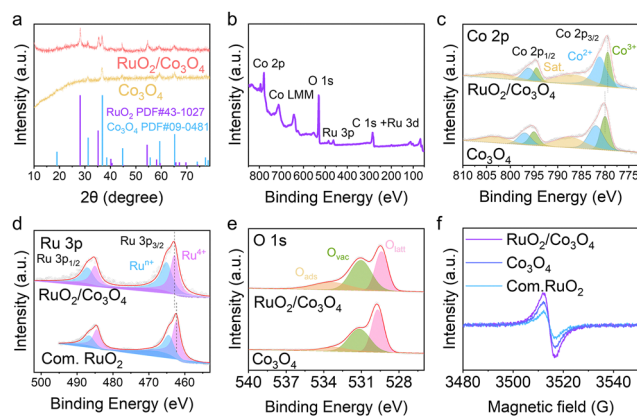


Fig. 3 (a) XRD patterns of RuO₂/Co₃O₄ and Co₃O₄. (b) The whole XPS spectrum of RuO₂/Co₃O₄. (c)–(e) The XPS spectra of (c) Co 2p, (d) Ru 3p, and (e) O 1s for RuO₂/Co₃O₄. (f) Electron paramagnetic resonance of RuO₂/Co₃O₄, com. RuO₂ and Co₃O₄.

the Ru 3p XPS spectra show two pairs of spin-orbit double peaks located at around 462.9 and 465.1 eV for Ru 3p_{3/2} and 485.1 and 487.2 eV for Ru 3p_{1/2}, which are assigned to the Ru⁴⁺ and Ru^{>4+} species.¹⁵ Compared to commercial RuO₂, the binding energies of RuO₂/Co₃O₄ exhibit a positive shift of *ca.* 0.6 eV, implying a partial charge transfer between RuO₂ and Co₃O₄, which can be attributed to the strong support and active phase synergy effect. Deconvolution of the O 1s spectra (Fig. 3e) identifies three components: lattice oxygen (O_{latt}, 529.3 eV), oxygen vacancies (O_{vac}, 531.0 eV), and adsorbed water (O_{ads}, 533.4 eV).¹⁶ Among them, the oxygen vacancy content of RuO₂/Co₃O₄ increased by 4% compared with cobalt tetroxide. This result is confirmed by the electron paramagnetic resonance (EPR) spectrum (Fig. 3f). This vacancy enrichment likely originates from charge compensation during Ru³⁺ ion exchange. Collectively, these results demonstrate significant electronic restructuring at the RuO₂/Co₃O₄ interface. The synergistic interaction between the phases can optimize the water dissociation kinetics and intermediate adsorption/desorption energetics, thereby accelerating overall water electrolysis efficiency.¹⁷

The OER activity of RuO₂/Co₃O₄ was systematically evaluated in 1 M KOH using a conventional three-electrode system, with comparative studies against pristine RuO₂/Co₃O₄ and commercial RuO₂. Linear sweep voltammetry (LSV) curves were *iR*-corrected and normalized to the reversible hydrogen electrode (RHE). The Ru content in RuO₂/Co₃O₄ was precisely controlled by varying ion-exchange durations, with inductively coupled plasma optical emission spectrometer (ICP-OES) analysis confirming the optimized mass ratio (Table S1, ESI†). After 9 hours of ion exchange, the catalyst exhibited peak performance, characterized by a high electrochemical active surface area (ECSA) and low charge-transfer resistance (Fig. S4 and S5, ESI†). As illustrated in Fig. 4a, RuO₂/Co₃O₄ requires an exceptionally low overpotential of 223 mV to deliver 100 mA cm⁻², significantly surpassing RuO₂/Co₃O₄ (350 mV) and commercial RuO₂ (400 mV). Impressively, even at a high current density of 200 mA cm⁻², RuO₂/Co₃O₄ maintains superior performance with minimal overpotential (Fig. 4b), outperforming benchmark catalysts across all tested current densities. Reaction kinetics analysis reveals a Tafel slope of 46.46 mV dec⁻¹ for RuO₂/Co₃O₄, markedly lower than Co₃O₄ (70.66 mV dec⁻¹) and commercial RuO₂ (87.63 mV dec⁻¹) (Fig. 4c), confirming accelerated OER kinetics enabled by hetero-interface engineering. Electrochemical impedance spectroscopy (EIS) further corroborates this enhancement, with RuO₂/Co₃O₄ exhibiting the smallest semicircle diameter (Fig. 4d), indicative of reduced charge-transfer resistance and faster interfacial kinetics. The ECSA, derived from double-layer capacitance (*C*_{dl}) measurements *via* cyclic voltammetry at varying scan rates (Fig. S6, ESI†), reaches 328.95 mF cm⁻² for RuO₂/Co₃O₄, exceeding Co₃O₄ (167.60 mF cm⁻²) and commercial RuO₂ (40.68 mF cm⁻²) by factors of 1.96 and 8.09, respectively (Fig. 4e).¹⁸ This substantial increase in *C*_{dl} directly correlates with electronic structure modulation at the RuO₂/Co₃O₄ heterointerface, which exposes abundant active sites and enhances charge-transfer efficiency.

The enhanced electrocatalytic activity may be attributed to the tip effect of the rough nanoneedles.¹² Densely packed

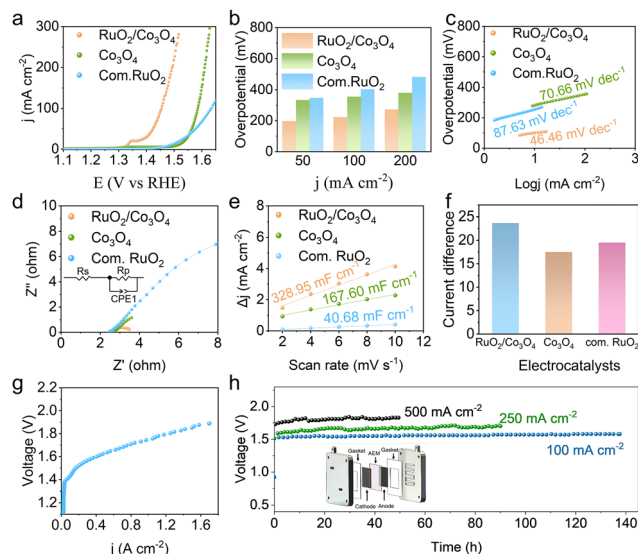


Fig. 4 (a) LSV curves, (b) overpotentials at 50, 100 and 200 mA cm⁻², (c) corresponding Tafel slopes, (d) EIS Nyquist plots, and (e) capacitive current density against the scan rate of RuO₂/Co₃O₄, Co₃O₄, and com. RuO₂ in 1.0 M KOH. (f) Current difference between the polarization curves in 1.0 M KOH solution with and without 1.0 M methanol for RuO₂/Co₃O₄, Co₃O₄ and com. RuO₂. (g) Polarization curves of RuO₂/Co₃O₄, which were measured by the use of an AEMWE cell in 1.0 M KOH with a scan rate of 10 mV s⁻¹. (h) Chronopotentiometric measurements of stability at 0.5 A cm⁻², 0.25 A cm⁻² and 0.1 A cm⁻². Inset is a diagram of an AEMWE electrolyzer.

nanoneedles can induce a strong local electric field, enriching OH⁻ ions at the electrode surface, exposing more active sites to OH⁻ ions, and promoting O₂ release, thus accelerating the alkaline oxygen evolution reaction (OER) process. To verify the enrichment of OH⁻ ions, methanol molecular probe experiments were conducted (Fig. S7, ESI†). The methanol oxidation reaction (MOR) follows a well-established mechanism in which methanol molecules nucleophilically attack electrophilic *OH species.^{19,20} The nucleophilic reagent methanol can easily adsorb the electrophilic reagent *OH in the process of the OER, which forms a competitive relationship with the adsorption of *OH by the OER. Therefore, the MOR is considered as an electronic probe assaying the adsorption of OER intermediates, that is, the increase of current density in the MOR is positively correlated with the coverage of intermediate *OH.^{21,22} The difference in current density due to the MOR is proportional to the charge transferred, which can be quantified by calculating the area between the curves (Fig. 4f). The current difference between the MOR and OER on RuO₂/Co₃O₄ nanoneedles is greater than that observed on Co₃O₄ and RuO₂, indicating a stronger MOR competitive reaction and validating enhanced *OH adsorption on RuO₂/Co₃O₄. To demonstrate the stability of RuO₂/Co₃O₄ in an alkaline environment, the catalyst stability was tested at a current density of 100 mA cm⁻². The voltage degradation of RuO₂/Co₃O₄ was found to be negligible after 100 hours (Fig. S8, ESI†).

After the OER stability test, a series of characterizations were executed to minutely explore the morphology or structure evolutions of the spent catalyst. XPS was also carried out to

investigate the chemical state and surface composition of the oxide after the stability test (Fig. S9, ESI†). It can be seen that the binding energy of Ru 3p has undergone a slight positive shift, indicating that Ru has undergone a slight oxidation during the OER process. SEM analysis was used to observe micro-morphological changes after testing, revealing that the nanowire array remained largely intact and that Ru, Co, and O elements were uniformly distributed throughout the catalyst (Fig. S10, ESI†), highlighting the robustness of the catalyst. Notably, the OER performance of RuO₂/Co₃O₄ outperforms most recently reported Ru-containing electrocatalysts (Fig. S10 and Table S2, ESI†). In addition, we used custom anion exchange membrane electrolysis (AEMWE) cells to evaluate water decomposition performance in alkaline media with high current density. Under continuous operation, the RuO₂/Co₃O₄ based AEMWE only needs 1.723 V battery voltage to achieve 1 A cm⁻² water decomposition current density (Fig. 4g). To assess its industrial relevance, extended stability tests were performed at current densities of 0.1, 0.25, and 0.5 A cm⁻² (Fig. 4h). The cell demonstrated excellent long-term stability, with negligible voltage fluctuations during 120 hours of operation, confirming the structural integrity and corrosion resistance of the RuO₂/Co₃O₄ catalyst under harsh alkaline conditions. These results suggest that RuO₂/Co₃O₄ exhibits excellent OER activity and significant stability due to the presence of abundant heterogeneous interfaces and densely packed nanoneedles.

In summary, we have developed highly efficient and stable RuO₂/Co₃O₄ heterogeneous nanoneedle electrocatalysts through an ion exchange reaction and a simple pyrolysis method. The optimal RuO₂/Co₃O₄ electrocatalyst achieves a minimal overpotential of 223 mV at 100 mA cm⁻². Furthermore, it exhibits exceptional OER stability, with no significant degradation observed at 100 mA cm⁻² over 100 hours, outperforming most recently reported state-of-the-art electrocatalysts. The experimental results demonstrate that the heterogeneous interface facilitates strong electron interactions, enhancing the OER activity. Additionally, the methanol oxidation molecular probe test confirms that the densely packed nanoneedles promote the enrichment of OH⁻ ions around the active sites, exposing more active sites to OH⁻ ions, thereby accelerating the release of O₂ bubbles. This study presents a viable approach for producing high-performance transition metal oxide catalysts for efficient water oxidation.

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Data availability

Data available within the article or its ESI†

Conflicts of interest

There are no conflicts to declare.

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