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Robust bifunctional oxygen electrocatalyst with a “rigid and flexible” structure for air-cathodes

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Abstract

The development of highly active air-cathodes with robust stability and a low price is of crucial significance for rechargeable Zn–air batteries and remains a great challenge. Herein, for the first time, we report a “rigid and flexible” material consisting of three-dimensional (3D) porous nickel-manganese oxide (Ni₆MnO₈) coupled with 1D ultrathin Au nanowires (Au-NWs) as an efficient bifunctional oxygen electrocatalyst, adopting α -naphthol-Au(III) as a precursor of Au-NWs and pre-formed Ni₆MnO₈ as a support. Ni₆MnO₈ acts not only as a robust carbon-free support that is stable in alkaline electrochemical conditions, but also as a highly active component for the oxygen evolution reaction (OER), while flexible Au-NWs contribute to the excellent oxygen reduction reaction (ORR) activity and act as a flexible conductive electronic network. The coupling of Ni₆MnO₈ and Au-NWs plays a complementary role in the two types of oxygen electrocatalytic reactions. Accordingly, their advantages have been optimally harnessed while overcoming their deficiencies. Moreover, a Zn–air battery assembled with such a rigid and flexible air-cathode has lower charge and discharge overpotentials and a higher cyclic stability than those with a mixed Pt/C+RuO₂ catalyst.

Introduction

Oxygen-reduction and oxygen-evolution reactions (ORR and OER) are two significant reactions ($\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \leftrightarrow 4\text{OH}^-$), with oxygen reduced by electrons while discharging and the reverse process occurring during charging in rechargeable zinc (Zn)–air batteries, a promising technology to cope with future energy demands by virtue of their theoretically high energy density (1084 Wh kg^{−1}), low-price, eco-friendly nature, and safety^{1–10}. However, Zn–air batteries in practical energy devices remain less efficient in output and are unsatisfactorily stable in cycling resulting from the sluggish kinetics of oxygen reactions and the poor stability of catalysts at the air-cathode^{11–14}. Additionally,

efficient bifunctional catalysts that are active for both ORRs and OERs is one of the great challenges faced in designing rechargeable Zn–air batteries^{15–20}. Thus far, the best-known catalysts for oxygen electrocatalysis in alkaline media are prohibitive Pt-based metals for ORRs and Ir/Ru-based metals for OERs^{21–23}, but neither catalyst has sufficient bifunctional properties. Therefore, the development of highly active and stable bifunctional catalysts in light of low-price transition metals is important for practically applying Zn–air batteries.

In contrast to all the other types of transition-metal alternatives, the oxides, encompassing perovskites (e.g., CaMnO₃, LaMnO₃)²⁴, spinels (e.g., CuCo₂O₄, ZnCo₂O₄)^{25,26}, pyrochlore oxides (e.g., Pb₂Ru₂O_{6.5}, Y₂[Ru_{2–x}Y_x]O_{7–y})^{7,27}, and oxysulfides (e.g., CoO_{0.87}S_{0.13})²¹, are potential bifunctional catalysts because of their chemical versatility and favorable stability in alkaline media. The electrocatalytic performances of metal oxides are limited by their intrinsically poor electrical conductivity, which can, however, be improved via supporting them on conductive

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materials. A synergetic combination of oxides with carbon materials is a general strategy for designing efficient bifunctional electrocatalysts^{28–35}. Notably, such carbon-supported metal oxides are electrochemically unstable, especially under harsh OER conditions because carbon oxidation/corrosion occurs at relatively low potentials ($C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^-$, $E_0 = 0.207$ V vs. standard hydrogen potential)^{36,37}. Carbon corrosion has been identified as a main issue that greatly affects the stability of catalysts^{11,38}. In this regard, exploring robust carbon-free bifunctional electrocatalysts while retaining satisfactory electrical conductivity and evident catalytic activity is vitally necessary^{36,38,39}. For instance, Chen et al. developed a new carbon-free bifunctional catalyst comprising $CaMnO_3$ and Pt clusters (Pt/ $CaMnO_3$) that exhibit evidently prolonged durability and optimized activity relative to that of carbon-supported Pt and $CaMnO_3$ alone³⁹. A similar result was also observed for a synergetic catalyst of Co_3O_4 and Ag particles (Ag/ Co_3O_4)⁴⁰. More recently, Goodenough et al. reported a robust Ni_3FeN -supported Fe_3Pt (Fe_3Pt/Ni_3FeN) that can enable Zn–air batteries to achieve long-term cycling stability with high efficiency as an air-cathode³⁶. Although these robust carbon-free-supported noble metal catalysts become markedly more stable, the morphology and structure of these catalysts are unsatisfactory because electrocatalysis is a type of structure sensitive reaction, especially for ORRs.

Herein, a new, low-cost and highly active bifunctional electrocatalyst is designed and fabricated, consisting of flexible Au nanowires cross-linked with rigid Ni_6MnO_8 microspheres (Au-NWs/ Ni_6MnO_8) as an efficient air-cathode. The Ni_6MnO_8 microspheres present a 3D hierarchically porous structure, while the Au nanowires have an ultrathin 1D anisotropic structure. Such “rigid and flexible” materials were prepared using in situ deposition of Au nanowires on the oxide support in the presence of α -naphthol. Unlike the numerous Au nanowires previously reported, the Au-NWs outlined here can be rapidly synthesized with ultrathin diameters. Strongly coupled Au-NWs/ Ni_6MnO_8 have a superior bifunctional electrocatalytic performance, in which the Au-NWs are active for ORRs and Ni_6MnO_8 for OERs, coinciding with the concept of “rigid and flexible coupling”. Meanwhile, Au-NWs/ Ni_6MnO_8 is electrochemically stable over the potential range of an air-cathode in an alkaline medium. The synergistic interaction of the 3D porous structure and the metallic 1D nanowires provides abundant catalytic active sites and facilitates mass and electron transport. Moreover, a Zn–air battery adopting Au-NWs/ Ni_6MnO_8 as the air-cathode exhibits a larger peak power density (118 mW cm^{-2}), a higher specific capacity ($768\text{ mAh g}_{Zn}^{-1}$) and a longer cycle life than that of a mixed Pt/C + RuO_2 air-cathode. This paper is the first to report the synthesis of rigid Ni_6MnO_8 -supported flexible

Au nanowires as an efficient synergistic catalyst for air-cathode reactions.

Materials and methods

Materials

Nickel (II) nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$), manganese (II) acetate tetrahydrate ($Mn(COOH)_2 \cdot 4H_2O$), and hydrogen tetrachloroaurate (III) tetrahydrate ($HAuCl_4 \cdot 4H_2O$) were purchased from Alfa Aesar. Hexamethylenetetramine (HMTA), α -naphthol ($C_{10}H_8O$), and ruthenium oxide (RuO_2) were supplied by Aladdin. Commercial Pt/C was purchased from Johnson Matthey Chemicals Ltd. All reagents and chemicals were used without further purification.

Synthesis of Ni_6MnO_8 samples

Typically, $Ni(NO_3)_2$ and $Mn(COOH)_2$ in a 3:1 molar ratio was dissolved into 20 mL of deionized water (metal-ion concentration 40 mM) with 560 mg of HMTA by continuously stirring. The mixture was then transferred to a Teflon-lined steel autoclave and heated in an oven at 80°C for 12 h. Once cooled to room temperature, the obtained precipitate was collected and washed several times with deionized water and subsequently dried at 60°C to yield the hierarchical $NiMn$ LDHs. Then, the resulting $NiMn$ LDHs were placed in a tube furnace and annealed in air at 600°C for 4 h at a heating rate of 5°C min^{-1} . After natural cooling to room temperature, the porous Ni_6MnO_8 hierarchical microspheres were collected.

Synthesis of Au-NWs/ Ni_6MnO_8 and Au-NWs/C samples

Typically, 25 mg of Ni_6MnO_8 powder (or carbon black) was added into a 10 mL mixture of deionized water and ethanol ($V_{\text{water}}:V_{\text{ethanol}} = 1:1$) with 144 mg (1 mM) of α -naphthol in an ultrasonic bath for 10 min to form a uniform solution. Then, 2.0 mL of 0.05 M $HAuCl_4$ solution was added into the above mixture and further stirred for 10 min. Finally, the mixture was treated by submersion in a water bath at 60°C for a few minutes. The resulting Au-NWs/ Ni_6MnO_8 and Au-NWs/C catalysts were then centrifuged and extensively washed with deionized water.

Synthesis of pure Au-NWs and Au-particles/ Ni_6MnO_8 samples

Pure Au-NWs were prepared using an ultrafast method. Specifically, 2.0 mL of 0.05 M $HAuCl_4$ solution was added into a mixture of 5 mL of deionized water and 5 mL of ethanol with 1 mM α -naphthol in an ultrasonic bath for 10 min to form a uniform solution, followed by submersion in a water bath at 60°C for a few minutes. For the synthesis of the Au-particles/ Ni_6MnO_8 catalyst, Au colloids were first synthesized in a trisodium citrate solution: a 20 mL mixed solution containing 0.10 mM $HAuCl_4$ and

0.25 mM trisodium citrate was prepared at room temperature, and NaBH_4 was also dissolved in deionized water; the resulting solution (0.01 M) was used as a reducing agent; with the dropwise addition of 0.5 mL of the NaBH_4 solution, the red-wine solution containing Au colloids was formed. Then, an appropriate aliquot of Au colloids was mixed with Ni_6MnO_8 in a beaker while being vigorously stirred for 30 min, resulting in the deposition of Au colloids on the Ni_6MnO_8 supports. Finally, the Au-particles/ Ni_6MnO_8 catalyst was obtained by filtration and washing with water to remove excess surfactant and reducing agent.

Physicochemical characterization

The phase purity and crystallinity of the products were identified using X-ray powder diffraction (XRD) on a Rigak Smartlab X-ray with $\text{Cu-K}\alpha$ radiation ($\lambda = 0.1541$ nm). Scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDX) were performed using a Hitachi S4800 SEM. Transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) were performed using a JEOL 2010F TEM/STEM operated at 200 kV. X-ray photoelectron spectroscopy (XPS) was performed using a Thermo VG Scientific ESCALAB 250 spectrometer with an $\text{Al-K}\alpha$ radiator. The binding energy (BE) was calibrated using the C 1s peak energy of 284.6 eV. The Brunauer–Emmett–Teller (BET)-specific surface area was measured at 77 K using a Micromeritics ASAP 2050 system. The electrical conductivity was measured using 4-probe conductivity measurements on an ST-2722 semiconductor resistivity of the powder tester (Suzhou Jingge Electronic Co., Ltd., China) under a pressure of 10 MPa.

Electrochemical measurements

Electrochemical measurements were carried out using a CHI 760E electrochemical analyzer (Shanghai, Chenghua Co.). A standard three-electrode system was used, including a rotating disk electrode (RDE) or rotating ring-disk electrode (RRDE) as the working electrodes (0.196 cm^2), a platinum wire as the auxiliary electrode, and a saturated calomel electrode protected by a Luggin capillary with KCl solution as the reference electrode. The catalyst ink was prepared by ultrasonically dispersing the mixture of 5 mg of catalyst, 1 mL of ethanol, and 20 μL of 5 wt.% Nafion solution; 10 μL of the catalyst ink was pipetted and spread onto the electrode. The loading of the studied catalysts was $250\text{ }\mu\text{g cm}^{-2}$. For the ORR test, the background current was measured under a N_2 atmosphere at an identical rotation speed and scan rate as for measurements conducted under O_2 . The ORR activities of the catalysts were measured via the RRDE voltammograms in 0.1 M KOH electrolyte at the

predefined rotation rate of 1600 rpm and a scan rate of 5 mV s^{-1} . Before testing, O_2 was passed through the electrolyte for at least 20 min to saturate the electrolyte with O_2 . To remove the capacitive current of the working electrode, the background current was measured by running the above electrodes in N_2 -saturated 0.1 M KOH and then was subtracted from the ORR polarization curve. The percentage of HO_2^- intermediate production (% HO_2^-) and electron transfer number (n) were determined using the following equations:

$$\%\text{HO}_2^- = \frac{200I_r}{NI_d + I_r} \quad n = \frac{4NI_d}{NI_d + I_r},$$

where I_d is the disk current, I_r is the ring current, and N is the current collection efficiency of the Pt ring, which was determined to be 0.37. For the OERs, the polarization curves were also measured in 0.1 M KOH solution recorded from 1.1 to 2.0 V at a scan rate of 5 mV s^{-1} . Note that high-purity O_2 is bubbled through the electrolyte during testing to fix the reversible oxygen potential (or ensure the $\text{O}_2/\text{H}_2\text{O}$ equilibrium at 1.23 V vs. RHE). To avoid the peeling of the catalyst that is caused by evolved O_2 adhesion, a rotation speed of 1600 rpm was used during the OERs.

The Zn–air battery tests were performed with a homemade Zn–air cell. The air-cathode consisted of hydrophobic carbon paper with a gas diffusion layer on the air-facing side and a catalyst layer on the water-facing side. The catalyst layer was made by loading catalyst ink onto the carbon paper by drop-casting, with a loading of 10 mg cm^{-2} for all the catalysts. A polished Zn plate with a thickness of 0.3 mm was used as the anode. A 0.2 M $\text{ZnCl}_2 + 6\text{ M KOH}$ mixed solution was used as the electrolyte. The gas diffusion layer had an effective area of 0.5 cm^2 and allows O_2 from the ambient air to reach the catalyst sites. A Land CT2001A system was used to perform the cycling test with a 5-min rest time between each discharge and charge at a current density of 10 mA cm^{-2} . Each discharge and charge period was set to be 20 min.

Results

Structure and composition of Au-NWs/ Ni_6MnO_8

Figure 1a presents a schematic diagram for the fabrication process of the Au-NWs/ Ni_6MnO_8 catalyst, which primarily involves three steps: (i) co-deposition of Ni and Mn precursors to form hierarchical NiMn layered double hydroxides (NiMn LDHs) with the aid of HMTA, in which HMTA was used as a hydrolysis agent to slowly alkalize the solution and homogeneously precipitate out bimetallic NiMn LDHs; (ii) pyrolysis treatment at 600°C in air to promote the formation of the hierarchically porous Ni_6MnO_8 phase; (iii) and ultrafast in situ growth of Au nanowires on the oxide support via a novel and simple water bath method in the presence of α -naphthol.

The experimental details are provided in the experimental section. The XRD pattern of NiMn LDHs (Fig. S1) shows diffraction peaks at 2θ of 9.5, 19.0, 34.7, 38.7, 44.6, and 60.0, which can be, respectively, indexed to (003), (006), (012), (015), (018), and (110) reflections of the rhombohedral LDH phase. Figure 1b shows the XRD patterns of the Au-NW, Ni_6MnO_8 , and Au-NWs/ Ni_6MnO_8 samples. As observed, all of diffraction peaks for the obtained oxide support are observed to be well geared into the face-centered cubic (fcc) murdochite-type Ni_6MnO_8 rigid structure (space group: $\text{Fm}\bar{3}\text{m}$ (225), JCPDS No. 83–1186, $a = b = c = 8.32 \text{ \AA}$). No other crystalline phase was detected, which indicates that the final product has a high purity. Murdochite-type Ni_6MnO_8 has a derived rock-salt structure, and one-eighth of the Ni^{2+} ions are replaced by Mn^{4+} ions and vacancies (Fig. 1c and Fig. S2)^{41,42}. This murdochite-type rigid structure was found to be chemically stable after being soaked in 0.1 M KOH solution for 2 weeks, as demonstrated by the XRD patterns (Fig. S3). There are five additional diffraction peaks of the Au-NWs/ Ni_6MnO_8 hybrid appearing at 38.3° , 44.5° , 64.7° , 77.7° , and 81.9° as compared to Ni_6MnO_8 ; they are consistent with the (111), (200), (220), (311), and (222) reflections of fcc Au (space group: $\text{Fm}\bar{3}\text{m}$ (225), JCPDS No. 65-8601, $a = b = c = 4.072 \text{ \AA}$). The XRD results

indicate the successful reduction of the Au(III) precursor with α -naphthol as the reducing agent.

Micro/nanostructures of the as-synthesized NiMn LDHs, Ni_6MnO_8 , and Au-NWs/ Ni_6MnO_8 were characterized specifically using electron microscopy technology. Representative SEM images (Fig. 2a and Fig. S4) of the NiMn LDHs display a 3D hierarchical porous architecture comprising dozens of interconnected sheet-like subunits. After thermal pyrolysis, the Ni_6MnO_8 sample retains the structure and morphology integrity of the hierarchical NiMn LDH microspheres, while the sheet-like subunits of the NiMn LDHs were completely transformed into porous ones (Fig. 2b and Fig. S5). The porous subunits packed with particles make the surface much coarser (Fig. S5), hinting at open and accessible mesopore channels, which should provide open pathways for mass transportation^{43,44}. Figure 2c and d and Fig. S6 display SEM images of Au-NWs/ Ni_6MnO_8 . After the decorating of Au nanowires, the Au-NWs/ Ni_6MnO_8 sample manifests a 3D interconnected architecture akin to the original Ni_6MnO_8 oxides. Remarkably, the randomly tortuous Au nanowires are uniformly dispersed on the surface of the oxides, filling the pores and bridging the boundary of the porous sheet-like subunits. The flexible Au nanowires can work conductive bridges to offer effective electron transport channels. Although Ni_6MnO_8 itself has a poor

conductivity ($2.46 \times 10^{-3} \text{ S m}^{-1}$), the Au-NWs/ Ni_6MnO_8 hybrid demonstrates a better electrical conductivity of approximately $1.25 \times 10^3 \text{ S m}^{-1}$ that can facilitate electron transport during electrocatalysis. To better investigate the structural features of Au-NWs/ Ni_6MnO_8 , TEM measurements were conducted, as presented in Fig. 2e and f and Fig. S7. Flexible nanowires with a high morphological yield (100%) and an ultrathin diameter of approximately 4 nm (Fig. S6d) were observed on the Ni_6MnO_8 surface. The high-resolution TEM (HRTEM) image and the corresponding fast Fourier transform (FFT) patterns show two types of crystalline domains of Au and Ni_6MnO_8 oriented along the [110] and [100] zone axes (Fig. 2g), respectively. The EDX elemental mappings (Fig. 2i and Fig. S8) reveal a uniform distribution of Ni, Mn, O, and Au in the STEM image (Fig. 2h), which demonstrates the homogeneous growth of Au nanowires on the porous Ni_6MnO_8 surface. The content of Au in the Au-NWs/ Ni_6MnO_8 is approximately 22 wt.%, which was demonstrated by the EDX spectrum (Fig. S9).

A nitrogen adsorption–desorption measurement was performed to ascertain the porosity of Au-NWs/

Ni_6MnO_8 . The adsorption–desorption curves (Fig. 3a) manifest representative type-IV isotherms with a distinctive hysteresis loop, which indicates the existence of microporous/mesoporous structures. The BET-specific surface area was calculated to be approximately $176 \text{ m}^2 \text{ g}^{-1}$. The surface state of the Au nanowires and Ni_6MnO_8 and the interaction between them were ascertained using XPS. The full XPS spectrum clearly indicates the co-existence of Au, Mn, Ni, and O elements in the Au-NWs/ Ni_6MnO_8 hybrid (Fig. S10). Figure 3b shows the high-resolution Au4f spectrum of Au-NWs/ Ni_6MnO_8 . The Au4f peaks centered at 83.7 and 87.4 eV are assigned to the spin-orbit doublet characteristic of metallic Au. Note that the Au4f peaks for Au-NWs/ Ni_6MnO_8 shifted to a lower BE by 0.48 eV in contrast to that of the non-supported Au nanowires, which was prepared via the direct α -naphthol reduction method (see Experimental for details). Given the similar morphology and surface properties of the Au particles in Au-NWs/ Ni_6MnO_8 and non-supported Au-NWs (Fig. S11), the Au4f-BE shift of Au-NWs/ Ni_6MnO_8 probably arose from the strong incorporation

Fig. 2 SEM images of **a** NiMn LDHs microspheres; **b** Ni_6MnO_8 microspheres; **c**, **d** Au-NWs/ Ni_6MnO_8 ; **e**, **f** TEM images of Au-NWs/ Ni_6MnO_8 ; **g** HRTEM image of Au-NWs/ Ni_6MnO_8 and the corresponding FFT patterns from the selected region of Ni_6MnO_8 and Au-NWs; **h** STEM image of Au-NWs/ Ni_6MnO_8 ; and **i** the corresponding EDX element mappings

between the oxide support and Au nanowires. The XPS analysis of the Au-NWs/ Ni_6MnO_8 also demonstrated that Ni (II) and Mn (IV) are the dominant species in the Ni_6MnO_8 (Fig. 3c, d). Additionally, a definite positive shift was found in the BE of the Ni2p and Mn2p peaks, for Au-NWs/ Ni_6MnO_8 relative to Au-free Ni_6MnO_8 . The positive shifts in the BE of the Ni2p and Mn2p peaks further demonstrate the presence of electron interactions between Au and Ni_6MnO_8 in Au-NWs/ Ni_6MnO_8 , consequently transferring electrons from Ni_6MnO_8 to metallic Au. Note that α -naphthol has little influence on the valence state of Ni_6MnO_8 because of its low reducing capacity. In contrast with numerous Au nanowires that have been reported previously, the Au-NWs outlined here have better structural advantages, and the α -naphthol-driven synthetic method is deemed to be more rapid and effective. Detailed comparisons are provided in Table S1. Notably, α -naphthol is critically significant in the formation of Au nanowires. In the absence of α -naphthol, the HAuCl_4 precursor cannot be reduced under the present HAuCl_4 - α -naphthol- Ni_6MnO_8 conditions, while in the presence of α -naphthol and without adding Ni_6MnO_8 , pure Au nanowires also can be obtained rapidly. Accordingly, α -naphthol is deduced to be able to not only serve as a reducing agent but also direct the formation of ultrathin Au nanowires. To confirm the rapid formation of Au nanowires, the reaction process was continuously

monitored using UV-Vis spectroscopy at the surface plasmon resonance (SPR) peak of the Au particles (approximately 550 nm). As Fig. 3e indicates, the intensity of the SPR peak progressively increases as the reaction progress until equilibrium occurs. The acquisition of the equilibrium point indicates the end of the reduction reaction. We found that it merely takes 130 s to completely reduce the HAuCl_4 precursor under the present reaction conditions. This phenomenon might stem from the strong molecular interaction between α -naphthol and HAuCl_4 that was ascertained from the UV-Vis spectra (Fig. 3f). When α -naphthol was incorporated into the HAuCl_4 solution, the characteristic absorption peak at 317 nm of the HAuCl_4 species is markedly blue-shifted. Moreover, as the nanowires were directed by α -naphthol-Au(III), due to the sufficient pre-interaction between α -naphthol and Ni_6MnO_8 support through the electrostatic binding, the Au nanowires capped by α -naphthol had the opportunity to come into intimate contact with the oxide support, resulting in the in situ deposition of the Au nanowires onto the Ni_6MnO_8 .

Bifunctional electrocatalytic activities for the OERs and ORRs

Given the unique structural advantages of the Au-NWs/ Ni_6MnO_8 hybrid, that is, inclusive of numerous mesopores, high BET surface area, and prominent electrical

Fig. 3 **a** N_2 adsorption-desorption isotherms of Au-NWs/ Ni_6MnO_8 microspheres; **b** high-resolution Au4f, **c** Ni2p, and **d** Mn 2p XPS spectra of Au-NWs/ Ni_6MnO_8 and Au-NWs; **e** the intensity of SPR peak changes as a function of time, the inset is the UV-Vis spectrum of a Au nanowire after a complete reaction; **f** UV-Vis spectra of HAuCl_4 , α -naphthol, and α -naphthol- HAuCl_4 complex solutions

conductivity, they should be very promising for electrocatalysis. First, the ORR activity of Au-NWs/Ni₆MnO₈ (Fig. 4a) was evaluated using a RDE. The performances of the Ni₆MnO₈ and Au-NWs samples are provided for comparison. Au-NWs/Ni₆MnO₈ shows significantly improved ORR activity in terms of its more positive half-potential ($E_{1/2} = 0.90$ V) as compared with Au-NWs (0.88 V) and Ni₆MnO₈ (0.62 V), suggesting that oxygen was more easily reduced on the Au-NWs/Ni₆MnO₈ catalyst. Note that ultrathin Au-NWs are an active component for ORRs, and their activity is higher than those of previously reported Au-based catalysts (Table S2). To probe the effect of Au-NWs on ORR performance, the Ni₆MnO₈-supported Au nanoparticles (Au-NPs/Ni₆MnO₈) were subjected to an ORR test. The detailed characterizations of Au-NPs/Ni₆MnO₈ are presented in Fig. S12. Au-NPs/Ni₆MnO₈ exhibited inferior ORR activity in comparison to the Au-NWs/Ni₆MnO₈ catalyst (Fig. S13), further verifying that the anisotropically ultrathin 1D nanostructure accounts for the high ORR activity of Au-NWs/Ni₆MnO₈. The anisotropic 1D nanowires possess many exposed surface atoms that can work as high-efficiency active sites, thus elevating the

atom utilization efficiency of the catalysts^{45,46}. Ni₆MnO₈ microspheres can act as a support and promoter to facilitate ORRs, due to their unique 3D hierarchically porous structure. Additionally, the Mn (IV) sites from Ni₆MnO₈ oxide for the enhanced ORR activity cannot be neglected. This is because Mn (IV) cations can effectively assist the charge transfer to adsorb oxygen on the catalyst surface, facilitating HO₂⁻ decomposition^{47,48}. Thus, the strong incorporation of Au-NWs with Ni₆MnO₈ (i.e., synergistic effect) makes hybridization a very promising ORR catalyst, even better than the commercial Pt/C catalyst (Fig. 4a). As Table S3 lists, the Au-NWs/Ni₆MnO₈ catalyst is also more active than the reported ORR catalysts. Additionally, Au-NWs/Ni₆MnO₈ has a smaller Tafel slope of 62 mV Dec⁻¹ (Fig. S14) than that of Au-NWs (63 mV Dec⁻¹), Ni₆MnO₈ (140 mV Dec⁻¹), and commercial Pt/C (74 mV Dec⁻¹), indicating a better kinetic process. To quantify the catalysts' ORR efficiencies, RRDE measurements were employed. Within a wide potential range (0.4–0.8 V), the average electron transfer number (n) and HO₂⁻ yield for Au-NWs/Ni₆MnO₈ are ca. 3.85 and 7.47% (Fig. 4b and Fig. S15), respectively, which are obviously superior to those for the Ni₆MnO₈ sample (2.74

Fig. 4 **a** ORR polarization curves of catalysts in O₂-saturated 0.1 M KOH (rotation rate: 1600 rpm; sweep rate: 5 mV s⁻¹); **b** bar plots of the electron transfer number and percentage of peroxide; **c** OER polarization curves of the catalysts in O₂-saturated 0.1 M KOH (rotation rate: 1600 rpm; sweep rate: 5 mV s⁻¹); **d** bar plots of the E_{onset} and $E_{1/2}$

and 37.5%). This fact further indicates that Au nanowire is a favorable conductive electronic network (n : 3.78 and HO_2^- yield: 10.5%). These values are very similar to those for the commercial Pt/C catalyst (3.88 and 5.90%), indicating a good four-electron ORR pathway for the Au-NWs/ Ni_6MnO_8 catalyst.

Apart from the remarkable ORR activity, the Au-NWs/ Ni_6MnO_8 catalyst also has very good OER activity. Figure 4c shows the OER polarization curves for Au-NWs/ Ni_6MnO_8 and other samples. Clearly, the Au-NWs/ Ni_6MnO_8 catalyst exhibits a lower overpotential and a higher current density over the provided potential range compared to the other references (Fig. 4d). At the current density of 10 mA cm^{-2} , Au-NWs/ Ni_6MnO_8 has a very low overpotential (E_{j10}) of 0.36 V, outperforming the state-of-the-art RuO_2 catalyst (0.39 V), and is even comparable to those of other non-noble metal catalysts (Table S4). Pure Au-NWs show a poor OER response, indicating that unsupported Au-NWs do not work as an active catalytic site for the OER. The excellent OER activity of Au-NWs/ Ni_6MnO_8 probably principally arise from the intrinsic OER property of Ni_6MnO_8 , as indicated by the lower onset-potential compared with that of Au-NWs. As shown in Fig. S16, the Tafel plots for the OER of

Au-NWs/ Ni_6MnO_8 exhibit a slope of 62 mV Dec^{-1} , lower than that of the Au-NW (101 mV Dec^{-1}), Ni_6MnO_8 (82 mV Dec^{-1}), and RuO_2 (76 mV Dec^{-1}) catalysts. To further explore the active site of Ni_6MnO_8 for OERs, we performed a theoretical investigation by calculating the free energies based on density functional theory. Figure 5 compares how the free energy of OER changes at the Ni sites (Fig. 5a) and the Mn sites (Fig. 5b) of Ni_6MnO_8 . Generally, OERs abide by the following four-electron step process:

It is seen that all the elementary reactions are positive free energy change (endothermic) at zero electrode potential. As the electrode potential increases to the equilibrium potential at 1.23 V, some elementary reactions (e.g., OH^* and O^* formation) become energetically downhill (exothermic). All the elementary reactions become downhill until the electrode potential increases to 2.13 V for the Ni sites and 2.48 V for the Mn sites on the Ni_6MnO_8 surface. This fact suggests the overpotential is

Fig. 5 Free energy diagrams for the OER obtained at zero potential ($U = 0$), equilibrium potential ($U = 1.23 \text{ V}$), and at the potential for which all steps are downhill on **a** Ni sites and **b** Mn sites; **c** the structures of the OER intermediates on the Ni sites and Mn sites

0.90 and 1.25 V on the Ni sites and Mn sites. It can be concluded that the overpotential on the Ni sites is lower than that on the Mn sites, indicating that the Ni sites have superior OER activity and are the preferred reaction active sites. Figure 5c shows the corresponding structures of OER intermediates on the Ni sites and Mn sites of Ni₆MnO₈.

Notably, Ni₆MnO₈ alone cannot explain such a good OER activity of the Au-NWs/Ni₆MnO₈ catalyst, which arises from its poor electrical conductivity. Previous studies demonstrated that some hydroxides, including NiFeOOH, NiOOH, and CoOOH, have better OER activities on a Au substrate than on glassy carbon; this phenomenon was attributed to the partial electron transfer from hydroxides to more electronegative Au^{49,50}. It is therefore reasonable to infer that Au-NWs improve the electrical conductivity of the catalytic active centers in Ni₆MnO₈ due to the difference of the work functions and the strong interfacial coupling between Au-NWs and Ni₆MnO₈. The results demonstrate the advantages of the

strongly coupled Au-NWs and Ni₆MnO₈ at boosting bifunctional oxygen electrocatalysis: Au-NWs bring both catalytic active sites for the ORR and a high electrical conductivity, which facilitates electron transport during electrocatalysis, whereas Ni₆MnO₈ is catalytically active for the OER due to its intrinsic OER property and improves mass transport by the 3D hierarchically porous structure. The stability of Au-NWs/Ni₆MnO₈ as a bifunctional catalyst was investigated for the ORR and the OER using the chronoamperometric method (Fig. 6a). Au-NWs/Ni₆MnO₈ shows better electrocatalytic stabilities during both the OER and ORR than those of the commercial Pt/C and RuO₂ catalysts after 30,000 s (Fig. 6b). More importantly, the Ni₆MnO₈-supported Au-NWs clearly improved the stability relative to that of the Au-NWs/C catalyst, which apparently arises from the preferable chemical stability and structural stability of Ni₆MnO₈. A favorable chemical stability would be beneficial to the electrochemical stability of catalysts⁴³. When cycling repeatedly at a wide potential range of ORRs and

OERs for 100 cycles at 0.1 M KOH (Fig. S17), there was no observable degradation of the electrochemical signal associated with Ni_6MnO_8 , demonstrating that Ni_6MnO_8 is electrochemically stable. Furthermore, 1D Au-NWs within the 3D hierarchically porous architecture impede agglomeration and dissolution of catalyst particles. The remarkable electrocatalytic activity and stability of Au-NWs/ Ni_6MnO_8 make it highly promising as a bifunctional oxygen catalyst, as further indicated by the overall oxygen electrode curves (Fig. 6c, d). The oxygen electrode activity ($\Delta E = E_{110} - E_{1/2}$) of Au-NWs/ Ni_6MnO_8 noticeably present the smallest value (0.69 V) of all the provided catalysts and is even comparable with that of other reported bifunctional electrocatalysts (Table S5), confirming that the Au-NWs/ Ni_6MnO_8 catalyst is one of the most efficient bifunctional catalysts.

Rechargeable Zn-air batteries

Using the prominent bifunctional performance of the Au-NWs/ Ni_6MnO_8 hybrid, a Zn-air battery was designed and assembled to evaluate its feasibility, as exhibited in Fig. S18. The open-circuit voltage (OCV) of the Au-NWs/ Ni_6MnO_8 -driven Zn-air battery is approximately 1.52 V (Fig. 7a), which is in the vicinity of the theoretical voltage (1.65 V). Two cells connected in series can work as an efficient energy supplier to power a red light-emitting diode (LED, 3.0 V). For comparison, a mixed Pt/C + RuO_2 catalyst (the mass ratio of Pt/C and RuO_2 was of 1/1) was also tested as a control air-cathode. Figure 7b shows the

discharge polarization curves and the corresponding power density curves. Au-NWs/ Ni_6MnO_8 exhibits a decent current density of 104.9 mA cm^{-2} at 1.0 V, which is superior to that of the mixed Pt/C + RuO_2 catalyst (70.2 mA cm^{-2}). The maximum power density of ca. 121 mW cm^{-2} exceeds that of the battery with Pt/C + RuO_2 (110 mW cm^{-2}) and many other reported bifunctional catalysts (Table S6). The specific capacity of the Au-NWs/ Ni_6MnO_8 -based battery was up to $760 \text{ mAh g}_{\text{Zn}}^{-1}$ at a current density of 5 mA cm^{-2} (Fig. 7c), corresponding to an energy density of $996 \text{ Wh kg}_{\text{Zn}}^{-1}$, which surpasses those of Pt/C + RuO_2 ($692 \text{ mAh g}_{\text{Zn}}^{-1}$; $892 \text{ Wh kg}_{\text{Zn}}^{-1}$) and previously reported state-of-the-art air-cathodes (Table S7). Moreover, the Au-NWs/ Ni_6MnO_8 -based battery demonstrated superior cycle stability compared to that of the mixed Pt/C + RuO_2 catalyst (Fig. 7d). For instance, the 1st cycle discharge-charge voltage gap is only 0.70 V, contributing to a high energy efficiency of 65%. After 80 cycles, both the voltage gap and the energy efficiency remain at high values, 1.02 V and 50.2% (Fig. 7e), respectively. Comparatively, the Pt/C + RuO_2 -based battery has a poor cycle life with a large overpotential increase after 20 cycles (Fig. 7f). After the charge/discharge cycles, the overall morphology and structure of the Au-NWs/ Ni_6MnO_8 cathode material were well preserved (Fig. S19). These results verify the excellent activity and stability of the Au-NWs/ Au_6MnO_8 catalyst as the air-cathode in rechargeable Zn-air batteries.

Discussion

In summary, we have developed a simple and efficient strategy for the synthesis of a strongly coupled Au-NWs/ Ni_6MnO_8 material with both rigidity and flexibility as a new, low-cost, and highly active air-cathode for rechargeable Zn–air batteries. The α -naphthol–Au(III) complex plays a critical role in regulating the morphology of Au nanocrystals and synthesizing Ni_6MnO_8 -supported Au nanowires. The synergistical integration of Ni_6MnO_8 that is active for OERs and Au nanowires that are active for ORRs endows the hybrid with a superior bifunctional electrocatalytic performance. The rigid Ni_6MnO_8 also makes the electrochemical properties more stable over the potential range of an air-cathode in an alkaline media, while the flexible Au nanowires offer effective electron transport channels as conductive bridges. The strong cross-link between the hierarchically porous Ni_6MnO_8 and Au nanowires provides an additional synergistic effect to further enhance electrocatalytic activity and stability, by virtue of its unique structural advantages. Moreover, the Au-NWs/ Ni_6MnO_8 -driven Zn–air battery can output a high OCV of 1.52 V, a high peak power density of 118 mW cm^{-2} , and a large specific capacity of $768 \text{ mAh g}_{\text{Zn}}^{-1}$. This work offers an innovative strategy for developing carbon-free bifunctional electrocatalysts that have many potential applications in metal–air batteries.

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Conflict of interest

The authors declare that they have no conflict of interest.

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