

Graphdiyne oxide-mediated synthesis of amorphous high-entropy sulfides for highly stable zinc-air batteries

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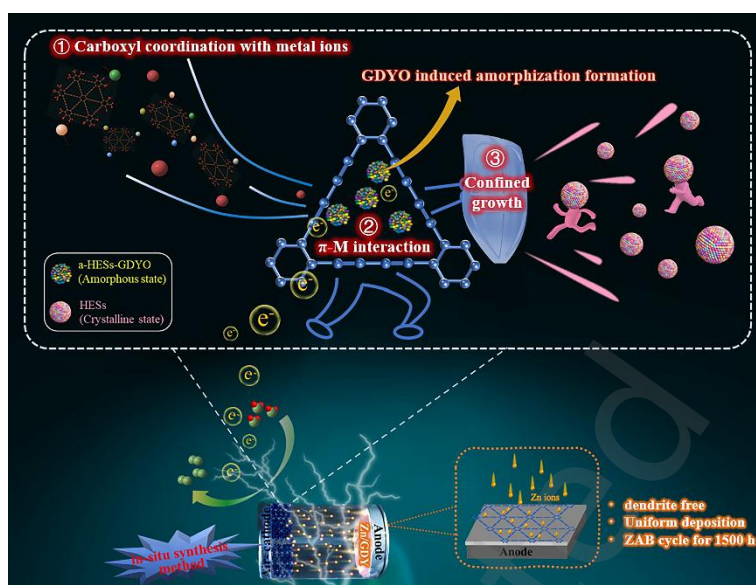
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Graphdiyne oxide (GDYO) directs the formation of amorphous high-entropy sulfides by coordinating metal ions, anchoring nuclei, and confining crystal growth. Compared with crystalline high-entropy sulfides, this method yields electrodes for zinc-air batteries that feature enhanced oxygen reduction activity, a 61% higher peak power density, and over 1500 hours of cycling stability.

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ABSTRACT: Developing efficient and durable air cathodes is pivotal yet challenging for high-performance rechargeable zinc-air batteries (ZABs). Herein, we present an innovative strategy that leverages oxidized graphdiyne (GDYO) as a multifunctional mediator to construct amorphous high-entropy sulfide-graphdiyne oxide composite (a-HESs-GDYO). The unique characteristics of GDYO, including its abundant oxygen-containing groups, electron-rich alkyne bonds, and triangular nanopores, exerts triple synergistic regulatory effects. This mechanism involves the coordinated dispersion of metal cations, electrostatic anchoring of metal nuclei, and confined growth within the pores, effectively addressing the common synthesis challenges of easy crystallization and elemental segregation encountered in amorphous high-entropy sulfides (a-HESs). Leveraging the GDYO-induced amorphous structure, the synergistic effect among multimetal components of high-entropy sulfides, as well as stable structural reconstruction and anti-agglomeration capability, a-HESs-GDYO delivers good dual-functional catalytic performance in zinc-air batteries. Specifically, the a-HESs-GDYO catalyst exhibits enhanced electrocatalytic activity towards the oxygen reduction reaction (ORR), showcasing a half-wave potential of 0.66 V (vs. RHE) and superior stability, representing an increase of 60 mV compared to crystalline HESs. When assembled as the air cathode of ZABs, the device demonstrates impressive performance, delivering a power density of 133 mW cm⁻², a specific capacity of 725 mAh g⁻¹, and long-term stability exceeding 1500 h of operation. This study provides an effective and general synthetic strategy for high-performance amorphous high-entropy catalysts and establishes a robust paradigm for their application in next-generation energy storage devices.

KEYWORDS: graphdiyne oxide, Zn-air batteries, high-entropy sulfides, amorphous, electrocatalysts

1. Introduction

The escalating global demand for sustainable energy, coupled with mounting environmental concerns, has driven intensive research into next-generation energy storage and conversion systems. Among these, rechargeable zinc–air batteries (ZABs) stand out for their high theoretical energy density ($1086 \text{ Wh}\cdot\text{kg}^{-1}$), inherent safety, cost-effectiveness, and environmental benignity, making them promising candidates for large-scale energy storage and portable electronics. However, the practical deployment of ZABs faces significant bottlenecks [1, 2]. The sluggish kinetics of the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER) at the air cathode result in considerable polarization and low energy efficiency, posing significant obstacle to their further development [3-7]. The zinc anode faces persistent issues such as dendrite growth, corrosion, and passivation, which severely compromise the cycling stability and operational safety of ZABs [8, 9]. Therefore, the design of efficient, stable, and low-cost bifunctional electrocatalysts for both ORR and OER, along with the development of effective strategies to stabilize the zinc electrode has become a key challenge in the ZABs field.

Recently, high-entropy materials (HEMs), particularly high-entropy sulfides (HESs), have recently garnered attention in electrocatalysis due to their unique "cocktail effect" and entropy-driven stabilization. Their high configurational entropy reduces the Gibbs free energy, which theoretically suppresses element segregation and phase separation, enhancing structural stability under electrochemical cycling [5-7, 10-13]. Particularly when oxygen-containing intermediates exhibit complementary adsorption behaviors at different metal sites, the synergistic effect of multiple active sites can disrupt the scaling relationships of oxygen-related reactions (e.g., $\ast\text{O}$, $\ast\text{OH}$, $\ast\text{OOH}$), resulting in higher intrinsic activity [14, 15]. However, driven by the thermodynamics to minimize surface energy, Reported HESs predominantly exist as crystalline phases. Crystalline high entropy materials, different exposed crystal planes possess distinct atomic arrangements, which imposes a crystal facet dependence on their catalytic activity. Moreover, their rigid lattice frameworks are susceptible to degradation from repeated volume changes during cycling, often compromising rate capability and long-term durability [16-18]. Conversely, amorphous materials, which lack long-range atomic order, possess abundant dangling bonds, unsaturated coordination sites and defect structures, offering inherently higher densities of active site [19, 20]. The structural flexibility of amorphous frameworks can better accommodate volume strain, thereby improving mechanical and structural robustness during electrochemical processes [21-24]. Furthermore, synthesizing a-HESs presents a promising avenue to circumvent the inherent limitations of their crystalline

counterparts [25]. However, the synthesis of phase-pure a-HESs remains a formidable challenge. Firstly, although the high mixing entropy of multi-component systems favors single-phase stability, metal atoms still tend to migrate and order during conventional synthesis processes (such as high-temperature sulfidation and heat treatment) [26, 27], leading to the formation of local crystalline domains or even complete crystallization, which makes it difficult to obtain the thermodynamically metastable pure amorphous phase. Second, while suppressing crystallization is critical, ensuring homogeneous mixing of five or more metal elements is equally important, further increasing the difficulty of synthesis.

Conventional synthesis routes, such as hydrothermal/solvothermal methods [28, 29], high-temperature solid-state reactions [30, 31], rapid quenching [32, 33], and chemical precipitation [34, 35], each has inherent shortcomings. Hydrothermal and solvothermal methods are prone to elemental segregation due to differences in hydrolysis and precipitation rates among multiple metal ions, typically yielding crystalline or partially crystalline products. High-temperature solid-state reactions require harsh conditions that strongly promote atomic ordering, making crystallization inevitable. Rapid quenching demands extremely high cooling rates as well as sophisticated equipment. Although chemical precipitation is operationally straightforward, it often suffers from elemental segregation and compositional inhomogeneity caused by variations in solubility products during multi-element co-precipitation, resulting in products that are frequently crystalline or mixed-phase. Consequently, existing synthesis strategies struggle to simultaneously achieve precise kinetic and thermodynamic control to obtain both an "amorphous state" and "homogeneous multi-element mixing". In this context, the use of multifunctional additives provides a feasible pathway for synergistically suppressing crystallization and elemental segregation.

Graphdiyne oxide (GDYO) is a functionalized derivative of graphdiyne (GDY), synthesized through the oxidation of the terminal acetylenes at the edges to form carboxyl groups [36-38]. GDYO not only preserves the integrity of GDY's sp and sp^2 hybridized two-dimensional structure but also incorporates carboxyl functional groups. This configuration imparts uniformly distributed and tunable electronic properties, a porous structure, high π -conjugation characteristics and abundant oxygen-containing functional groups [39-45]. These electron-withdrawing groups can coordinate with many metal ions and exhibit significant hydrophilicity. The unique structural features of GDYO render it an ideal regulatory carrier for the synthesis of various functional materials. For instance, Xu et al. employed GDYO as a substrate,

leveraging its self-terminating electron transfer process with the metal precursor RuCl_3 , alongside the electrostatic adsorption effect of GDYO's abundant acetylenic bonds and the confinement effect of triangular pores, successfully fabricating Ru@GDYO with high metal loading and small size [46]. Yao et al. modified SnO_2 using GDYO as a functional additive, leveraging the interaction between the oxygen-containing groups of GDYO and PbI_2 to suppress the crystallinity of PbI_2 . This yielded a perovskite conductive layer with fewer defects, higher conductivity, and better-matched energy levels [47]. Wang et al. modified the zinc anode using GDYO, where the abundant triangular pores in the GDYO framework facilitated a uniform electrolyte flux, and electrostatic interactions between the acetylenic bonds and metallic zinc promoted uniform planar deposition of metallic Zn [48].

Herein, we propose an innovative GDYO-mediated strategy to tackle this dual synthesis challenge. GDYO's versatile chemical structure enables multifunctional control: the carboxyl groups can selectively coordinate with various metal ions, ensuring their uniform dispersion; the alkyne bonds can electrostatically anchor and inhibit the agglomeration of nascent metal-sulfide nuclei; and its nanoscale pores can provide a spatially confined environment that retards the ordered growth of these nuclei. Leveraging these features, we introduce a facile, in-situ synthesis route for preparing homogeneous amorphous high-entropy sulfide-graphdiyne oxide composite (a-HESs-GDYO). This "triple-effect synergistic regulation" exerted by GDYO overcomes the hurdles of "easy crystallization" and "elemental segregation", allowing for the controllable fabrication of well-defined a-HESs under mild conditions. The resulting a-HESs-GDYO catalyst, benefiting from its amorphous nature and compositional synergy, demonstrates significantly enhanced ORR electrocatalytic activity. When employed as an air cathode in ZABs, it delivers superior battery performance including a high-power density of 133 mW cm^{-2} and an extended cycle life exceeding 1500 hours, especially when coupled with a GDY-modified Zn anode. This work not only presents a generalizable and effective strategy for synthesizing high-performance a-HESs but also establishes a paradigm for designing advanced materials for next-generation metal-air batteries.

2. Experimental

2.1. Synthesis of graphdiyne (GDY)

The entire procedure was carried out under a nitrogen atmosphere. In the three-necked flask of the polymerization apparatus, 10 mL of TMEDA, 16 mg of CuI , and 40 mL of a pyridine solution were added. After the dry desilication of HEB, 200 mg of the monomer HEB was dissolved in 50 mL of pyridine solution and transferred to a constant pressure addition funnel, with the funnel's valve adjusted accordingly. The solution was then added dropwise to the three-necked flask over a period of more than 8 hours. The mixture was heated at 50°C for 12

hours in the dark and allowed to react for three days. The resulting powder was washed with ammonia to remove excess CuI and then rinsed with distilled water until neutral. Finally, GDY powder was obtained through vacuum drying.

2.2. Synthesis of graphdiyne oxide (GDYO)

GDYO was obtained through the acid oxidation of GDY. Briefly, 100 mg of GDY powder was carefully mixed with 1.2 mL of concentrated H_2SO_4 in an ice bath for 10 minutes. Next, 1.8 mL of 30 wt% H_2O_2 was slowly added while stirring vigorously. The mixed solution was allowed to react at room temperature for 12 hours, resulting in a brown suspension, referred to as the graphdiyne oxide solution. Finally, GDYO powder was obtained by freeze-drying the graphdiyne oxide solution.

2.3. Synthesis of Zn/GDY

Copper foil serves as the catalyst for the coupling reaction, while zinc foil (Zn foil: $85 \times 3.4 \times 2 \text{ mm}$) acts as the growth substrate for graphdiyne. The copper foil is subjected to ultrasonic treatment in 6 M HCl (to remove surface oxides), H_2O (to eliminate HCl residues), and acetone (to remove moisture), each for 15 minutes, and is then stored in acetone for later use. Under nitrogen protection, 50 mL of a pyridine solution containing 5 mg of HEB is slowly added to 50 mL of a pyridine solution containing an appropriate amount of copper foil and zinc foil (this process takes 2~3 hours to complete), followed by allowing the mixture to react for 24 hours at 50°C in the dark. After cooling, the zinc foil is removed and washed sequentially with acetone, hot DMF (80°C), and acetone to eliminate surface organic solvents and oligomers, and then air-dried, ultimately yielding a zinc electrode modified with graphdiyne, labeled as Zn/GDY.

2.4. Synthesis of HESs

Initially, a high-entropy glycerate salt template was synthesized using a simple solvothermal method. Equal molar amounts (0.5 mmol) of metal nitrates ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) were dissolved in 15 mL of isopropanol, followed by the addition of 3 mL of glycerol. The uniformly mixed solution was transferred to a 25 mL stainless steel autoclave and subjected to solvothermal reaction at 150°C for 10 hours. The resulting powder was collected to serve as a template for the synthesis of metal sulfides, and was named as P-M. Subsequently, 100 mg of the synthesized metal glycerate was dispersed in 50 mL of ethanol, and 200 mg of thioacetamide was added. After stirring the mixture for 30 minutes, it was transferred to a 25 mL stainless steel autoclave for a solvothermal reaction at 160°C for 8 hours. The reactants were centrifugally washed to obtain HESs.

2.5. Synthesis of a-HESs-GDYO

Initially, the precursor was synthesized using a simple solvothermal method. GDYO (20 mg) was mixed with 2 mg of equimolar (0.5 mmol) metal nitrates ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) in mass ratios of 15:1,

10:1, 5:1, and 1:1, respectively, in 15 mL of isopropanol. Subsequently, 3 mL of glycerol was added, and the resulting homogeneous solution was transferred to a 25 mL stainless steel autoclave for a solvothermal reaction at 150 °C for 10 hours. The obtained powders were collected and used as precursors for metal sulfide synthesis, designated as P-M-GDYO-15, P-a-M-GDYO, P-M-GDYO-5 and P-M-GDYO-1, respectively. Then, 10 mg of each precursor powder was dispersed in 50 mL of ethanol, and 4 mg of thioacetamide was added to each. After stirring the mixture for 30 minutes, it was transferred to a 25 mL stainless steel autoclave for a solvothermal reaction at 160°C for 8 hours. The products were washed by centrifugation to yield HESs-GDYO-15, HESs-GDYO-10 (a-HESs-GDYO), HESs-GDYO-5, and HESs-GDYO-1.

2.6. Synthesis of mechanically mixed c-HESs/GDYO

To keep the metal loading in c-HESs/GDYO consistent with that in a-HESs-GDYO, 10 mg of GDYO and 1 mg of HESs were vigorously stirred in 20 mL of deionized water for 4 h. The reactants were then centrifuged and washed to obtain c-HESs/GDYO.

3. Results and discussion

3.1 Synthesis and Characterization of Materials

The amorphization synthesis of high-entropy sulfides is facilitated by graphdiyne oxide (GDYO), which serves as a structure-directing agent due to its unique structural and chemical properties. A schematic representation of the preparation process is illustrated in **Fig. 1(a)**. Initially, GDYO and five metal salts (Fe, Ni, Co, Cr, and Mn, with a mass ratio of $m_{\text{GDYO}}/m_{\text{M}}=10:1$) are dispersed in an isopropanol solution and thoroughly mixed under stirring. The strong coordination interactions between the abundant oxygen-containing functional groups (such as carboxyl and hydroxyl groups) on GDYO and the metal cations lead to the formation of a stable coordination complex. Notably, the carboxyl groups on GDYO facilitate selective coordination with various metal cations, while a continuous three-dimensional (3D) network structure is established through cross-linking among these functional groups. Subsequently, the resulting coordination complex undergoes sulfidation, ultimately yielding amorphous high-entropy sulfides with a 3D network architecture. The transmission electron microscopy (TEM) image of a-HESs-GDYO displays amorphous carbon with a layered structure consistent with the morphology of GDYO (**Fig. 1(b)**), corroborating the observation that only the characteristic peaks of carbon were detected in XRD pattern (**Fig. S1**). The high-resolution TEM image (**Fig. 1(c)**) reveals no obvious metal particles or discernible lattice fringes of metal species, while the corresponding selected-area electron diffraction (SAED) pattern (**Fig. 1(d)**) exhibits characteristic diffuse diffraction rings, indicating the successful synthesis of an amorphous high-entropy sulfide-graphdiyne oxide (a-HESs-GDYO) composite. The high-angle annular dark field-scanning-

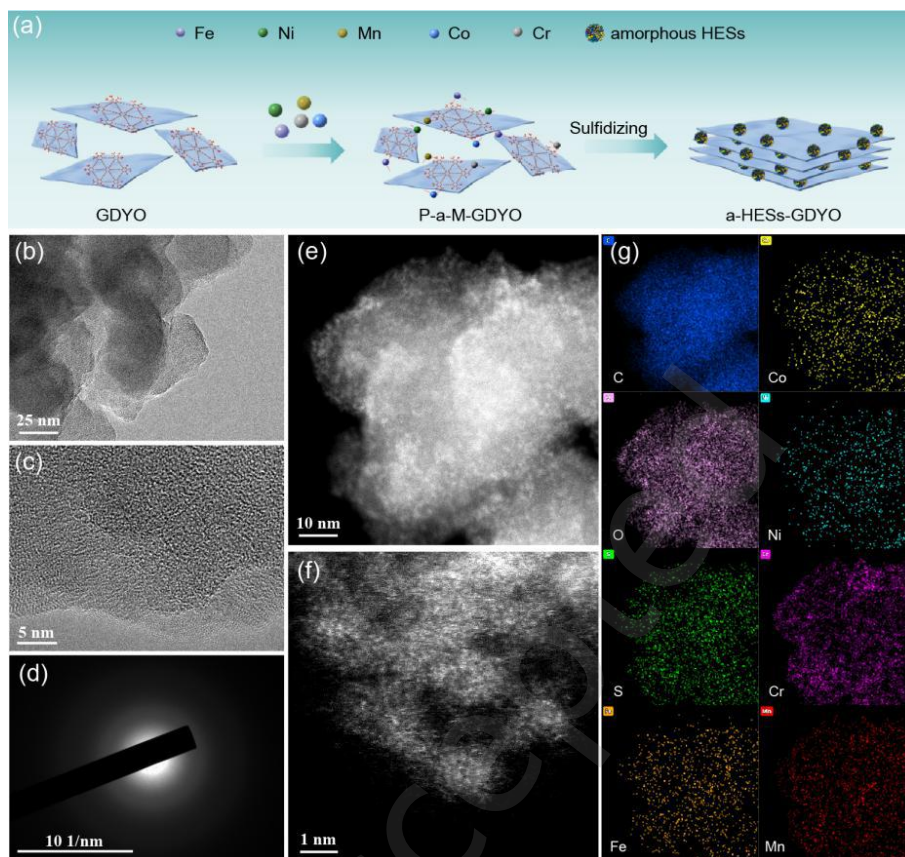


Fig. 1 (a) Synthesis process of a-HESs-GDYO, (b) Transmission Electron Microscopy (TEM) image, (c) High-Resolution Transmission Electron Microscopy (HRTEM) image, (d) Selected Area Electron Diffraction (SAED) pattern, (e-f) Aberration-Corrected Scanning Transmission Electron Microscopy (AC-STEM) images, and (g) Elemental mapping images of a-HESs-GDY.

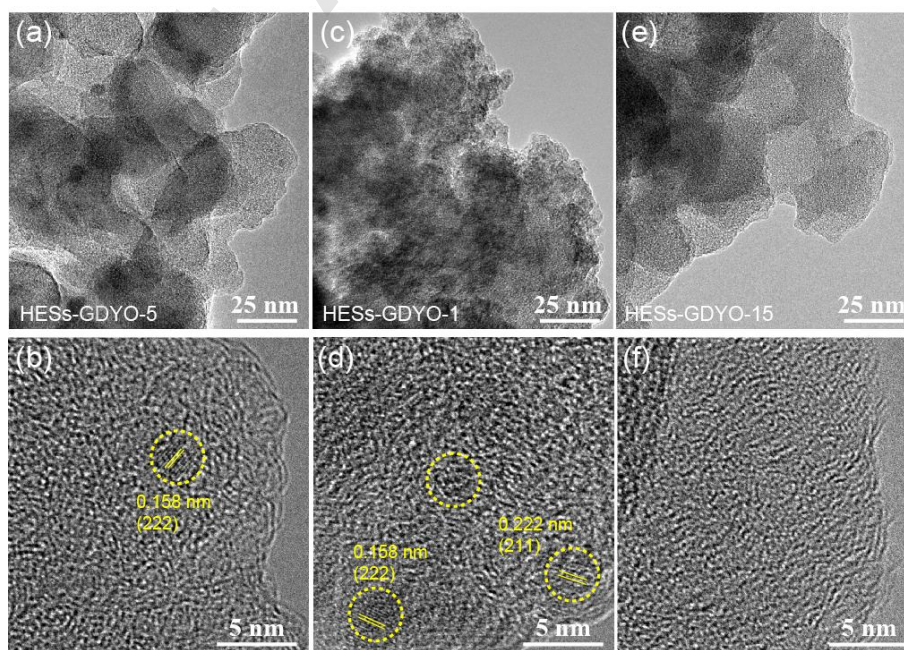


Fig. 2. TEM and HRTEM images of (a,b) HESs-GDYO-1, (c,d) HESs-GDYO-5 and (e,f) HESs-GDYO-15.

transmission electron microscopy (HAADF-STEM) image in **Fig. 1(e)** clearly shows a uniformly distributed population of bright dots, attributed to metal species. The atomic-resolution HAADF-STEM image in **Fig. 1(f)** further reveals that the average size of these nanoparticles is less than 2 nm, with no distinct lattice fringes, consistent with the results obtained from SAED. Additionally, the energy-dispersive X-ray spectroscopy (EDS) image shows that C, O, S, Fe, Ni, Co, Cr, and Mn are distributed throughout the structure (**Fig. 1(g)**) with the concentrations of each metal element approaching an equimolar ratio (1.23:1.15:1.15:1.23:1, **Fig. S2**), further confirming the successful fabrication of the amorphous high-entropy sulfides.

To investigate the effect of GDYO on material structure, single-component metal sulfides were initially synthesized, followed by the preparation of their corresponding single-metal sulfide-GDYO composite samples through the incorporation of GDYO to the reaction system. XRD results (**Fig. S3**) indicated that all prepared single-metal sulfides exhibited crystalline phases, with the exception of CrS, which was found to be amorphous. The crystalline phases were identified as FeS₂ (JCPDS#01-079-0617), Co₃S₄ (PDF#02-1361), MnS (PDF#03-1062), and Ni₃S₄ (PDF#08-0106). The successful synthesis of amorphous single-metal sulfides, achieved with the addition of GDYO as a functional modifier further demonstrates that GDYO effectively promotes the formation of an amorphous structure. To elucidate the role of GDYO in inducing the synthesis of amorphous high-entropy sulfides, we designed a series of variable experiments by adjusting the amount of GDYO added to the reaction system. When no GDYO was incorporated, the resulting metal salt precursor exhibited an aggregated microspherical structure (**Fig. S(4)**), which transformed into agglomerated nanoparticles after

sulfidation (**Fig. S5(a)**). The XRD results (**Fig. S6**) demonstrate that the structure of the obtained pure high-entropy samples is consistent with that of the single-metal FeS₂ (PDF#01-079-0617), which matches the results reported in the literature. High-resolution transmission electron microscopy (HRTEM) images revealed distinct lattice fringes at 0.158 nm and 0.222 nm, corresponding to the (222) and (211) crystal planes of FeS₂ (**Fig. S5(b)**) [49]. Selected-area electron diffraction (SAED) patterns displayed sharp diffraction spots (**Fig. S7**), confirming the product as crystalline high-entropy sulfides (pure HESs). Elemental mapping further demonstrated that all metals elements are uniformly distributed at a nearly equimolar ratio (**Fig. S8**). The influence of GDYO dosage on the structure and morphology of the resulting high-entropy sulfides was further investigated by systematically tuning the mass ratio of GDYO to metal precursors ($m_{\text{GDYO}}/m_{\text{M}}$). As shown in **Figs. 2(a) and 2(b)**, at $m_{\text{GDYO}}/m_{\text{M}} = 1:1$ (HESs-GDYO-1), the product transformed from the aggregated particles observed in the GDYO-free sample into dispersed nanoparticles with a size of approximately 2 nm. HRTEM images reveal that the lattice fringes remain consistent with those of pristine HESs, indicating that at this ratio, GDYO effectively suppresses particle agglomeration during high-temperature sulfidation. When the ratio was increased to 5:1 (HESs-GDYO-5), the product maintained a similar dispersed morphology (**Figs. 2(c) and 2(d)**). However, upon further increasing the ratio to 10:1 (a-HESs-GDYO) or 15:1 (HESs-GDYO-15), no visible metal particles or lattice fringes were observed in the HRTEM images (**Figs. 2(e) and 2(f)**), suggesting a complete transformation to the amorphous state. XRD results (**Fig. S9**) further corroborate this evolution: at $m_{\text{GDYO}}/m_{\text{M}} = 10:1$ or 15:1, no characteristic diffraction peaks corresponding to metal compounds are detected, confirming its fully amorphous nature; in contrast, when the ratio decreases to 5:1, 1:1, and 0.5:1, crystalline

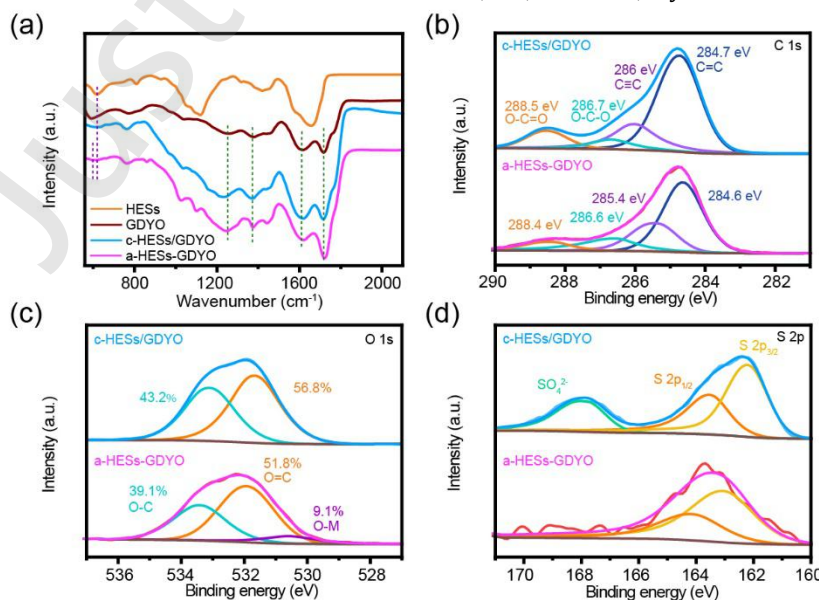


Fig. 3 (a) FT-IR spectra of a-HESs-GDYO and references, (b) C 1s XPS spectra, (c) O 1s XPS spectra, (d) S 2p XPS spectra of a-

HESs-GDYO and mechanically mixed HESs/GDYO.

diffraction peaks attributable to metal species emerge in the XRD patterns, indicating that insufficient GDYO dosage fails to effectively suppress crystalline phase formation. Collectively, these results demonstrate that GDYO can effectively induce the formation of amorphous structures through surface interactions, and enable a controllable transformation of high-entropy sulfides from crystalline to amorphous states by precisely adjusting its dosage, thereby playing a critical structure-directing role during the synthesis process.

To investigate the mechanism by which GDYO induces the synthesis of amorphous high-entropy sulfides through specific interactions, we prepared composite samples of pure high-entropy sulfides (HESs) with GDYO (denoted as c-HESs/GDYO) using a mechanical mixing method and conducted a comparative analysis. The X-ray diffraction (XRD) patterns (**Fig. S10**) revealed that c-HESs/GDYO retained the characteristic diffraction peaks of HESs, although their intensity significantly decreased compared to pure HESs. This phenomenon may be attributed to the reduced particle size of HESs, which is caused by the dispersing effect of GDYO. High-magnification transmission electron microscopy (TEM) images (**Fig. S11(a)**) show that HESs nanoparticles, with sizes of approximately 5–10 nm, are uniformly dispersed on the GDYO substrate surface. This indicates a transition from agglomerated to uniformly dispersed nanoparticles on the GDYO surface due to mechanical mixing. However, their size remains larger than that of the in-situ synthesized a-HESs-GDYO sample (approximately 2 nm) prepared under the same conditions. This size difference can be ascribed to the confinement effect of triangular pores in GDYO during the in-situ synthesis process. These results demonstrate that the alkynyl groups on the GDYO surface effectively inhibit particle agglomeration through electrostatic adsorption, promoting the uniform anchoring of HESs, while its uniform pore structure provides spatial constraints that suppress crystal growth. The high-resolution TEM image of c-HESs/GDYO (**Fig. S11(b)**) reveals lattice fringes with an interplanar spacing of 0.178 nm, confirming that mechanical mixing achieves good dispersion and stabilization of crystalline high-entropy sulfides while maintaining their crystal structure. This conclusion is further corroborated by the selected-area electron diffraction results (**Fig. S12**). Moreover, to clarify the role of carboxyl groups in the formation of amorphous high-entropy sulfides, graphene oxide (GO) and GDY were employed as functional additive to replace GDYO. As shown in **Fig. S13(a-c)**, under identical synthesis conditions, distinct lattice fringes are observed in the HRTEM images of the samples prepared with GO instead of GDYO. This finding indicates that the mere presence of carboxyl groups is insufficient to induce amorphization of high-entropy sulfides. In contrast, when GDY is used as the additive (**Figs. S13(d-f)**), no lattice fringes are detected in either the

HRTEM or FFT images, highlighting that both alkyne linkages and pore structures are essential for the successful synthesis of amorphous high-entropy sulfides. In summary, the comparative results highlight the crucial role of GDYO with its unique structural advantages, in facilitating the amorphization of high-entropy sulfides.

The results of the infrared spectroscopy analysis (**Fig. 3(a)**), reveal distinct interaction characteristics between GDYO and high-entropy sulfides. In the pure GDYO sample, characteristic peaks at 1718 cm^{-1} , 1613 cm^{-1} , 1377 cm^{-1} , and 1250 cm^{-1} correspond to the stretching vibrations of C=O, and C=C, as well as the bending vibrations of C-O and O-H, indicating a high abundance of carboxyl functional groups in the material. For the pure high-entropy sulfides, the absorption peak at 619 cm^{-1} corresponds to the stretching vibration of the metal-sulfur bond (M-S), while the peak at 1123 cm^{-1} is attributed to the vibration of the S-O bond. In the a-HESs-GDYO composite sample, the characteristic peaks of GDYO, including those related to carboxyl groups and carbon-carbon double bonds, shift towards lower wavenumbers, suggesting potential coordination between the carboxyl groups and metal ions. Additionally, the vibration peak of the M-S bond shifts to 612 cm^{-1} , further confirming the presence of chemical interactions between GDYO and high-entropy sulfides, likely originating from the coordination between carboxyl groups and metal ions. In contrast, the infrared spectrum of the mechanically mixed sample shows no significant changes in the positions of the characteristic peaks of GDYO and high-entropy sulfides, and the S-O vibration peak at 1123 cm^{-1} is not observed, indicating that the two components exhibit only physical interaction without forming effective chemical interactions. X-ray photoelectron spectroscopy (XPS) was employed to further investigate the surface functionalization of a-HESs-GDYO. In **Fig. 3(b)**, the C 1s spectrum of the physically mixed c-HESs/GDYO is deconvoluted into four subpeaks at 284.5 eV (C-C), 285.2 eV ($\text{C}\equiv\text{C}$), 286.9 eV (C-O), and 288.5 eV (C=O), which aligns with that of pure GDYO (**Fig. S14**), confirming that only physical mixing occurs between the two components. Conversely, the C 1s spectrum of a-HESs-GDYO exhibits significant changes: the characteristic peak attributed to carboxyl carbon (C=O, 288.4 eV) disappears, and the entire C 1s spectrum broadens noticeably, with an overall binding energy shift towards lower energy. This indicates that the carboxyl groups in GDYO coordinate with metal ions, leading to a reduction in the electron cloud density of the carbon framework. The O 1s spectrum of a-HESs-GDYO (**Fig. 3(c)**) displays a characteristic peak of metal-oxygen bonds (M-O) at 530.0 eV, which is absent in the mechanically mixed sample, indicating the formation of a metal-carboxyl coordination structure during the in-situ synthesis process. Additionally, the S 2p spectrum of the physically mixed c-HESs/GDYO (**Fig. 3(d)**) can be

deconvoluted into three peaks at 163.2 eV, 164.3 eV and 168.5 eV, corresponding to S 2p_{3/2}, S 2p_{1/2} and sulfur oxides, respectively [50, 51]. The peak for sulfur oxides at 168.5 eV suggests that high-entropy sulfide undergoes surface oxidation during synthesis or exposure to air. However, this oxidation peak is not detected in a-HESs-GDYO, further proving that the strong interfacial interaction between GDYO and high-entropy sulfide effectively suppresses the oxidation of the sulfide and enhances the chemical stability of the material. These results indicate that a strong interfacial chemical interaction is established between GDYO and high-entropy sulfide through metal-carboxyl coordination in the a-HESs-GDYO composite material.

3.2. Formation mechanism of a-HESs-GDYO

Based on the experimental results presented, we propose that the formation mechanism of GDYO-induced amorphous high-entropy sulfides can be divided into three distinct steps. First, the carboxyl functional groups abundant on the surface of GDYO engage in strong coordination interactions with metal ions (such as Fe³⁺, Ni²⁺, Co²⁺, Cr³⁺, and Mn²⁺), forming a three-dimensional cross-linked 'GDYO-metal ion' composite precursor. The carboxyl functional groups provide uniform coordination sites for metal ions, facilitating their homogeneous dispersion at the molecular level. Simultaneously, the spatial constraints imposed by the coordination bonds effectively suppress the free diffusion of metal ions, thereby laying the foundation for uniform multimetal nucleation. Second, the FeNiCoCrMn-glycerate precursor nuclei formed during the subsequent reaction are anchored onto the GDYO surface via electrostatic adsorption by the sp-C (alkynyl) bonds and uniformly distributed along the sp-C chains. The uniform pore channels of GDYO provide a physical confinement space for the growth of these sub-nanometer nuclei—the nuclei progressively fill one

triangular pore and extend into adjacent pores until the entire hexagonal unit (theoretical aperture of ~1.1 nm) is fully occupied [52-56]. These sp-C framework and pore-confining effect effectively inhibits the migration and aggregation of nuclei before and after sulfidation, preventing their growth into larger crystals via Ostwald ripening. Third, the strong coordination between GDYO and metal ions persists throughout the entire sulfidation process, and the three-dimensional network continuously disrupts the ordered growth of the high-entropy sulfide lattice. Due to differences in hydration radii and diffusion rates among the five metal ions, elemental segregation tends to occur under unconstrained conditions. However, the multi-metal synergistic coordination by carboxyl groups and the pore-confinement effect uniformly anchor ions of varying sizes within the GDYO framework, effectively suppressing this tendency and ensuring molecular-level uniform dispersion of each ion. The sustained coordination hinders the long-range ordered arrangement of metal ions according to specific rules, ultimately stabilizing the sulfide product in the amorphous state. The effective functioning of the above three synergistic effects depends on a sufficient GDYO dosage. When the GDYO amount is insufficient (e.g., $m_{\text{GDYO}}/m_{\text{M}} \leq 5:1$), both the density of coordination sites and the number of pore channels are significantly reduced. The spatial confinement provided by GDYO becomes insufficient to cover all nucleating metal species. Some metal ions or initial nanocrystals that are not effectively anchored can freely diffuse and collide in solution, gradually growing via Ostwald ripening. Once the nanocrystal size exceeds the effective confinement size of the GDYO triangular pores (theoretical ~5.5 Å), they escape the pore constraints and grow freely in three-dimensional space, arranging into a crystal lattice according to the minimum-energy principle, ultimately forming crystalline high-entropy sulfides. This comparative result confirms, from the opposite perspective,

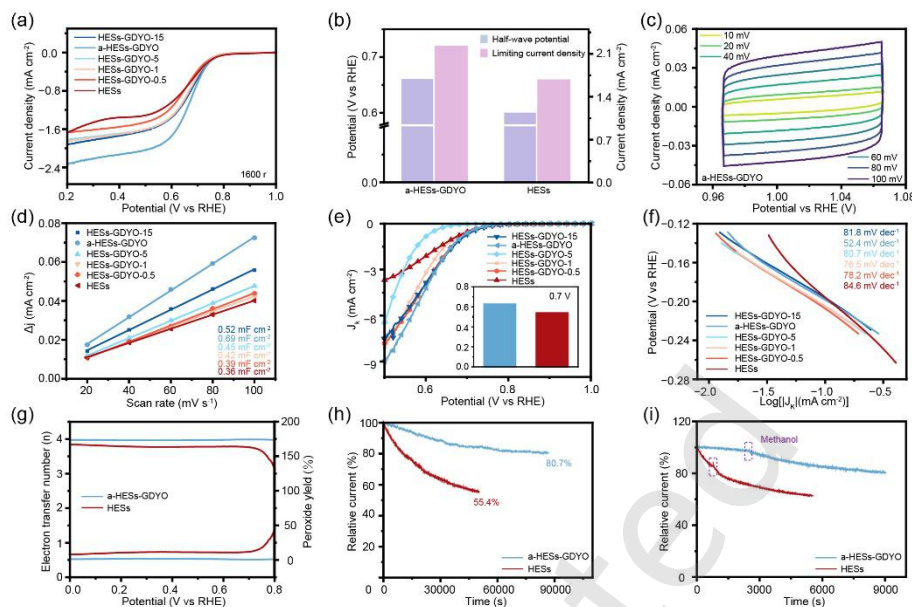


Fig. 4 (a) Linear sweep voltammetry (LSV) curves of samples with different GDYO loadings in O_2 -saturated 0.1 M KOH solution at a rotation rate of 1600 rpm; (b) Onset potential (E_{onset}) and half-wave potential ($E_{1/2}$) of a-HESs-GDYO and HESs; (c) Cyclic voltammetry (CV) curves of a-HESs-GDYO at different scan rates; (d) Electrochemical active surface area; (e) ORR kinetic current density, and (f) ORR Tafel slope of samples with different GDYO loadings; (g) Rotating ring-disk electrode (RRDE) polarization curves of a-HESs-GDYO and HESs; (h) Chronoamperometric (i-t) curves, and (i) methanol tolerance test results of a-HESs-GDYO and HESs.

the irreplaceable role of GDYO in the amorphization process.

3.3. Electrochemical performance

The ORR performance of the samples was evaluated through rotating disk electrode (RDE) measurements in O_2 -saturated 0.1 M KOH electrolyte. As shown in **Fig. 4(a)** and **Fig. 4(b)**, a-HESs-GDYO ($m_{GDYO}/m_{HESs} = 10:1$) exhibited optimal performance with a half-wave potential ($E_{1/2}$) of 0.66 V, which is notably higher than that of other composite counterparts: pure HESs ($E_{1/2} = 0.60$ V), HESs-GDYO-0.5 (0.5:1, $E_{1/2} = 0.64$ V), HESs-GDYO-1 (1:1, $E_{1/2} = 0.65$ V), HESs-GDYO-5 (5:1, $E_{1/2} = 0.65$ V), HESs-GDYO-15 (15:1, $E_{1/2} = 0.65$ V), and physically mixed c-HESs/GDYO ($E_{1/2} = 0.56$ V) (**Fig. S15(a)**). These results demonstrate that the incorporation of GDYO significantly enhances the ORR activity of high-entropy sulfides, likely due to the GDYO-induced amorphous structure exposing more accessible active sites. Furthermore, the ORR performance of pristine single-metal sulfides and their corresponding amorphous single-metal sulfide counterparts was evaluated. Pristine single-metal sulfides exhibit relatively poor ORR activity, with half-wave potentials ($E_{1/2}$) of 0.57 V (CoS), 0.38 V (FeS₂), 0.56 V (CrS), 0.55 V (MnS), and 0.58 V ((Ni₃S₄), all lower than that of high-entropy sulfide (HESs), which show a more positive $E_{1/2}$ of 0.60 V (**Figs. S16(a) and S16(b)**). A similar trend is observed for the amorphous systems, where a-HESs-GDYO exhibits a significantly higher $E_{1/2}$ of 0.66 V than the amorphous single-metal sulfide/GDYO counterparts. These

comparisons indicate that the cooperative interaction among multiple metal components is indispensable. The results confirm that a significant synergistic effect exists among the high-entropy multi-metal components. Although the $E_{1/2}$ value of a-HES-GDYO remains lower than that of commercial Pt/C (0.86 V, **Fig. S17(a) and S17(b)**), the catalyst exhibits superior long-term stability, retaining 80.7% of its initial current after 90,000 s compared with approximately 73% retention for Pt/C after 20,000 s. The relatively low $E_{1/2}$ and limiting current density may be associated with the strong hydrophilicity and two-dimensional layered structure of GDYO, which can hinder oxygen mass transport under static rotating disk electrode (RDE) testing conditions. To clarify the mechanism underlying this activity enhancement, cyclic voltammetry (CV) curves were measured at different scan rates within the non-Faradaic region (**Fig. 4(c) and S18**). The electrochemical active surface area (ECSA) was quantified by calculating the double-layer capacitance (C_{dl}). As presented in **Fig. 4d**, a-HESs-GDYO exhibited a C_{dl} value of 0.69 $mF \cdot cm^{-2}$ —approximately twice that of pure HESs (0.36 $mF \cdot cm^{-2}$) and significantly higher than those of other composites: HESs-GDYO-5 (0.39 $mF \cdot cm^{-2}$), HESs-GDYO-1 (0.42 $mF \cdot cm^{-2}$), HESs-GDYO-5 (0.45 $mF \cdot cm^{-2}$), HESs-GDYO-15 (0.52 $mF \cdot cm^{-2}$) and physically mixed c-HESs/GDYO (0.23 $mF \cdot cm^{-2}$) (**Fig. S15(b)**). This improvement is attributed to the abundant edge sites, defects, and dangling bonds generated by the amorphous structure [57–61], which increase the density of active sites and enable a-HESs-GDYO-10 to provide more active sites for

electrochemical reactions. A further analysis of ORR reaction kinetics (before and after GDYO incorporation) is shown in **Fig. 4(e)**. a-HESs-GDYO exhibited the lowest Tafel slope of 52.4 mV dec^{-1} , lower than that of pure HESs (84.6 mV dec^{-1}) and other composites: HESs-GDYO-0.5 (76.5 mV dec^{-1}), HESs-GDYO-1 (78.2 mV dec^{-1}), HESs-GDYO-5 (80.7 mV dec^{-1}), and HESs-GDYO-15 (81.8 mV dec^{-1}). This indicates that GDYO incorporation significantly improves reaction kinetics. Additionally, the kinetic current density of a-HESs-GDYO at 0.70 V was calculated to be $0.63 \text{ mA}\cdot\text{cm}^{-2}$ (**Fig. 4(f)**)—substantially higher than that of pure HESs ($0.54 \text{ mA}\cdot\text{cm}^{-2}$) and the mechanically mixed c-HESs/GDYO ($0.37 \text{ mA}\cdot\text{cm}^{-2}$) (**Fig. S15(c)**)—further confirming its excellent ORR reaction kinetics. To assess the effect of GDYO incorporation on the ORR selectivity of high-entropy sulfides, rotating ring-disk electrode (RRDE) measurements were performed to determine the electron transfer number (n) and hydrogen peroxide (H_2O_2) yield. As shown in **Fig. 4(g)**, compared with pure HESs ($n = 3.84$, H_2O_2 yield $>10\%$), a-HESs-GDYO exhibited a higher average electron transfer number (~ 3.98) and a lower H_2O_2 yield ($<2\%$). This demonstrates that the in-situ incorporation of GDYO not only enhances reaction kinetics but also significantly improves catalyst selectivity, favoring the more desirable four-electron transfer pathway. This enhanced selectivity is likely due to the amorphous structure—compared to crystalline structures—providing more abundant active sites and a more optimized electronic structure. Beyond selectivity and kinetics, catalyst stability is critical. The stability of a-HESs-GDYO was evaluated via chronoamperometry at 0.45 V vs. reversible hydrogen electrode (RHE). As shown in Figure 4h, after continuous operation for $90,000 \text{ s}$, the ORR current retention rate of a-HESs-GDYO remained as high as 80.7% . In contrast, the current retention rate of pure HESs dropped to 55.4% after only $50,000 \text{ s}$ of testing. This result fully confirms that GDYO incorporation significantly enhances the long-term operational stability of the catalyst. To further evaluate the selectivity and anti-interference capability of the active sites of the a-HESs-GDYO toward ORR, we perform a methanol tolerance test using methanol as a representative small-molecule interference probe. During the stability test, 15 mL of methanol was added to the electrolyte (final concentration: 10 mM). As shown in **Fig. 4(i)**, the current of a-HESs-GDYO showed only a slight fluctuation after methanol addition and quickly recovered, retaining 80.6% after $9,000 \text{ s}$ of continuous operation. In contrast, pristine HESs exhibited a much more pronounced current response upon methanol addition, and its current retention decreased to 62.5% after $6,000 \text{ s}$ of operation. Those results indicate that the in-situ incorporation of GDYO significantly enhances the methanol tolerance of the catalyst toward methanol interference and reflects improved ORR selectivity and operational robustness.

In 1 M KOH solution, the OER activity of single-metal

sulfides, high-entropy sulfides, and their corresponding amorphous samples was further evaluated. **As shown in Fig. S19(a)**, the overpotentials at 10 mA cm^{-2} (η_{10}) for CoS and Ni_3S_4 are 330 mV and 397 mV , respectively, while CrS, FeS_2 and MnS exhibit relatively poor OER activity. When five metal elements are combined to form a crystalline high-entropy sulfide, the material shows significantly OER activity with an η_{10} of 239 mV . Similarly, among the amorphous samples, the amorphous single-metal sulfides (CoS, Ni_3S_4 , CrS, FeS_2 and MnS) still display limited OER activity (**Fig. S19(b)**), whereas the amorphous high-entropy sulfide (a-HESs-GDYO) exhibits a markedly OER performance with η_{10} of 340 mV . These results indicated a pronounced synergistic effect among the multiple metal components in high-entropy system. Furthermore, the OER performance of HESs synthesized with different amounts of GDYO was further investigated. **As shown in Fig. S19(c)**, HESs-GDYO-10 (a-HESs-GDYO) exhibits the best OER activity ($\eta_{10} = 340 \text{ mV}$), outperforming HESs-GDYO-15 ($\eta_{10} = 383 \text{ mV}$), HESs-GDYO-5 ($\eta_{10} = 370 \text{ mV}$), HESs-GDYO-1 ($\eta_{10} = 359 \text{ mV}$), HESs-GDYO-0.5 ($\eta_{10} = 359 \text{ mV}$), and even commercial RuO_2 ($\eta_{10} = 390 \text{ mV}$, **Fig. S17(c)**). To exclude the influence of different metal loadings on OER activity, the mass of metal species across all samples was normalized and obtained the corresponding OER polarization curves (**Fig. S19(d)**). The results show that HESs-GDYO-10 (a-HESs-GDYO) exhibits the highest intrinsic OER activity, with a mass activity of 26.3 mA mg^{-1} at an overpotential of 400 mV , which is higher than those of HESs-GDYO-15 (13.53 mA mg^{-1}), HESs-GDYO-5 (6.57 mA mg^{-1}), HESs-GDYO-1 (3.23 mA mg^{-1}), HESs-GDYO-0.5 (1.88 mA mg^{-1}) and the mechanically mixed c-HESs/GDYO (6.07 mA mg^{-1}).

In addition, the Tafel slopes of all materials was calculated. **As shown in Fig. S19(e)**, a-HESs-GDYO has the smallest Tafel slope (67.1 mV dec^{-1}), indicating the fastest OER kinetics among the tested samples. The electrochemical active surface area (ECSA) of all samples from CV curves recorded at different scan rates in the non-Faradaic region was further estimated. **As shown in Fig. S19(f)**, a-HESs-GDYO possesses the largest C_{dl} value (3.01 mF cm^{-2}), much higher than that of the mechanically mixed c-HESs/GDYO (0.77 mF cm^{-2}), indicating that amorphous high-entropy sulfide has a larger electrochemical active surface area compared to its crystalline counterpart. The intrinsic activity of a-HESs-GDYO was evaluated using ECSA-normalized polarization curves. **As shown in Fig. 19(g)**, the ECSA-normalized specific activity of a-HESs-GDYO at an overpotential of 350 mV is 9.0 mA cm^{-2} , nearly twice that of c-HESs/GDYO (5.6 mA cm^{-2}), demonstrating its higher intrinsic OER activity. In addition, electrochemical impedance spectroscopy (EIS) was employed to further reveal the reaction kinetics and electron-transfer ability associated with the favorable OER performance of a-HESs-GDYO. **From Fig. S19(h)**, the

charge-transfer resistance (R_{ct}) of a-HESs-GDYO is about 21.2 Ω , much smaller than that of c-HESs/GDYO (81.2 Ω), HESs-GDYO-15 (33.5 Ω), HESs-GDYO-5 (55.2 Ω), HESs-

GDYO-1 (98.7 Ω), HESs-GDYO-0.5 (100.3 Ω), and HESs (37.1 Ω), confirming the fast charge-

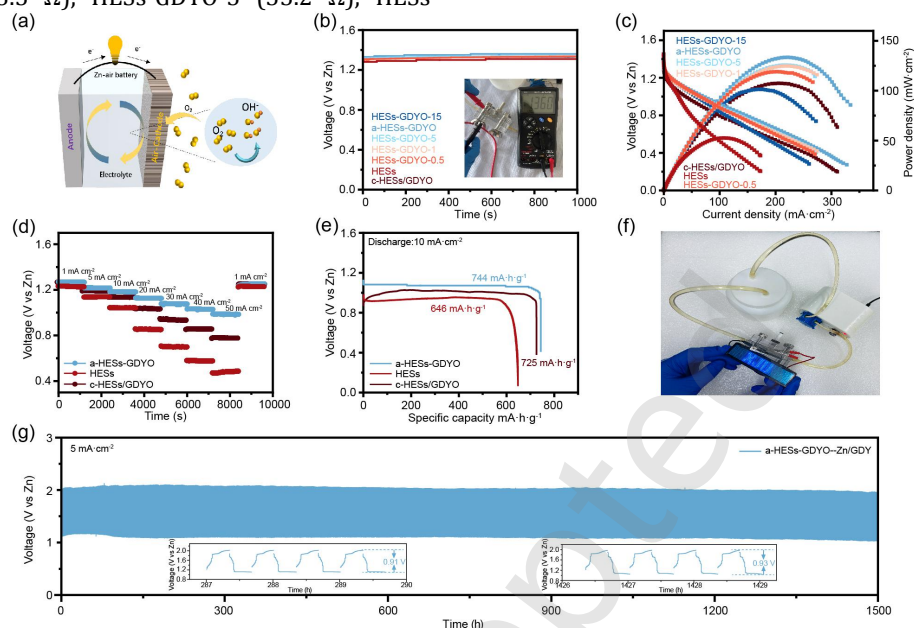


Fig. 5. (a) Schematic diagram of aqueous zinc-air battery; (b) Open circuit voltage diagram, (c) polarization and corresponding power density curves of pure HESs, a-HESs-GDYO and HESs-GDYO-x; (d) The discharge curves of a-HESs-GDYO and pure HESs at different current densities were obtained, (e) the constant current discharge curve at 10 mA cm⁻² current density (specific capacity); (f) The physical map of LED display driven by ZAB; (g) The charge-discharge cycle curve of rechargeable zinc-air battery with a-HESs-GDYO as air cathode at 5 mA cm⁻².

transfer capability of a-HESs-GDYO. Furthermore, the durability of the a-HESs-GDYO catalyst was evaluated by stepwise chronopotentiometry. As shown in Fig. S19(i), the overpotentials of a-HESs-GDYO at 10 mA cm⁻², 50 mA cm⁻², 100 mA cm⁻² and 200 mA cm⁻² are consistently lower than those of c-HESs/GDYO, and the catalyst remains stable during operation. Notably, after continuous testing at 200 mA cm⁻² for 10 h, the degradation of a-HESs-GDYO is negligible, whereas c-HESs/GDYO shows a clear decay trend. The stability of a-HESs-GDYO is also far superior to that of commercial RuO₂ (Fig.17(d)), which retains only about 34% of its initial current density after constant-voltage operation for 10,000 s.

3.4. Zn-air batteries performance

To evaluate the practical application potential of the material in zinc-air batteries (ZABs), we assembled ZABs using the a-HESs-GDYO catalyst as the air cathode (loading: 0.5 mg cm⁻²), a polished zinc plate as the anode, and a 6.0 M KOH + 0.2 M zinc acetate electrolyte (Fig. 5(a)). For comparative analysis, pure HESs, a physically mixed c-HESs/GDYO, and in-situ synthesized HESs-GDYO with varying GDYO contents (HESs-GDYO-x) were also employed as cathodes. As illustrated in Figs. 5(b) and 5(c), the ZAB assembled with pure HESs exhibited an open-circuit voltage (OCV) of 1.31 V and a power density of 52 mW cm⁻². In contrast, the ZAB assembled with the mechanically mixed c-HESs/GDYO achieved an OCV of 1.34

V and a power density of 107 mW cm⁻² (Fig. S20). This preliminary result confirms that the incorporation of GDYO enhances battery performance, which is attributed to the electron-rich alkynyl groups in GDYO that effectively anchor high-entropy nanoparticles and suppress their agglomeration. Notably, the amorphous in-situ synthesized a-HESs-GDYO catalyst delivered enhanced performance, with an OCV of 1.36 V and a high power density of 133 mW cm⁻². This performance not only outperforms that of the physically mixed c-HESs/GDYO but also surpasses those of in-situ synthesized crystalline counterparts and commercial noble metal catalysts: HESs-GDYO-0.5 (1.33 V, 119 mW cm⁻²), HESs-GDYO-1 (1.34 V, 124 mW cm⁻²), HESs-GDYO-5 (1.34 V, 125 mW cm⁻²), HESs-GDYO-15 (1.33 V, 101 mW cm⁻²), and commercial Pt/C//RuO₂ (1.41V, 125 mW cm⁻²), as shown in Figs. S21(a) and S21(b). The enhanced performance of a-HESs-GDYO is likely derived from its higher intrinsic activity and more exposed active sites, which result from its amorphous structure compared to crystalline materials (e.g., HESs-GDYO-x and c-HESs/GDYO), which is consistent with its larger electrochemical active surface area (ECSA).

To assess the rate performance of the ZABs, galvanostatic discharge tests were conducted at current densities ranging from 1 to 50 mA cm⁻² (1, 5, 10, 20, 30, 40, 50 mA cm⁻²), with each current density maintained for 20 minutes (Fig. 5(d) and S21(c)). At low current densities (1

and 5 mA cm^{-2}), the discharge voltages of a-HESs-GDYO and pure HESs were almost identical. However, as the current density increased ($10\text{--}50 \text{ mA cm}^{-2}$), both samples maintained stable voltage platforms, but the gap in their discharge voltages widened significantly. Specifically, at a high current density of 50 mA cm^{-2} , the discharge voltage of a-HESs-GDYO remained above 1.0 V, while that of pure HESs dropped to 0.47 V. This indicates that a-HESs-GDYO possesses superior rate performance and reversibility, implying that a-HESs-GDYO possesses a faster charge transfer and mass transport capability during high current discharge processes. This is primarily attributed to the characteristics of its amorphous structure, where the highly disordered electronic arrangement in a-HESs-GDYO may lead to a broader distribution of electronic states, thereby exposing more active sites and accelerating the charge transfer rate. In addition, the a-HESs-GDYO catalyst achieved a specific capacity of $725 \text{ mA}\cdot\text{h g}^{-1}$ at a current density of 10 mA cm^{-2} (**Fig. 5(e)**), which is higher than that of pure HESs ($646 \text{ mA}\cdot\text{h g}^{-1}$) and noble metal catalysts (694 mAh g^{-1} , **Fig. S21d**). Furthermore, a ZAB assembled with a-HESs-GDYO as the air cathode successfully powered a blue LED display (operating voltage range: 1–5 V, **Fig. 5(f)**), providing direct evidence of its practical power supply capability. To further evaluate the stability of a-HESs-GDYO-based ZABs, charge-discharge cycling tests were performed using a LAND test system at a current density of 5 mA cm^{-2} . As illustrated in **Fig. S22**, the ZABs assembled with an unmodified Zn anode and an a-HESs-GDYO air cathode demonstrates exceptional charge-discharge cycle stability. Specifically, this battery can operate continuously and stably for 680 h while maintaining a voltage gap of 0.96 V throughout the entire cycling process, reflecting its outstanding electrochemical reliability during long-term operation. This performance significantly surpasses that of two control groups: pure HESs-based ZABs (300 h), mechanically mixed c-HESs/GDYO-based ZABs (400 h), even exceeding This performance significantly surpasses that of pure HESs-based ZABs (300 h), and mechanically mixed c-HESs/GDYO-based ZABs (400 h), even exceeding commercial Pt/C//RuO₂ (380 h, **Fig. S21(e)**) and other air electrodes reported in the literature (**Table S1**). These comparative data clearly indicate that the design, composition, and structural characteristics of the air cathode are critical factors that directly influence the charge-discharge cycle stability and overall electrochemical performance of ZABs. Compared to ZABs based on pure HESs and mechanically mixed c-HESs/GDYO air cathodes, a-HESs-GDYO-based ZABs exhibit remarkably superior charge-discharge cycle stability. The primary reason for this stability enhancement can be attributed to the effective incorporation of GDYO and the unique amorphous structure formed: the layered structure of GDYO provides a stable supporting framework for the air cathode, ensuring structural integrity during repeated electrochemical

reactions, while the amorphous structure effectively inhibits the agglomeration and structural collapse of active materials during the repeated charge-discharge process. The synergistic effect of these two factors significantly enhances the structural stability and catalytic durability of the air cathode. The validity of this proposed mechanism is further corroborated by TEM images of the samples following cycling stability tests, which visually represent the structural changes of various cathode materials after prolonged operation. Specifically, after undergoing continuous charge-discharge cycling tests, both pure HESs (**Fig. S23(a) and S23(b)**) and mechanically mixed c-HESs/GDYO (**Fig. S23(c) and S23(d)**) exhibit significant agglomeration in their respective TEM images, directly leading to a degradation in their catalytic performance. In contrast, the a-HESs-GDYO sample maintains its intact amorphous structure even after 680 h of continuous cycling (**Fig. S23(e) and S23(f)**), with no notable crystallization or structural damage observed. Additionally, to track the evolution behavior of the amorphous structure during prolonged cycling, the structural evolution of a-HESs-GDYO after 680 h cycling was further characterized via XRD and XPS. As displayed in **Fig. S24**, after cycling, the characteristic diffraction peaks of the high-entropy sulfides in both the pristine HESs and c-HESs/GDYO samples (located at approximately 28.4° , 32.9° , 40.6° , 47.3° , 56.1° , and 64.0°) disappeared completely, indicating significant structural reconstruction during electrochemical cycling. Meanwhile, new diffraction peaks emerged at 23.0° , 24.1° , 28.5° , 29.9° , 36.0° , and 38.6° , which can be indexed to transition metal oxides and oxyhydroxides, including Cr₃O₈ (PDF#07-0267) and (Co,Ni)O(OH) (PDF#29-0491). Notably, the XRD pattern of the pristine a-HESs-GDYO exhibited only the characteristic peaks of the carbon substrate, with no observable diffraction signals attributable to metallic compounds, confirming its amorphous nature. After prolonged of charge-discharge cycling, in addition to the carbon peaks, new diffraction peaks assignable to Cr₃O₈ appeared at 28.4° and 32.9° , along with a weak signal at 38.6° corresponding to (Co, Ni)O(OH). These new diffraction peaks are consistent with those observed for the cycled HESs and c-HESs/GDYO samples, suggesting that the amorphous a-HESs-GDYO also undergoes a reconstruction toward crystalline transition metal oxides/oxyhydroxides during long-term operation. These newly formed high-valence species are widely recognized as the primary active components for OER. Furthermore, X-ray photoelectron spectroscopy (XPS) was employed to analyze the surface chemical valence states of the a-HESs-GDYO electrode after 680 h of continuous charge-discharge cycling. The ex-situ high-resolution XPS spectra acquired during the continuous charge-discharge cycle are presented in **Fig. S25**. After prolonged cycling, the XPS peaks of Fe 2p, Ni 2p, Co 2p, and Cr 2p in the a-HESs-GDYO sample all exhibited pronounced positive shifts,

indicating an increase in the valence states of the metal species. This change can be attributed to the structural reconstruction of sulfides that occurs during continuous charge–discharge cycling (the OER process), when the material acts as the air cathode in zinc–air batteries. This reconstruction promotes the formation of high-valence transition metal oxides or oxyhydroxides, which is consistent with the XRD detection results. These results further reveal that, in contrast to crystalline high-entropy sulfides, the amorphous flexible framework of a-HESs-GDYO possesses abundant dangling bonds and defect sites, which provide a larger number of active centers for catalytic reactions. Such structural features not only accelerate charge transfer at the cathode/electrolyte interface but also enhance ionic diffusion kinetics during electrochemical processes, thereby significantly improving the reaction efficiency [62]. Meanwhile, the amorphous nature effectively accommodates volume expansion and stress accumulation during prolonged charge–discharge cycling, helping maintaining the stability of the active interface between the catalyst and the electrolyte. Overall, the synergistic effect between GDYO and the amorphous structure is the key factor endowing a-HESs-GDYO with exceptional stability as an air-cathode catalyst in zinc–air batteries over extended cycling operation.

It is well established that, aside from the air cathode, the uneven deposition of zinc atoms on the anode's surface during extended charge and discharge cycles can lead to the formation of zinc dendrites [2]. The uncontrolled growth of these dendrites may not only penetrate the battery separator, triggering internal short circuits and safety hazards, but also result in significant anode corrosion and fragmentation, ultimately leading to irreversible battery failure. Previous work has systematically investigated and verified the mechanism by which the GDYO modification layer suppresses Zn dendrites. Briefly, the GDYO layer synergistically inhibits dendrite growth and improves cycling stability by providing a uniform ionic flux, abundant carboxyl- Zn^{2+} coordination nucleation sites, reversible Zn^{2+} capture/release through its porous structure, and a physical barrier against electrolyte corrosion. Given that GDYO and GDY share essentially similar structural characteristics, the GDY-modified Zn anode is expected to exhibit the same protection mechanism [63]. To further substantiate the structural advantages of the a-HESs-GDYO air cathode, we modified the zinc anode by in-situ growing a GDY film on its surface (denoted as Zn/GDY), thereby fabricating a novel anode with stable zinc deposition performance to mitigate the adverse impact of the zinc anode on the performance of zinc–air batteries. As shown in **Fig. 5(g)**, the zinc–air batteries (ZABs) configured with a-HESs-GDYO as the cathode and Zn/GDY as the anode (a-HESs-GDYO//Zn/GDY) exhibit extraordinary long-term cycle stability, functioning stably for over 1500 h—more

than twice that of the ZABs assembled with an a-HESs-GDYO cathode and an unmodified Zn anode. This significant enhancement in cycle stability is likely attributed to the unique structural advantages of GDY, which provide numerous zinc-philic sites for anchoring Zn atoms during the deposition process (Schematic diagram is shown in **Fig. S26**). These sites effectively induce uniform Zn deposition on the anode surface, suppressing uneven nucleation of Zn and thereby inhibiting the formation and growth of Zn dendrites. Scanning Electron Microscopy (SEM) observations further corroborated this mechanism (**Fig. S27**), as the GDY-modified zinc plate exhibited uniform Zn deposition with no detectable sharp zinc dendrites even after 1500 h of continuous testing. Moreover, under identical testing conditions at a current density of 5 mA cm^{-2} , ZABs assembled with an a-HESs-GDYO cathode and a Zn/GDY anode deliver an initial charge–discharge voltage gap of 0.91 V. After 1500 h of continuous operation, the voltage gap only slightly rises to 0.93 V, with a negligible increment of merely 0.02 V. By contrast, pristine HESs-based ZABs show a voltage gap increase from 0.83 V to 1.01 V (a 0.17 V increment) after only 300 h of operation. Similarly, ZABs based on mechanically mixed c-HESs/GDYO present a voltage gap elevation from 0.93 V to 1.08 V (a 0.15 V increment) within 400 h (**Fig. S28**). These systematic experimental results not only further highlight the unique advantages of a-HESs-GDYO as an air cathode in rechargeable zinc–air batteries but also confirm that the synergistic effect between the a-HESs-GDYO cathode and the Zn/GDY anode is crucial for substantially improving the overall cycle stability and reliability of the battery system.

4. Conclusion

In summary, we have developed a GDYO-mediated strategy to controllably synthesize amorphous high-entropy sulfides-graphdiyne oxide (a-HESs-GDYO) composites under mild conditions. The results demonstrate an inherent triple-effect synergistic regulatory mechanism of GDYO: carboxyl group coordination enables the uniform dispersion of multi-metal precursors; electron-rich alkyne bonds electrostatically anchor nascent metal-sulfide nuclei and inhibit agglomeration; and triangular nanopores provide spatial confinement to suppress long-range crystalline ordering. This integrated mechanism enables precise control over the nucleation and growth of multi-metal sulfide species, simultaneously overcoming the dual synthetic challenges of facile crystallization and elemental segregation commonly encountered in amorphous high-entropy materials. Benefiting from the multimetal synergistic effect that accelerates ORR/OER kinetics, the GDYO-induced amorphous structure featuring enlarged electrochemically accessible surface areas and expedited charge transport, as well as robust structural reconstruction and anti-agglomeration capability, the as-synthesized a-HESs-GDYO composite exhibits outstanding

bifunctional catalytic activity and remarkable zinc–air battery performance. When applied in zinc–air batteries, the catalyst achieves a high-power density of 133 mW cm⁻², and a specific capacity of 725 mAh g⁻² in the zinc–air battery configuration. Notably, when matched with a GDY-modified zinc anode, the assembled battery delivers an exceptional cycling stability of over 1500 h, representing a fivefold improvement over the baseline system. Overall, this work proposes a universal and rational design strategy that integrates precursor coordination, nucleation regulation, and spatial confinement at the material synthesis level. This approach opens up new opportunities for the rational design of amorphous high-entropy functional materials and is expected to promote their application in advanced energy storage and conversion technologies, especially in the field of metal-air batteries.

Electronic Supplementary Material: Supplementary material (Detailed characterization methods, electrochemical measurements, Zinc-air batteries test method, XRD, EDS, SEM, TEM, electrochemical test data graphs and charts) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94909124>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Author contribution statement

Renhe Guo: Writing – review & editing, Writing – original draft, Formal analysis, Data curation. Wei Su: Formal analysis, Data curation. Yan Lv: Formal analysis, Data curation. Na Liang: Formal analysis, Data curation. Xiuli Zhang: Formal analysis, Data curation. Jixi Guo: Formal analysis, Data curation. Huibiao Liu: Writing – review & editing, Funding acquisition, Formal analysis, Data curation. Zhiyu Jia: Formal analysis, Data curation. Dianzeng Jia:

Formal analysis, Data curation.

Use of AI statement

None

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Electronic Supplementary Material

Graphdiyne oxide-mediated synthesis of amorphous high-entropy sulfides for highly stable zinc-air batteries

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1. Characterization methods

Transmission electron microscopy (TEM) images of the as-synthesized catalysts were obtained using a JEM-2100F/X-Max80T. Field emission scanning electron microscope (FE-SEM) images were acquired with a Nova Nano SEM 450. Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images and energy dispersive X-ray spectroscopy (EDS) mapping images were attained on a FEI Titan 80–300 (acceleration voltage, 300 kV). Powder X-ray diffraction (XRD) measurements are recorded with a Philips PW-1830 X-ray diffractometer using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) at 30 kV and 40 mA. X-ray photoelectron spectroscopy (XPS, VG Scientific ESCALab 220i-XL (Al K α radiation)) was used to determine the surface chemical properties of the material. The percentage of element content was analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES, Optima 8000). Raman spectra are recorded on a Lab RAM HR800 instrument with Nd: YAG laser source of 532 nm. Fourier transform infrared spectroscopy (FT-IR) spectra were recorded using a German Bruker VERTEX70 infrared spectrum microscope. The absorption spectra of the Ru K-edge were measured by 1W1B beamline of Beijing Synchrotron Radiation Facility (BSRF, China) in fluorescence mode.

2. Electrochemical measurements

The catalyst ink was prepared by dispersing 5 mg of the as-prepared catalyst in 1 mL of a mixed solvent system, which consisted of 600 μL isopropanol, 380 μL ultrapure water, and 20 μL Nafion solution. The mixture underwent ultrasonication for 1 h to ensure homogeneous dispersion. For electrode preparation, 10 μL of the catalyst ink was precisely deposited onto either a polished glassy carbon rotating disk electrode (RDE, Pine Research Instrumentation) or a rotating ring-disk electrode (RRDE, Pine Research Instrumentation), followed by air-drying. This procedure resulted in a catalyst loading of approximately $0.25 \text{ mg}\cdot\text{cm}^{-2}$ for RDE and $0.210 \text{ mg}\cdot\text{cm}^{-2}$ for RRDE. For oxygen evolution reaction (OER) studies, 10 μL of the catalyst ink was uniformly deposited onto polished glassy carbon, resulting in a catalyst loading of $0.25 \text{ mg}\cdot\text{cm}^{-2}$. Electrochemical ORR performance was assessed using a CHI 760E electrochemical workstation (Shanghai Chenhua Instruments Company) integrated with a Pine Modulated Speed Rotator, employing a standard three-electrode system at room temperature. The electrochemical cell comprised a graphite rod (Tianjin Aida Hengsheng Instruments Company) as the counter electrode and an Ag/AgCl electrode (3 M KCl, Tianjin Aida Hengsheng Instruments Company) as the reference electrode. The electrolyte was O₂-saturated 0.1 M KOH solution for ORR and 1 M KOH solution for OER. ORR performance was evaluated using identical procedures, with the prepared catalyst serving as the working electrode in each test. Before electrochemical measurements, the catalyst electrode was activated via CV scans over a potential window from -1 to 0 V for 10 cycles at a scan rate of $100 \text{ mV}\cdot\text{s}^{-1}$ in N₂-saturated 0.1 M KOH electrolyte. ORR current densities were collected by LSV in O₂-saturated 0.1 M KOH aqueous solution in the voltage range of 0.1 to -1.0 V at $5 \text{ mV}\cdot\text{s}^{-1}$ with a rotation rate of 1600 rpm. The disk electrode was rotated at various rates from 400 to 2025 rpm. Durability tests were performed in O₂-saturated 0.1 M KOH solution via chronoamperometric response measurement of samples at 0.5 V with a rotation rate of 1600 rpm. Electrochemical impedance spectroscopy (EIS) measurements were performed at open-circuit potential using an AC voltage with a 5 mV amplitude in a frequency range from 100 KHz to 0.1 Hz. All measured potentials were converted to the reversible hydrogen electrode (RHE) using the Nernst equation (ORR: $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.0591 \times \text{pH} + 0.198$; OER: $E_{\text{RHE}} =$

$E_{\text{Hg/HgO}} + 0.0591 \times \text{pH} + 0.098$).

The linear sweep voltammetry (LSV) experiments were performed with a scan rate of $5 \text{ mV}\cdot\text{s}^{-1}$ at various disk rotation speeds of 400, 625, 900, 1225, and 1600 rpm. The kinetic current density at different potentials were calculated by using Koutecky-Levich Eqs.:

$$J^{-1} = J_L^{-1} + J_K^{-1} \quad \text{Eq. (1)}$$

Here J is the measured current density ($\text{mA}\cdot\text{cm}^{-2}$), J_L and J_K are the diffusion-limiting current density ($\text{mA}\cdot\text{cm}^{-2}$) and kinetic current density ($\text{mA}\cdot\text{cm}^{-2}$).

3. Zinc-air batteries testing:

The rechargeable Zn-air battery was assembled with 6.0 M KOH as the electrolyte. Carbon paper with an electrocatalyst loading of 1 mg cm^{-2} and a Zn plate were used as the air cathode and anode, respectively. All Zn-air battery tests, including discharge/charge cycling curves, galvanostatic discharge/charge curves, and power density profiles, were conducted on home-made cells at room temperature.

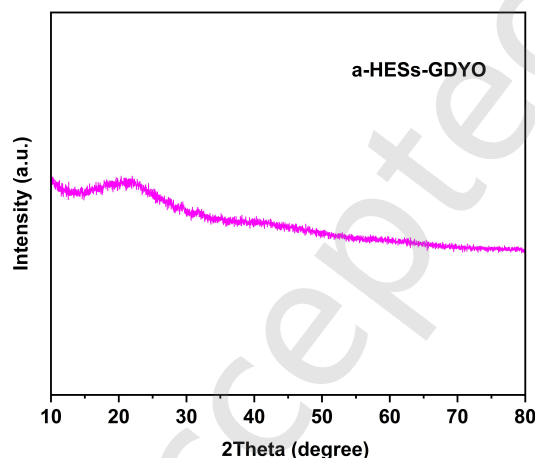


Fig. S1 XRD patterns of a-HESs-GDYO.

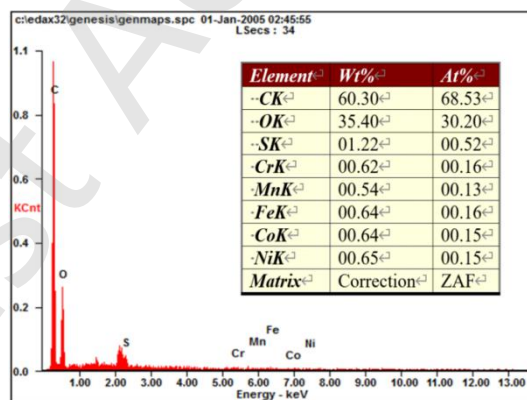


Fig. S2 Energy-dispersive X-ray spectroscopy (EDS) of a-HESs-GDYO.

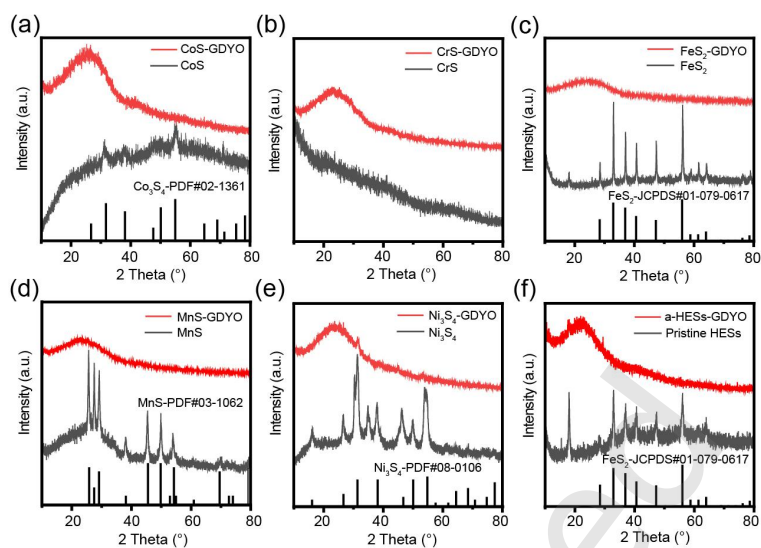


Fig. S3 The XRD patterns of single-component metal sulfides (a) CoS, (b) CrS, (c) FeS₂, (d) MnS, (e) Ni₃S₄ and (f) HESs, with corresponding amorphous single-metal sulfides.

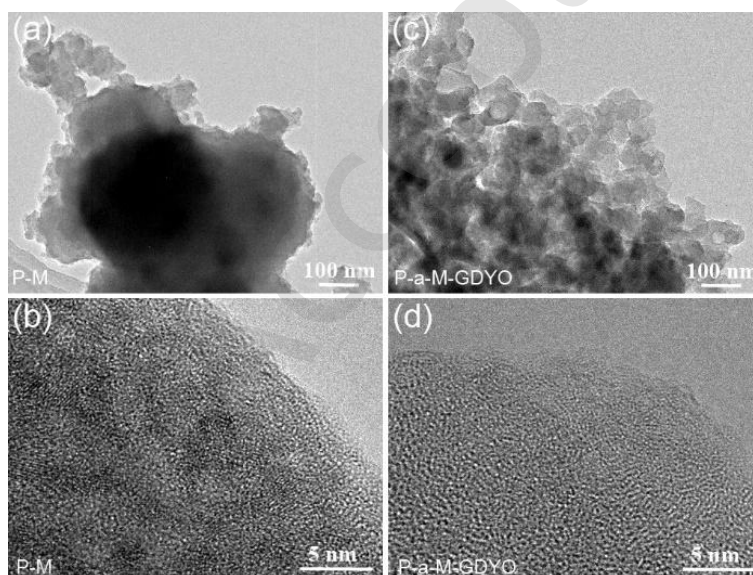


Fig. S4 TEM and High-resolution TEM images of (a-b) P-M, and (c-d) P-a-M-GDYO.

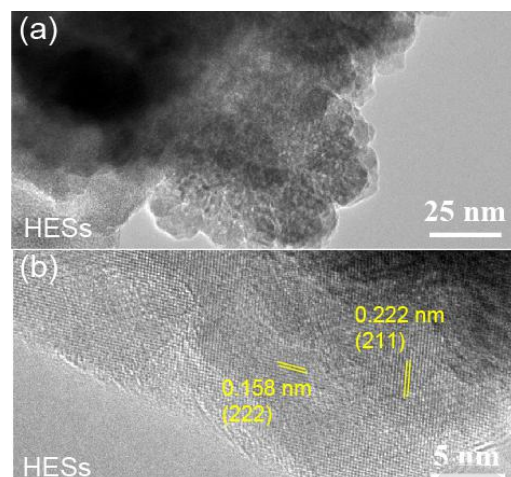


Fig. S5 TEM and High-resolution TEM images of pure HESs.

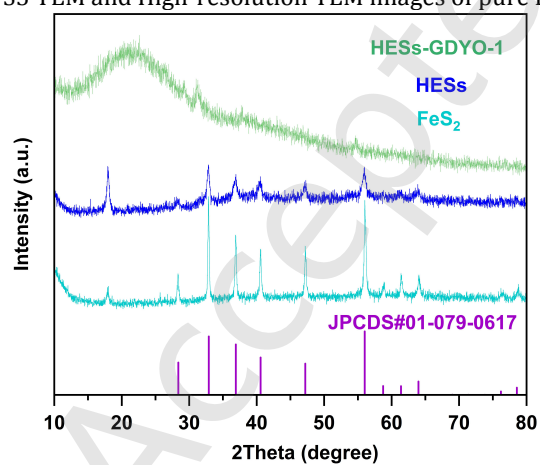


Fig. S6 XRD patterns of HESs-GDYO-1, HESs and FeS₂.

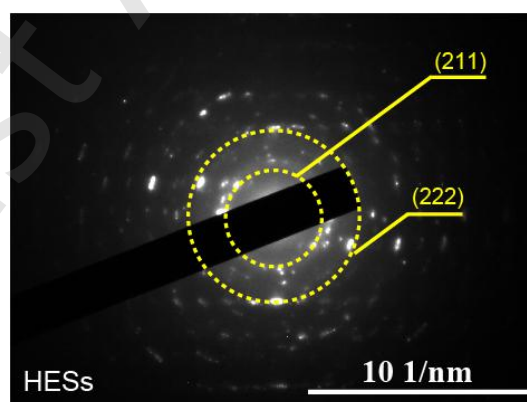


Fig. S7 Selected area electron diffraction images of HESs.

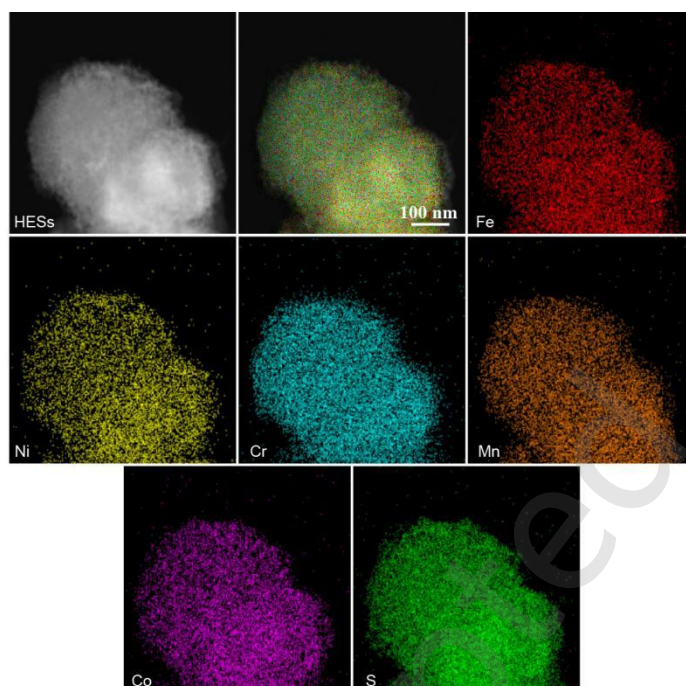


Fig. S8 Elemental mapping images of HESs.

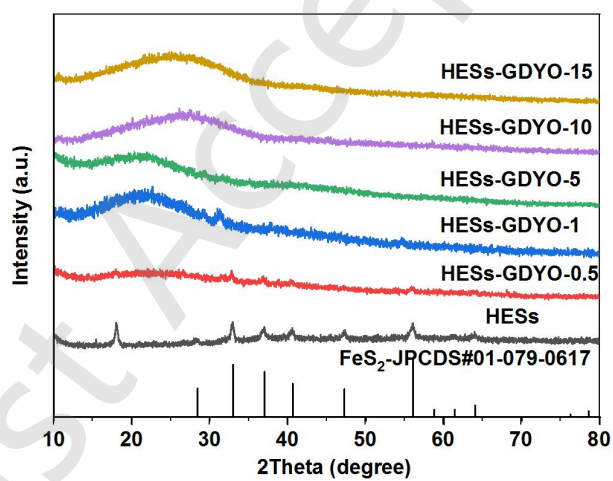


Fig. S9 XRD pattern of HESs-GDYO-x (x=0.5, 1, 5, 10, 15) and HESs

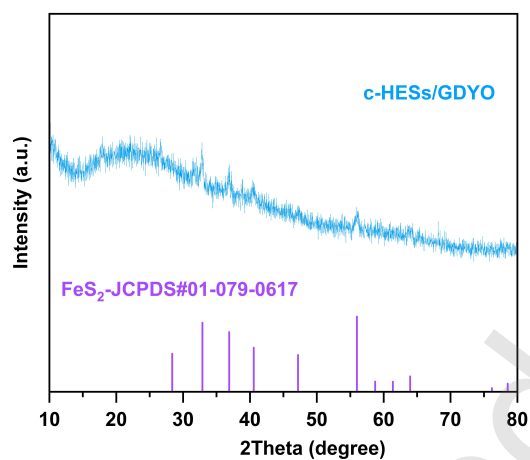


Fig. S10 XRD patterns of c-HESs/GDYO.

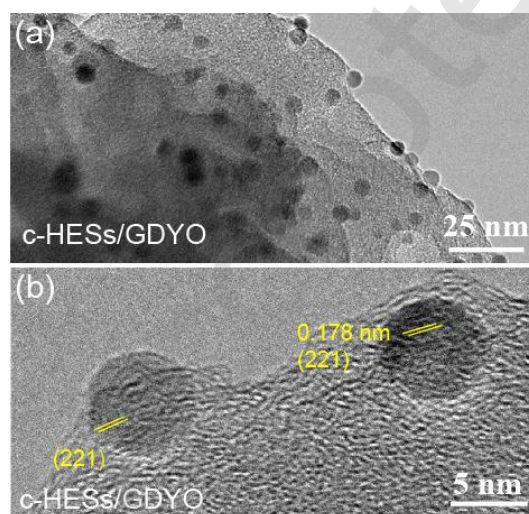


Fig. S11 TEM and High-resolution TEM images of c-HESs/GDYO.

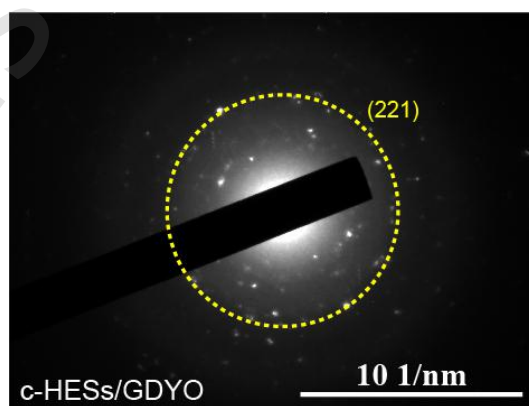


Fig. S12 Selected area electron diffraction images of c-HESs/GDYO.

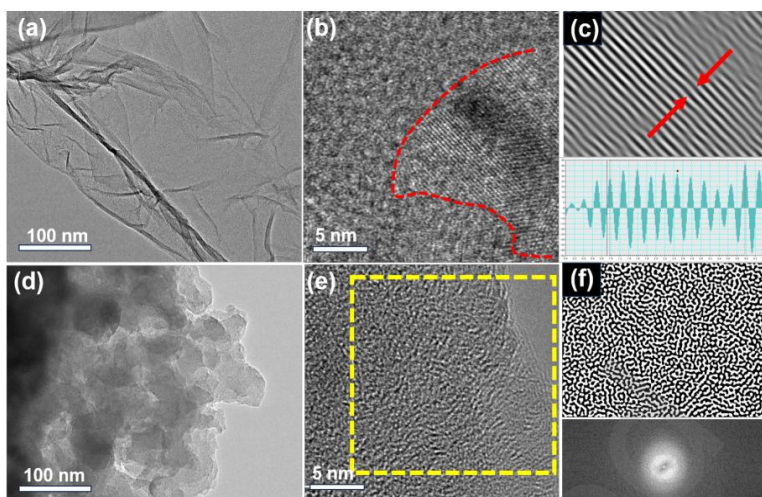


Fig. S13 (a) TEM, (b) HRTEM, (c) FFT images of the sample prepared with GO as additive; (d) TEM, (e) HRTEM, (f) FFT images of the sample prepared with GDY as additive.

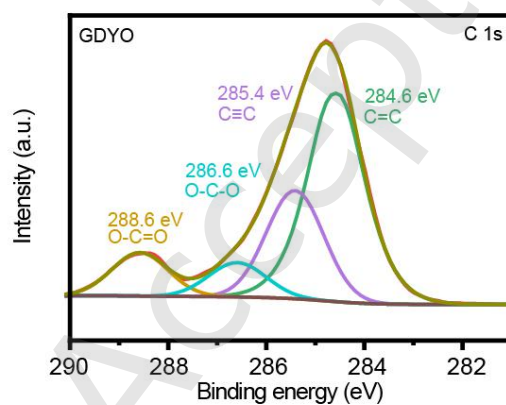


Fig. S14 C 1s XPS spectrum of GDYO.

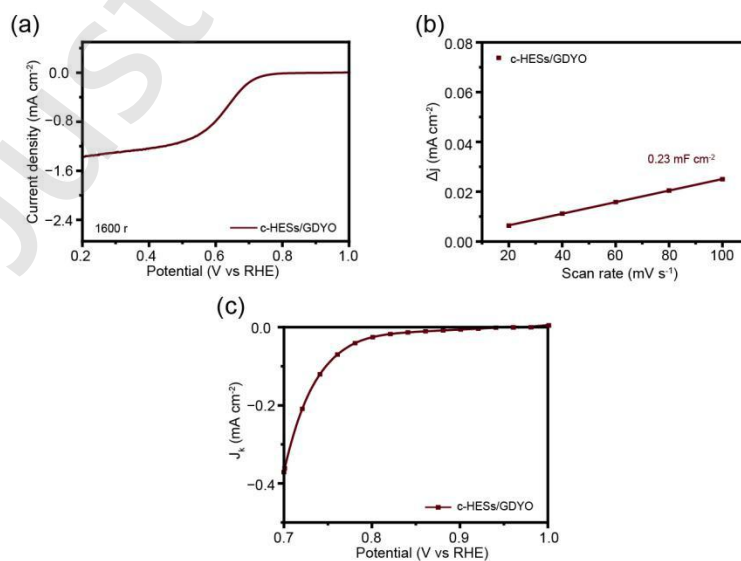


Fig. S15 (a) Linear sweep voltammetry (LSV) curves of samples with c-HESs/GDYO loadings in O_2 -saturated 0.1 M KOH solution at a rotation rate of 1600 rpm; (b) Electrochemical active surface area; (c) ORR kinetic current density.

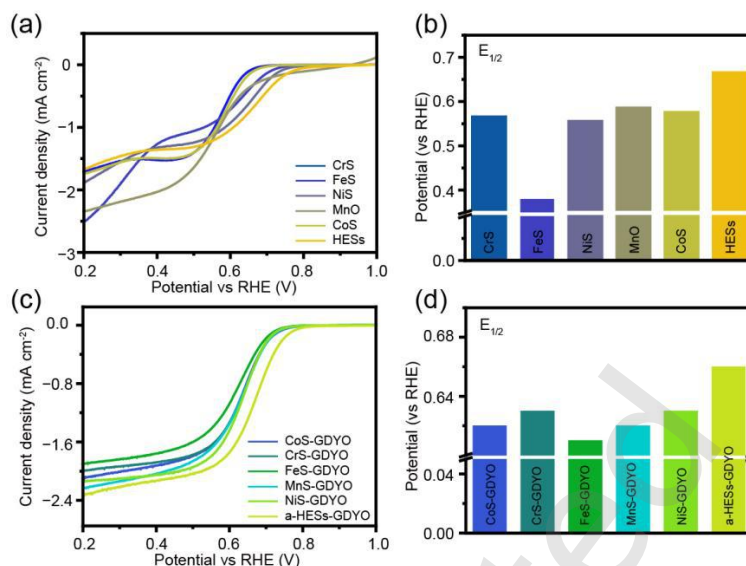


Fig. S16 (a) LSV curves, (b) half-wave potential ($E_{1/2}$) of Single-component metal sulfides (FeS, CoS, NiS, etc.), (c) LSV curves, (d) half-wave potential ($E_{1/2}$) of the corresponding amorphous single-metal sulfide-GDYO composite samples.

Under identical conditions (O_2 -saturated 0.1 M KOH), we evaluated the ORR performance of all samples. The results (**Figs. S16(a) and S16(b)**) show that each single-metal sulfide exhibits poor ORR activity, with half-wave potentials of 0.57 V (CoS), 0.38 V (FeS), 0.56 V (CrS), 0.55 V (MnS), and 0.58 V (NiS), respectively. When the five metal components were combined to form the high-entropy sulfide, the half-wave potential shifted positively to 0.60 V. A similar trend was observed in the amorphous systems (**Figs. S16(c) and S16(d)**): the a-HESs-GDYO composite exhibited significantly superior ORR activity ($E_{1/2} = 0.66$ V vs. RHE) compared to all amorphous single-metal sulfide counterparts, including a-FeS-GDYO ($E_{1/2} = 0.61$ V), a-CoS-GDYO ($E_{1/2} = 0.62$ V), a-MnS-GDYO ($E_{1/2} = 0.62$ V), a-CrS-GDYO ($E_{1/2} = 0.63$ V), and a-NiS-GDYO ($E_{1/2} = 0.63$ V). These comparative results clearly demonstrate that, regardless of GDYO-induced amorphization, the catalytic activity of single-metal systems cannot match that of the multi-metal high-entropy sulfide, fully validating the significant synergistic effect among the high-entropy multi-metal components.

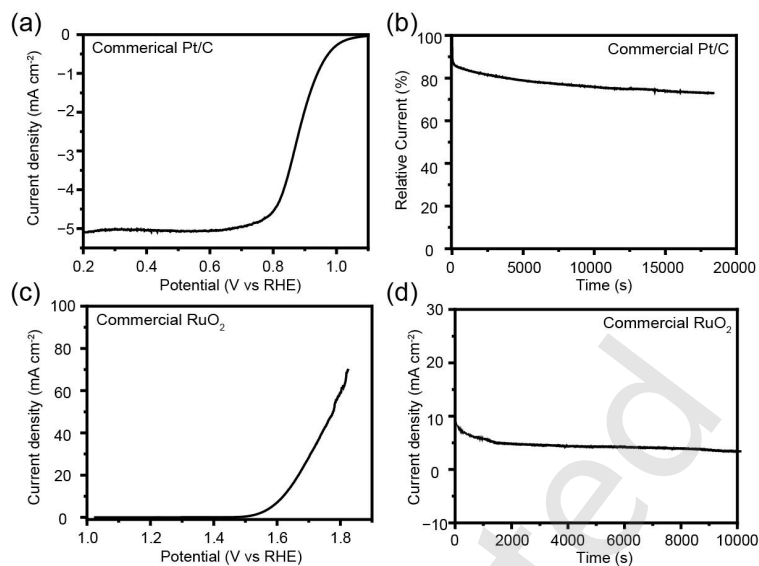


Fig. S17 (a) LSV, (b) stability test of commercial Pt/C for ORR (vs. RHE), (c) LSV, (d) stability test of commercial RuO₂ for OER at 1.62 V (vs. RHE).

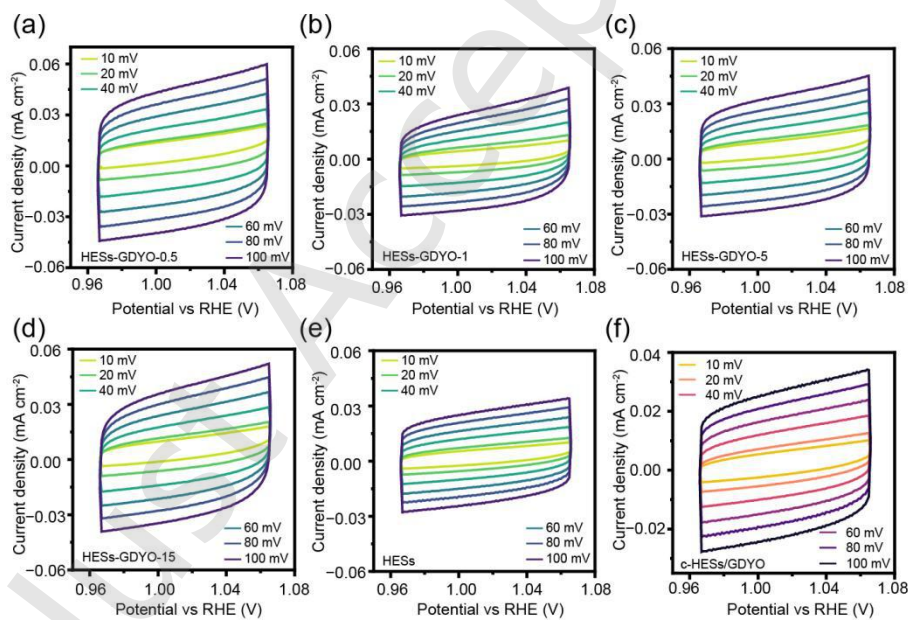


Fig. S18 Cyclic voltammetry (CV) curves of HESs-GDYO-x, HESs and c-HESs/GDYO at different scan rates.

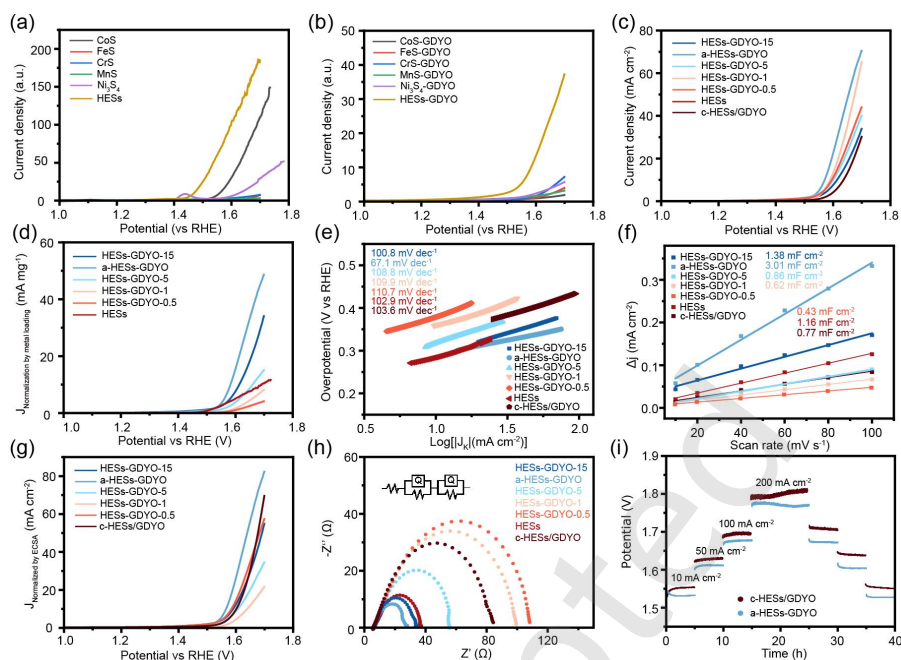


Fig. S19. Electrocatalytic OER performance of various catalysts in 1M KOH. (a, b) LSV curves of single-component metal sulfides (crystalline vs. amorphous). (c, d) LSV curves of HESs-GDYO-*x* (*x* = 0.5, 1, 5, 10, 15) and c-HESs/GDYO, with (c) raw and (d) metal-loading-normalized current densities. (e) Tafel slopes of HESs-GDYO-*x* and c-HESs/GDYO. (f) Double-layer capacitance (*C_{dl}*) values of HESs-GDYO-*x*, c-HESs/GDYO, and pristine HESs. (g) ECSA-normalized LSV curves of HESs-GDYO-*x* and c-HESs/GDYO. (h) Nyquist plots (EIS) of HESs-GDYO-*x*, c-HESs/GDYO, and pristine HESs. (i) Step-potential chronoamperometric responses of a-HESs-GDYO and c-HESs/GDYO (without iR-correction).

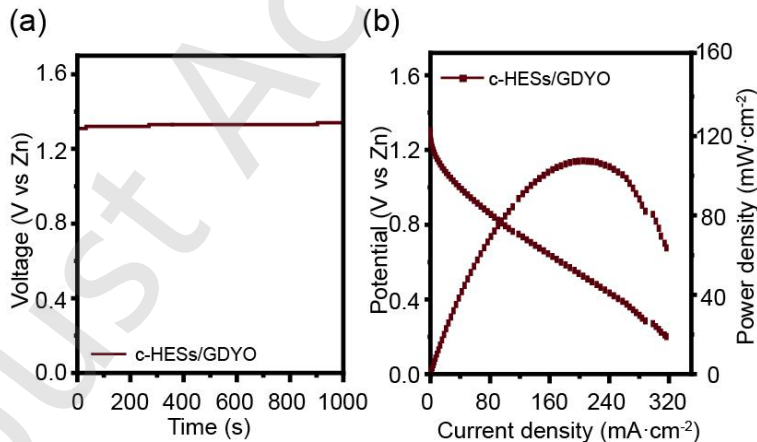


Fig. S20 (a) Open circuit voltage diagram, (b) polarization and corresponding power density curves of c-HESs/GDYO.

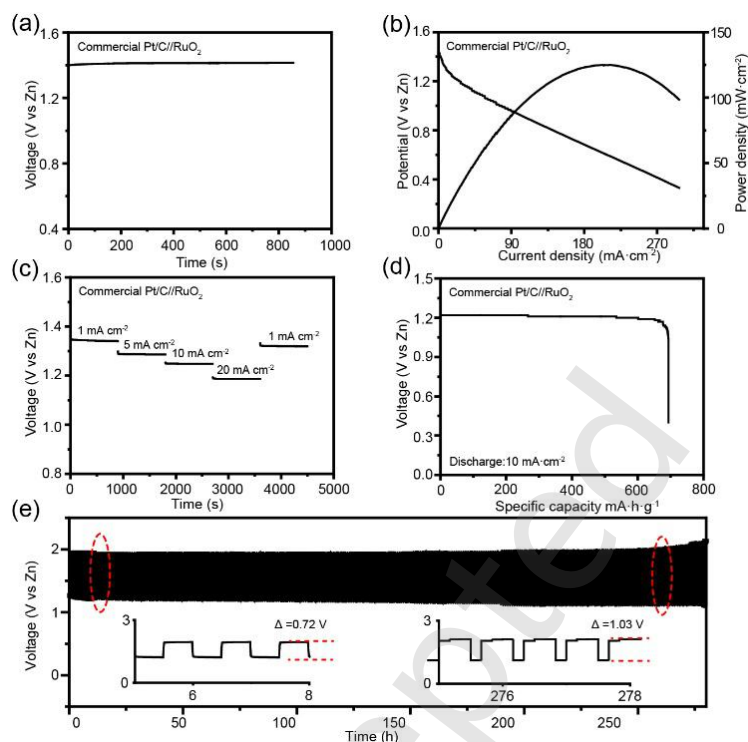


Fig. S21 (a) The open-circuit voltage (OCV), (b) Power density, (c) The rate performance, (d) The galvanostatic discharge curves, (e) The galvanostatic discharge curves of zinc-air batteries assembled with the commercial Pt/C//RuO₂ at a current densities of 10 mA·cm⁻².

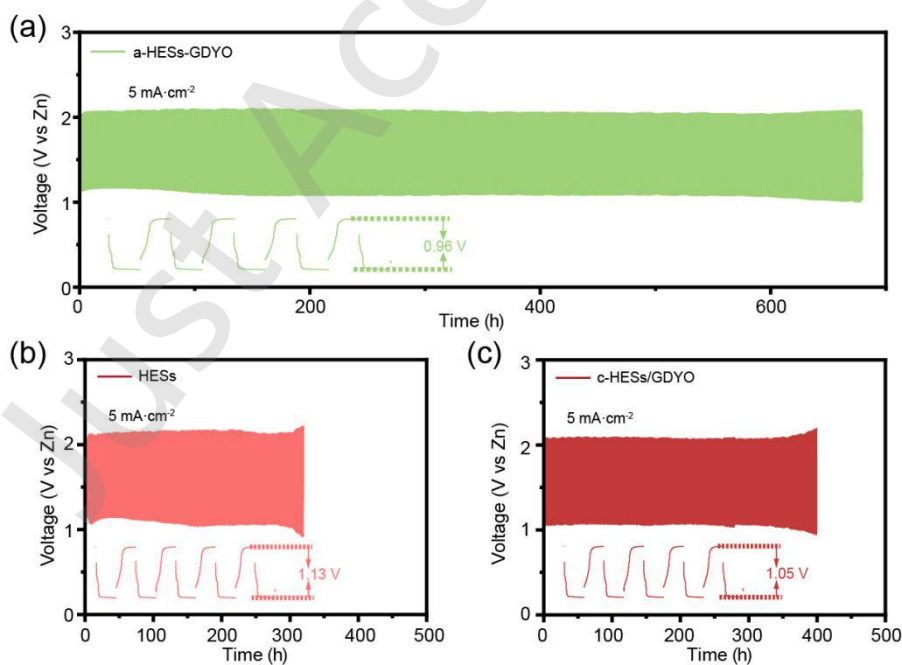


Fig. S22 Charge-discharge cycling curves of rechargeable ZABs with unmodified Zn anodes at 5 mA cm⁻²: (a) a-HESs-GDYO, (b) HESs as the air cathode, (c) c-HESs/GDYO as the air cathode.

Table S1. The zinc-air batteries performance comparison of a-HESs-GDYO with other state of the art catalysts.

Electrocatalyst	Time (h)	Current Density (mA cm ⁻²)	Power density (mWcm ⁻²)	References
a-HESs-GDYO	680	5	133	This work
Ce-Co ₃ O ₄	290	2	63.4	[1]
Fe-N ₃ S ₁ /CB	333.3	10	131.5	[2]
ReS ₂ /NiFe-LDH	300	5	26.5	[3]
Fe _{1.2} (CoNi) _{1.8} S ₆ MES	140	10	124	[4]
CoNi-SAs/NC	332	5	101.4	[5]
Pt-SCFP/C-12	80	5	122	[6]
CoNiMOF/rGO	120	10	97	[7]
CoFe-SNC	135	10	76.5	[8]
FeNiCo@NC-P	135	10	112	[9]
S _{5.84%} -LCO	100	2	92	[10]
Nb ₂ CO ₂ @COF	120	5	75	[11]
FePc@N,P-DC	50	5	120	[12]

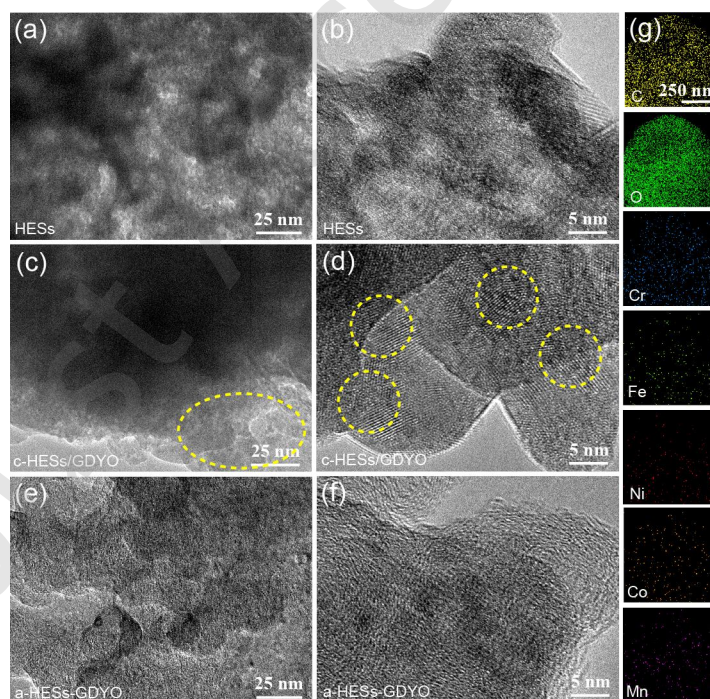


Fig. S23 TEM and HRTEM images: (a,b) pure HESs after 300 h charge-discharge cycling test, (c,d) c-HESs/GDYO after 400 h charge-discharge cycling test, (e,f) a-HESs-GDYO after 680 h charge-discharge cycling test, (g) element mapping of a-HESs-GDYO after 680 h charge-discharge cycling test.

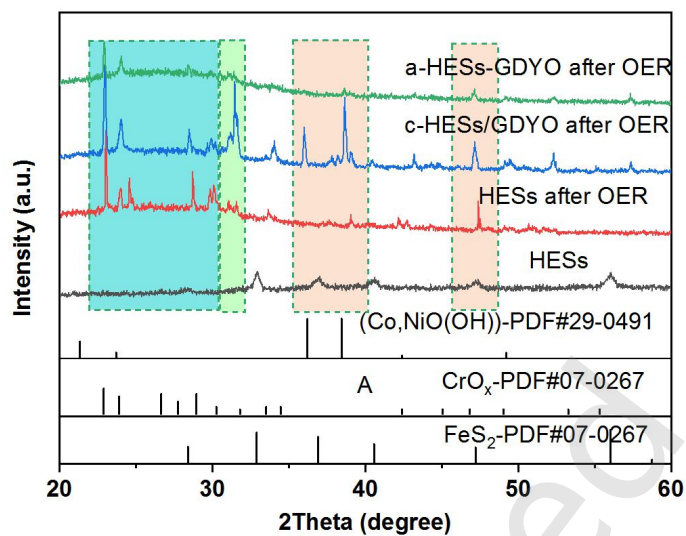


Fig. S24 X-ray diffraction pattern of pristine HESs, a-HESs-GDYO, c-HESs/GDYO as air electrode of zinc-air batteries after 1500 h continuous charge-discharge cycle stability test.

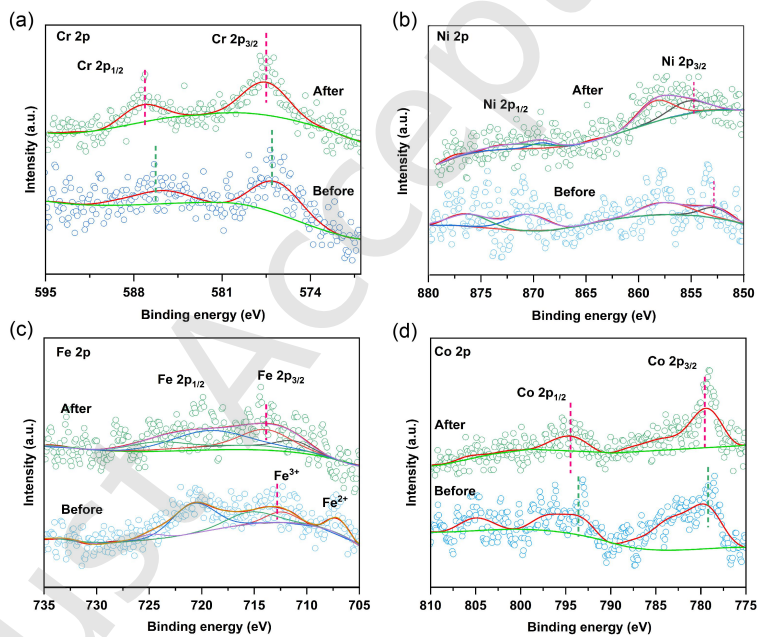


Fig. S25 XPS spectra of (a) Cr 2p, (b) Ni 2p, (c) Fe 2p, (d) Co 2p of a-HESs-GDYO after 1500 h continuous charge-discharge cycle stability test.

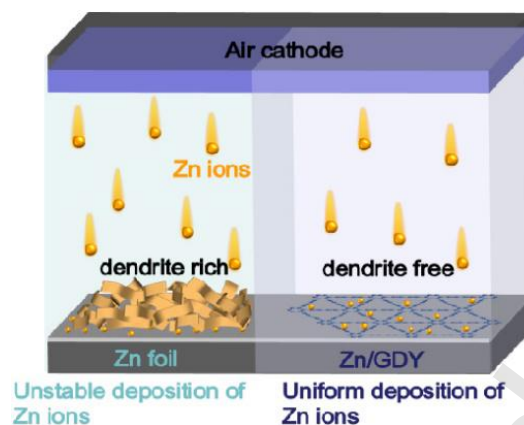


Fig. S26 Schematic illustration of the Zn deposition process on Zn foil versus Zn/GDY anode during long-term cycling.

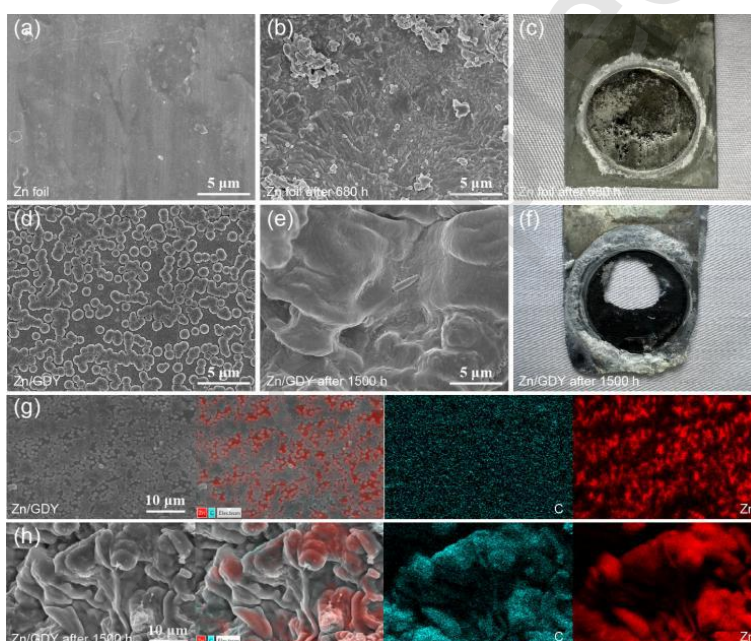


Fig. S27 SEM images of (a) Zn foil and (d) Zn/GDY; (b) The SEM and (c) digital photos image of the Zn foil after 680 hours of cycling at 5 mA cm^{-2} of the rechargeable zinc-air battery with Zn foil as the negative electrode; (e) The SEM and (f) digital photos image of the Zn/GDY after 1500 h of cycling at 5 mA cm^{-2} of the rechargeable zinc-air battery with Zn foil as the negative electrode; Elemental mapping images of (g) Zn/GDY and (h) Zn/GDY after 1500 h.

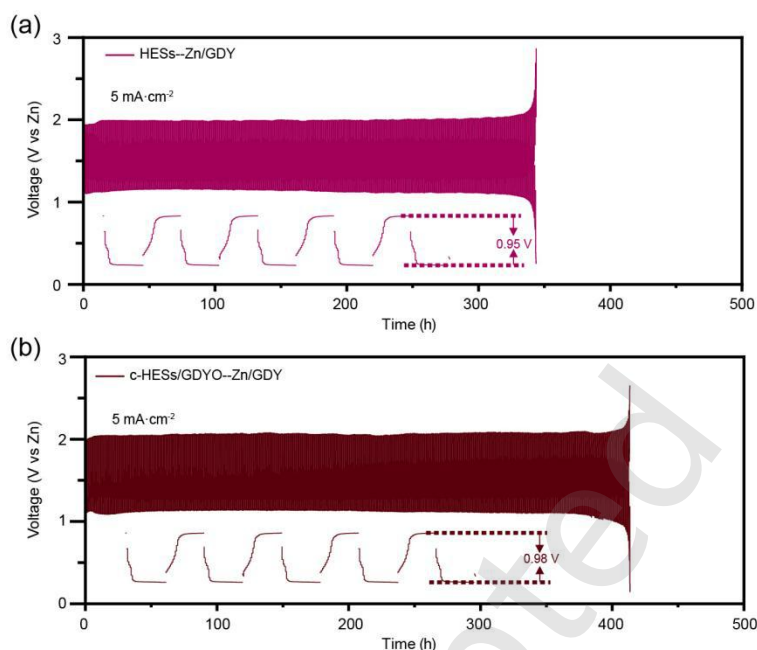


Fig. S28 Charge-discharge cycle curve of rechargeable ZABs assembled with GDY modified Zn anode of (a) HESs, (b) c-HESs/GDYO.

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