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Introduction

The rapid expansion of modern communities creates substantial energy demand, which is mainly based on traditional fossil fuels, including coal, petroleum and natural gas. However, these non-renewable energy carriers inevitably result in relevant environmental pollution.¹ Therefore, exploring clean energy carriers and developing highly efficient energy conversion techniques is urgently needed.²⁻⁴ During the past few years, hydrogen production based on electrocatalysis has drawn extensive attention due to its high energy economy and environmental benignity.5,6 Overall water splitting, namely, the coupled hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), has been considered as the most direct path to generate hydrogen via electricity.7,8 However, the sluggish anodic OER process with relatively high overpotential severely hinders the total efficiency of water electrolysis.9-13 Therefore, discovering alternative pathways to replace the

Sulfurization-induced edge amorphization in copper-nickel-cobalt layered double hydroxide nanosheets promoting hydrazine electrooxidation[†]

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The electrocatalytic hydrazine oxidation reaction (HzOR) has drawn extensive attention due to its high energy conversion efficiency and wide applications in hydrazine-assisted water splitting and direct hydrazine fuel cells (DHFC). In this study, a ternary copper–nickel–cobalt layered double hydroxide (CuNiCo LDH) nanosheet array catalyst with sulfurization-induced edge amorphization was fabricated as a highly efficient electrocatalyst for HzOR. The amorphous species at the edge region remarkably enrich the coordinatedly unsaturated metal atoms, which are catalytically active for the electro-oxidation reactions. In addition, the optimal ratio of ternary metal ions further modulates the electronic structure and optimizes the HzOR kinetics, thereby realizing improved catalytic activity. With the combined merits of enriched active species, large surface area, enhanced charge transfer behavior, and favorable reaction kinetics as well as its robust microstructure, a synergistically optimized HzOR catalyst with high activity and superior durability was achieved, which could be applied for hydrogen production *via* hydrazine-assisted water splitting and for generating electricity from DHFC.

sluggish OER process is required to further improve the efficiency and lower the cost of electrocatalytic hydrogen production, among which HER coupled with the electro-oxidation of energy-containing chemicals is considered to be promising.

Among energy-containing small molecules, hydrazine (N_2H_4) is a highly available chemical with high energy density, and it has been widely used as a fuel for aerospace technology as well as in direct hydrazine fuel cells (DHFCs).14-16 Compared with other energy-containing carbonaceous chemicals, such as methanol and urea, the electro-oxidation of hydrazine produces only nitrogen and water; therefore, it avoids the emission of carbon dioxide, a chemical that causes the greenhouse effect.17 Therefore, developing advanced electrocatalysts for HzOR is of great importance to realize high-efficiency hydrogen production from hydrazine-assisted water splitting or generate electricity directly via DHFC devices. Unfortunately, HzOR is a complex reaction involving multi-electron/proton transfer; thus, it possesses sluggish reaction kinetics.18-20 To date, in addition to expensive noble metal-based catalysts, transition metal compounds have received substantial attention to be potentially used as HzOR catalysts; among these, metallic copper, cobalt, nickel and their sulfides are deemed to be highly efficient in hydrazine electro-oxidation.21-34 For example, Sun and colleagues presented a single-crystalline Ni ultrathin nanosheet array which is highly active for both HzOR and HER.32 Following this study, a single-crystalline-alloyed NiCo nanosheet array catalyst with synergistic merits of a 2D ultrathin structure, large

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surface area, intimate connection to the conducting substrate and high intrinsic activity was reported by the same group; it could serve as a highly efficient electrocatalyst for HzOR.33 In addition, Zhou et al. reported a hierarchical cobalt-nickel sulfide nanosheet array catalyst derived from layered double hydroxide (LDH), in which the enhanced conductivity and ion transport in the hierarchical nanostructure effectively promoted the activity for HzOR.34 Introducing amorphous species is an effective way to further enrich the active sites; meanwhile, the balance between the active site density and the intrinsic conductivity should be considered.³⁵ In this work, we propose a ternary CuNiCo LDH nanosheet array catalyst with sulfurization-induced edge amorphization which provides enriched active sites for hydrazine electro-oxidation. Benefiting from the amorphous species on the edges, abundant coordinatedly unsaturated metal atoms can be introduced, providing enriched active sites for hydrazine electro-oxidation. In addition, the synergistic effect between ternary metals further optimizes the electronic structure of the product, thereby realizing enhanced HzOR performance.

Experimental section

Materials

The chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used as received without further purification.

Synthesis of LDH nanosheet arrays

The CuNiCo LDH nanosheet arrays grown on Ni foam (NF) were prepared by a hydrothermal method. Firstly, the total metal amounts of Ni(NO₃)·6H₂O, Co(NO₃)·6H₂O and Cu(NO₃)·3H₂O in 4 mmol were dissolved in 30 ml of deionized (DI) water containing 8 mmol hexamethylenetetramine and stirred for 15 min to form a homogeneous solution. The Ni foam (about 3 cm \times 3 cm \times 1 mm, 100 mesh) was ultrasonically cleaned with acetone for 20 min to remove the surface organics, rinsed in 2 M HCl solution to remove the oxide layer on the surface, and washed with DI water. Then, the Ni foam was placed into a Teflon-lined stainless-steel autoclave (50 ml) and maintained at 100 °C for 10 h. The as-obtained product was washed with DI water for the next experiments. By changing the ratio of Cu : Ni : Co salts (Ni = Co), pristine, 1%, 5%, and 10% Cucontaining LDH arrays were prepared.

Synthesis of sulfurized LDH (S-LDH) nanosheet arrays

First, 0.4 mmol thioacetamide (TAA) were dissolved in 30 ml DI water and stirred for 10 min; then, it was transferred into a 50 ml Teflon-lined stainless-steel autoclave. Then, the asprepared LDH nanosheet arrays grown on Ni foam were placed into the solution and maintained at 120 °C for 5 h. For the synthesis of sulfurized nickel foam (S-NF), bare NF was used as the precursor with the same reaction conditions. The asobtained product was washed with DI water and ethanol several times and dried overnight under vacuum.

Structural characterizations

The X-ray diffraction (XRD) data of the samples were obtained by a Philips X'Pert Pro Super diffractometer at a scan rate of 10° min⁻¹ in the 2θ range from 5° to 80° with Cu Ka ($\lambda = 1.54178$ Å) as the X-ray source. The scanning electron microscopy (SEM) was performed on a JEOL JSM-6700F SEM. The transmission electron microscope (TEM) images were collected by a JEM-2100 TEM at an acceleration voltage of 200 kV. The high resolution TEM (HRTEM) images were acquired by a JEOL-2010 TEM at an acceleration voltage of 200 kV. A PerkinElmer 7300DV ICP emission spectroscope was used for the inductively coupled plasma optical emission spectrometry (ICP-OES) analyses to identify the concentration of copper as Cu/(Cu + Ni + Co)%. The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and the corresponding elemental mapping analyses were carried out on an FEI Tecnai G2 F20 TEM. X-ray photoelectron spectroscopy (XPS) analysis was tested by VGESCALAB MKII with Mg K α (K α = 1253.6 eV) as the X-ray source.

Electrocatalytic study

All the electrochemical tests were performed on an electrochemical workstation (CHI660E) in a three-electrode system. Also, all the measured potentials were converted to reversible hydrogen electrode (RHE) according to the formula: $E_{\nu s.RHE} = E_{\nu s.Hg/HgO} + E_{\nu s.Hg/HgO}^{\circ} + 0.059$ pH. The as-prepared S-LDH nanosheet arrays grown on Ni foam were used as a working electrode, a Hg/HgO electrode was used as a reference electrode, and a platinum network (2 cm × 2 cm, 60 mesh) was used as a counter electrode. The cyclic voltanmetry (CV) and linear sweep (LSV) tests were performed at a rate of 50 mV S⁻¹ in 0.1 M KOH + 20 mM hydrazine solution. The electrochemical impedance spectroscopy (EIS) was tested at 0.4 V νs . RHE from 10^{-1} to 10^{-5} Hz. The chronoamperometry was operated at 0.7 V νs . RHE for 4 hours.

Results and discussion

With the aim of fabricating sulfurized CuNiCo LDH nanosheet arrays with edge amorphization, ternary CuNiCo LDH nanosheet arrays grown on Ni foam were first prepared via a one-step hydrothermal route by reacting soluble Cu/Ni/Co salts and hexamethylenetetramine (HMT) in water. During the synthesis, the hydrolysis of HMT could offer an alkaline environment, leading to the formation of the metal hydroxide. X-ray diffraction (XRD) patterns of the as-formed products are shown in Fig. 1a, where the samples are named LDH-1/2/3/4 according to the concentration of the incorporated Cu (0%, 1%, 5% and 10%, respectively); the sulfurized samples are labeled as S-LDH-1/2/3/ 4 accordingly. As can be seen, a typical layered structure can be identified in the XRD patterns, which is consistent with previous results for the LDH structure. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images further confirm the two-dimensional (2D) morphologies of the products (Fig. 1b, c, S2 and S3[†]), where the lateral size of the nanosheets is on the micrometer scale and the thin



Fig. 1 (a) XRD patterns of the CuNiCo LDH nanosheet arrays. (b and c) SEM and TEM images of LDH-3. (d) XRD patterns of the sulfurized CuNiCo LDH nanosheet arrays with edge amorphization. (e and f) SEM and TEM images of S-LDH-3. (g and h) HRTEM images of S-LDH-3. (i) Corresponding SAED pattern. (j) HAADF-STEM image and the elemental distribution maps of Cu, Ni, Co, O and S in S-LDH-3.

nanosheet morphology can be identified. The as-obtained CuNiCo LDH nanosheet arrays were then sulfurized by a hydrothermal treatment with thioacetamide (see Experimental section, ESI[†]). Of note, the color of the samples changed from green to black after the sulfurization (Fig. S4[†]), suggesting the homogeneous sulfurization of the samples. XRD analyses were first applied to investigate the structural information of the samples after sulfurization. As indicated in Fig. 1d, the sulfurized sample without Cu incorporation (S-LDH-1) shows a negligible difference in peak location compared with the nonsulfurized nanosheet arrays; meanwhile, the (003) peak of the Cu-incorporated samples exhibits an obvious right-shift, indicating shrinkage of the interlayer spacing. Detailed analysis reveals that the interplanar spacing of the (003) facets decreased from 9.5 Å to 7.6 Å, which is very close to the value of layerstructured α -Ni(OH)₂ (JCPDS card no. 33-0429). The obvious shrinkage of the interlayer spacing may arise from the formation of amorphous M^{II} (M = Cu, Ni, Co) sulfides, which weakens the interaction between the layers and the intercalated anions. Additionally, only one peak can be observed in the small degree region; this is caused by the *c*-axis orientation, which is a typical phenomenon in 2D materials, including LDH.36 The apparent orientation in the XRD patterns is mainly derived from the layered structure with large lateral size and ultrathin thickness.^{37,38} In addition, we performed XRD analyses on powdered S-LDH samples which were separated from the NF substrate via vigorous ultrasonic treatment. As shown in Fig. S5,† in addition to the peaks originating from the crystalline LDH phase, broad peaks in the range of 15 to 40° can be observed, confirming the

existence of amorphous species. The SEM image shows that the sulfurized LDH-3 (S-LDH-3) maintains the nanosheet array structure (Fig. 1e). It can be seen that the thickness of the nanosheets shows an obvious increment, which may be caused by the surface sulfurization/amorphization. In addition, the surface of the sulfurized nanosheets becomes rough, which can lead to enhancement of the surface area with more exposed active sites. The TEM image of S-LDH-3 further confirms the nanosheet morphology with increased thickness (Fig. 1f). A similar phenomenon was revealed for the products with various Cu concentrations (Fig. S6 and S7[†]). High-resolution TEM (HRTEM) analysis was operated to further study the detailed morphological and structural information of a nanosheet separated from S-LDH-3. As indicated in Fig. 1g and S8,† clear interfaces at the edge area of the nanosheet can be identified, where the edge exhibits no crystal fringes and the internal area is crystalline; this reveals the edge amorphization in S-LDH-3. The HRTEM image with higher magnification shows an interplanar distance of 0.27 nm with six-fold symmetry, which is consistent with the (100) plane of the LDH structure (Fig. 1h).^{39,40} Of note, the selected area electron diffraction (SAED) pattern (Fig. 1i) shows typical six-fold spots with a bright halo around the central spot, thereby confirming the singlecrystalline feature with the presence of amorphous species; this is consistent with the results of the HRTEM analysis.35 In order to further investigate the compositional information of S-LDH-3, high-angle annular dark field scanning electron microscopy (HAADF-STEM) and the corresponding elemental mapping analysis were conducted. As shown in Fig. 1j, Cu, Ni, Co, and O are uniformly distributed on the whole nanosheet, while S is mainly located at the edge of the nanosheet and the protruding surfaces; this confirms the amorphous edge feature of the nanosheets. In addition, inductively coupled plasma optical emission spectrometry (ICP-OES) was performed to identify the percentages of Cu, Ni and Co in the sulfurized CuNiCo LDH nanosheets. As can be seen in Fig. S12,† the concentration of copper in S-LDH-3 was determined to be 4.5%, which matches well with the added ratio of the Cu salt precursor. Additionally, the Ni: Co ratios for all the tested samples are approximately 3 : 1; therefore, they provide an ideal material system for studying the role of Cu dopant in hydrazine electro-oxidation.

To identify the valence information of the product, X-ray photoelectron spectroscopy (XPS) was conducted on S-LDH-3. The XPS survey spectrum verifies the co-existence of Cu, Ni, Co, S and O in S-LDH-3 (Fig. S13†). Detailed valence information of these elements can be investigated from their high-resolution spectra. As can be seen in Fig. 2a, the binding energies at 931.7 eV and 951.9 eV can be attributed to low-valence $Cu^{+/0}$ and $Cu^{+/0}$, respectively,^{41,42} which suggests the generation of Cu_xS species. Additionally, the binding energies of the Ni $2p_{3/2}$ and Ni $2p_{1/2}$ regions can be indexed to two sets of peaks (Fig. 2b), respectively. The peaks at 852.2 eV and 869.5 eV can be identified as Ni²⁺ ions, while the peaks at 855.2 eV and 873.0 eV can be designated as Ni³⁺ species.^{34,35,43} In addition, the broad peaks located at 860.8 eV and 879.4 eV are the satellite peaks. It is worth noting that the concentration of Ni³⁺ species is higher



Fig. 2 XPS spectra of S-LDH-3: (a) copper, (b) nickel, (c) cobalt, and (d) sulfur.

than that of Ni²⁺. The existence of high-valence Ni³⁺ ions can be attributed to the formation of amorphous species during the sulfurization in which the Ni ions are partially unsaturated, as previously reported.³⁵ Of note, the enrichment of the high-valence species is well accepted to be catalytically active for electro-oxidation reactions, which is beneficial for promoting HzOR performance. Additionally, the Co 2p profiles (Fig. 2c) at 780.5 eV and 796.2 eV can be deconvoluted to Co $2p_{3/2}$ and Co $2p_{1/2}$ for Co³⁺, accompanied by peaks at 782.3 eV and 797.0 eV, which are designated as the Co²⁺ species; this confirms the co-existence of Co²⁺ and Co³⁺.^{44–46} For the S 2p spectrum, the peaks located at 161.7 eV and 163.0 eV can be assigned as the S²⁻ species (Fig. 2d), which is consistent with the binding energy of metal–sulfur bonds.^{7,47}

A three-electrode system was used to evaluate the catalytic properties of HzOR. Typically, the sulfurized LDH nanosheet arrays with edge amorphization served as the working electrodes, with a Hg/HgO electrode and platinum gauze as the reference electrode and counter electrode, respectively. As shown in Fig. 3a, the linear sweeping voltammetry (LSV) curves obtained in 0.1 M KOH solution containing 20 mM hydrazine show that Cu plays an important role in regulating the HzOR activity. For S-LDH-3, an ultralow onset potential of 0.21 V vs. RHE can be identified for triggering HzOR, suggesting the highest activity among the tested catalysts. Of note, the ultralow onset potential is much lower than that of most previously reported catalysts based on transition metal compounds and their composites (Table 1).18,22,48-52 The low onset potential may arise from the presence of amorphous edges with abundant active sites as well as the enriched high-valence species in S-LDH-3. As listed in Table 1, the S-LDH-3 catalyst with 4.5% Cu incorporation exhibits higher HzOR behavior; it achieves a high current density of 185.1 mA cm⁻² at 1.0 V vs. RHE. Of note, this value is roughly 1.8 to 2.6 times higher than those of the other sulfurized samples and, remarkably, 24.7 to 29.9 times higher than those of the non-sulfurized catalysts; it is even much higher than those of state-of-the-art catalysts, as listed in Table 1,^{18,22,34,48-52} further confirming the excellent HzOR activity and indicating that both Cu incorporation and sulfurizationinduced edge amorphization can strongly regulate the HzOR process. That is, Cu incorporation may effectively tune the electronic structures and optimize the adsorption energies of hydrazine and reaction intermediates,16,26 and the introduction of the amorphous sulfide species can result in more coordinatedly unsaturated metal ions with high catalytic activity,35 therefore synergistically facilitating the HzOR process. The reaction kinetics was further investigated by analyzing the Tafel plots of the products. As revealed in Fig. 3b, S-LDH-3 possesses a small Tafel slope of 73.3 mV per decade, which is much smaller than those of the other S-LDHs (95.2 to 122.0 mV per decade) and LDHs (155.5 to 171.2 mV per decade); this confirms the kinetically favorable features of S-LDH-3 in catalyzing the HzOR process. The favorable HzOR behavior of S-LDH-3 can be attributed to the optimal concentration of the Cu dopant, which can effectively modulate the electronic structure of the catalyst, as well as the edge amorphization feature, which can enrich the active surface sites for HzOR catalysis.

As discussed in the introduction, HzOR can substitute OER in water electrolysis and couple with HER to achieve much higher efficiency in generating hydrogen. To verify the structural benefits of S-LDH-3 in hydrazine-assisted water splitting, the electro-oxidation behaviors in electrolytes with and without hydrazine were measured for S-LDH-3 and the non-sulfurized LDH-3. As shown in Fig. 3c, the HzOR onset potential of S-LDH-3 is 1.12 V lower than that of the OER, and the current density of S-LDH-3 at 1.4 V vs. RHE reaches 309 mA cm⁻²; this is over 7 times higher than that of the non-sulfurized LDH nanoarray, which confirms the structural merits of sulfurization-induced edge amorphization in the ternary CuNiCo LDH nanoarrays. In addition, the onset potential of S-LDH-3 outperforms that of the non-sulfurized LDH-3, showing a 570 mV decrement. The favorable HzOR reaction kinetics can be further verified by analyzing the electrochemical impedance spectra (EIS). As indicated in Fig. 3d, all the tested nanoarray catalysts exhibit relatively low series resistances (R_s) in the range of 16.8 to 20.6 Ω at 0.4 V vs. RHE, which are mainly attributed to the highly conductive Ni foam skeleton.53,54 Of note, the sulfurized samples show smaller R_s values, which may benefit from the higher conductivity of the sulfide layer than of the hydroxide matrix. In addition, S-LDH-3 exhibits a smaller radius of curvature of the semicircle, indicating a smaller charge transfer resistance (R_{ct}) during the HzOR catalysis. A smaller R_{ct} can guarantee fast electron transfer during the electrochemical processes; particularly, herein, it can electrochemically connect more surface sites and therefore accelerate the rate of hydrazine electro-oxidation.35 Therefore, the favorable HzOR reaction kinetics of the sulfurized LDH catalyst with edge amorphization is confirmed. Additionally, to eliminate the influence of the electrochemical surface area (ECSA) in evaluating the intrinsic



Fig. 3 (a) LSV curves for evaluating the HzOR activity. Inset: the electrolyzer cell. (b) Corresponding Tafel plots. (c) Comparison of the polarization curves of S-LDH-3 and LDH-3 in 0.1 M KOH with 20 mM hydrazine (solid lines) and 0.1 M KOH (dashed lines). (d) Nyquist plots measured at 0.4 V vs. RHE. (e) The estimation of C_{dl} . (f) LSV curves normalized by C_{dl} .

activity toward HzOR, the electrochemical double-layer capacitances ($C_{\rm dl}$) were measured for the tested catalysts (Fig. 3e). As listed in Table S2,† the LDH-based nanoarray catalysts before and after sulfurization exhibit similarly high $C_{\rm dl}$ values in the range of 4.1 to 5.2 mF cm⁻², which can be attributed to the large surface area of the 2D nanosheet array. As is well accepted,

Table 1 Comparison of HzOR performance. All the data were measured in 0.1 M KOH solution with various hydrazine concentrations as indicated

Catalyst	[V vs. RHE]	J_{geo} (a) 1.0 V vs. RHE [mA cm ⁻²]	$J_{C_{\text{cl}}}$ (a) 1.2 V νs . RHE [A F ⁻¹]	hydrazine in electrolyte	Reference
S-LDH-1	0.24	92.1	27.0	20 mM	This work
S-LDH-2	0.23	103.8	31.6	20 mM	This work
S-LDH-3	0.21	185.1	48.4	20 mM	This work
S-LDH-4	0.27	72.4	17.7	20 mM	This work
LDH-1	0.78	7.1	4.1	20 mM	This work
LDH-2	0.78	6.4	4.9	20 mM	This work
LDH-3	0.78	7.5	4.8	20 mM	This work
LDH-4	0.78	6.2	3.3	20 mM	This work
S-NF	1.02	1.1	3.4	20 mM	This work
Bare NF	0.93	3.0	10.4	20 mM	This work
Fe ₂ MoC/N-doped carbon	0.45	1.7	0.1	100 mM	18
Cu/graphene	0.85	2.0	_	10 mM	22
(Co, Ni) ₉ S ₈ nanoarray	0.05	9.2	_	20 mM	34
Graphene nanohill	0.64	10.0	_	50 mM	48
Cu nanocube/graphene	0.81	0.5	_	10 mM	49
Ni ₃ S ₂ /Ni foam	0.86	9.0	_	10 mM	50
Phosphatized Cu ₂ Ni/C	0.52	42.4	_	20 mM	51
Cu nanocluster/C	0.71	7.5	—	100 mM	52

larger C_{dl} values, or equivalently, larger ECSA, can provide more surface active sites to be involved in the electrochemical processes, including HzOR. Interestingly, the C_{dl} values of the S-LDHs exhibit negligible changes compared with the nonsulfurized samples, indicating that the ECSA is not increased during the sulfurization process. In fact, the increment of the thickness of the nanosheets contributes little to the surface area because the surface area of the nanosheets is mainly contributed by the lateral area rather than the edges. During the sulfurization process, the edges of the nanosheets become thicker due to the formation of amorphous sulfides, while the quantity and the lateral area of the nanosheets remain nearly unchanged. By means of normalizing the LSV curves by the C_{dl} values, the intrinsic HzOR activity of the catalysts can be judged without the influence of the surface area.⁵⁵ As shown in Fig. 3f and Table 1, S-LDH-3 exhibits the highest HzOR activity among the tested samples; it achieves a high normalized current density of 48.4 A F^{-1} at 1.2 V vs. RHE, showing 1.5 to 14.7 fold enhancement compared to the other LDH-based nanoarray catalysts. Therefore, the optimal sulfurized LDH nanoarray catalyst with edge amorphization is confirmed.

To further investigate the HzOR behavior of S-LDH-3, the polarization curves measured in the electrolytes containing different concentrations of hydrazine were analyzed. As revealed in Fig. 4a, the HzOR activity of S-LDH-3 shows an obvious dependence on the concentration of hydrazine, and the low onset potential of 0.2 V *vs.* RHE can be identified even in the electrolyte containing 2 mM hydrazine, indicating the superior

electro-oxidative ability of the catalyst. The nearly linear relationship between the current density and the concentrations of hydrazine can be further identified in Fig. 4b, where a positive correlation can be observed in the range from 2 mM to 14 mM at 0.7 V *vs.* RHE; this indicates that the hydrazine electro-oxidation process is controlled by the diffusion step.

In addition, chronoamperometry tests were performed to evaluate the electrochemical stability of S-LDH-3, which is crucial for practical applications. As shown in Fig. 4c, the HzOR current of S-LDH-3 decreases slightly from 50.5 mA cm⁻² to 46.4 mA cm⁻² in the first 4 hours, resulting in a 91.9% retention of the HzOR activity. To eliminate the influence of the decreased concentration of hydrazine, the electrolytes were replaced by fresh electrolyte every 4 hours. As can be seen, the HzOR current can be recovered by refreshing the electrolyte. In detail, the current density after 16 hour continuous operation reached 50.2 mA cm^{-2} , demonstrating excellent electrochemical stability with 99.4% current retention. After 20 hour HzOR operation, the current density can be identified as 46.6 mA cm^{-2} , which is slightly larger than that after 4 hour catalysis. Therefore, the superior HzOR stability can be verified. The morphology and chemical composition of S-LDH-3 after the stability test were studied by TEM and XPS analyses. As shown in Fig. S17,† the TEM image of S-LDH-3 after the 20 hour stability test reveals that the nanosheet morphology is maintained, confirming its good structural stability. Additionally, the XPS data of Cu, Ni and Co, revealed in Fig. 4d-f, demonstrate their mixed valence feature, further verifying the chemical stability of the catalyst. In



Fig. 4 (a) Polarization curves of S-LDH-3 in 0.1 M KOH with various concentrations of hydrazine. (b) The current density at 0.7 V vs. RHE obtained from LSV as a function of concentration. (c) Chronoamperometry curve of S-LDH-3 at a potential of 0.7 V vs. RHE in 0.1 M KOH solution containing 20 mM hydrazine. The arrows indicate the replacement of the electrolyte with fresh electrolyte. (d–g) XPS spectra of Cu, Ni, Co and S after continuous HzOR operation.

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3 T. Zhang and T. Asefa, Adv. Mater., 2019, 31, 1804394.

- 4 J. Xie, J. Zhang, S. Li, F. Grote, X. Zhang, H. Zhang, R. Wang, Y. Lei, B. Pan and Y. Xie, *J. Am. Chem. Soc.*, 2013, 135, 17881– 17888.
- 5 D. Yan, Y. Li, J. Huo, R. Chen, L. Dai and S. Wang, *Adv. Mater.*, 2017, **29**, 1606459.
- 6 Y. Liang, Y. Yu, Y. Huang, Y. Shi and B. Zhang, J. Mater. Chem. A, 2017, 5, 13336-13340.
- 7 J. Xie, H. Zhang, S. Li, R. Wang, X. Sun, M. Zhou, J. Zhou,
 X. W. Lou and Y. Xie, *Adv. Mater.*, 2013, 25, 5807–5813.
- 8 H. Jin, C. Guo, X. Liu, J. Liu, A. Vasileff, Y. Jiao, Y. Zheng and S.-Z. Qiao, *Chem. Rev.*, 2018, **118**, 6337–6408.
- 9 T. E. Mallouk, Nat. Chem., 2013, 5, 362-363.
- 10 Z. W. Seh, J. Kibsgaard, C. F. Dickens, I. Chorkendorff, J. K. Nørskov and T. F. Jaramillo, *Science*, 2017, **355**, 146.
- 11 B. Zhang, X. Zheng, O. Voznyy, R. Comin, M. Bajdich, M. García-Melchor, L. Han, J. Xu, M. Liu, L. Zheng, F. P. García de Arquer, C. T. Dinh, F. Fan, M. Yuan, E. Yassitepe, N. Chen, T. Regier, P. Liu, Y. Li, P. De Luna, A. Janmohamed, H. L. Xin, H. Yang, A. Vojvodic and E. H. Sargent, *Science*, 2016, 352, 333–337.
- 12 J. Xie, X. Zhang, H. Zhang, J. Zhang, S. Li, R. Wang, B. Pan and Y. Xie, *Adv. Mater.*, 2017, **29**, 1604765.
- 13 Y. Sun, S. Gao, F. Lei, J. Liu, L. Liang and Y. Xie, *Chem. Sci.*, 2014, **5**, 3976–3982.
- 14 N. V. Rees and R. G. Compton, *Energy Environ. Sci.*, 2011, 4, 1255–1260.
- 15 G. E. Evans and K. V. Kordesch, Science, 1967, 158, 1148.
- 16 M. Sun, Z. Lu, L. Luo, Z. Chang and X. Sun, *Nanoscale*, 2016, 8, 1479–1484.
- 17 J.-Y. Zhang, H. Wang, Y. Tian, Y. Yan, Q. Xue, T. He, H. Liu, C. Wang, Y. Chen and B. Y. Xia, *Angew. Chem., Int. Ed.*, 2018, 57, 7649–7653.
- 18 K. Ojha, E. M. Farber, T. Y. Burshtein and D. Eisenberg, *Angew. Chem., Int. Ed.*, 2018, 57, 17168–17172.
- 19 Y. Meng, X. Zou, X. Huang, A. Goswami, Z. Liu and T. Asefa, *Adv. Mater.*, 2014, **26**, 6510–6516.
- 20 W. Yang, T.-P. Fellinger and M. Antonietti, J. Am. Chem. Soc., 2011, 133, 206–209.
- 21 H. Wang, Y. Ma, R. Wang, J. Key, V. Linkov and S. Ji, *Chem. Commun.*, 2015, **51**, 3570–3573.
- 22 C. Liu, H. Zhang, Y. Tang and S. Luo, *J. Mater. Chem. A*, 2014, 2, 4580–4587.
- 23 H.-F. Wang, C. Tang, B. Wang, B.-Q. Li and Q. Zhang, Adv. Mater., 2017, 29, 1702327.
- 24 J. Zhang, X. Cao, M. Guo, H. Wang, M. Saunders, Y. Xiang, S. P. Jiang and S. Lu, *ACS Appl. Mater. Interfaces*, 2019, **11**, 19048–19055.
- 25 Q. Sun, L. Wang, Y. Shen, M. Zhou, Y. Ma, Z. Wang and C. Zhao, *ACS Sustainable Chem. Eng.*, 2018, **6**, 12746–12754.
- 26 Z. Wang, L. Xu, F. Huang, L. Qu, J. Li, K. A. Owusu, Z. Liu, Z. Lin, B. Xiang, X. Liu, K. Zhao, X. Liao, W. Yang, Y.-B. Cheng and L. Mai, *Adv. Energy Mater.*, 2019, **9**, 1900390.
- 27 J. Wang, Y. Li and Y. Zhang, Adv. Funct. Mater., 2014, 24, 7073-7077.
- 28 X. Yan, Y. Liu, K. R. Scheel, Y. Li, Y. Yu, X. Yang and Z. Peng, *Front. Mater. Sci.*, 2018, **12**, 45–52.

addition, sulfur can still be detected after 4 hours, suggesting that the sulfide layer is relatively stable in the electro-oxidative environment (Fig. 4g). Of note, the quantitative analysis demonstrates that the ratio of S : TM (i.e., total metal) decreases from 1:2.21 for the fresh catalyst to 1:5.32 for the postcatalysis sample, indicating decreased S content during longterm HzOR operation. The decreased content of S can be attributed to the surface reconstruction during the HzOR process, which is a common phenomenon in electrocatalytic oxidation reactions such as OER and the urea oxidation reaction (UOR). That is, the amorphous sulfides at the edge region can be partially dissolved and transformed into oxy-hydroxide species. Meanwhile, compared to OER and UOR, the triggering of HzOR requires a much lower potential. Therefore, only limited dissolution of sulfur occurs during the long-term HzOR catalysis, leading to the retention of amorphous sulfides in the catalyst, even after stability tests. Therefore, the sulfurized CuNiCo LDH nanosheet array catalyst with edge amorphization was identified to exhibit remarkable activity and durability toward hydrazine electro-oxidation.

Conclusions

Paper

In summary, a ternary CuNiCo LDH nanosheet array catalyst with sulfurization-induced edge amorphization was fabricated; it exhibits improved catalytic activity and robust durability toward hydrazine electro-oxidation. The amorphous species at the edges of the nanosheets could provide abundant coordinatedly unsaturated metal atoms for HzOR and enhance the electrical conductivity during catalysis. Additionally, the optimal concentration of the Cu dopant was identified, further leading to the discovery of a highly efficient and durable HzOR catalyst with a high current density, smaller Tafel slope, low overpotential and superior stability. This work provides a promising HzOR catalyst for hydrazine-assisted water splitting and direct hydrazine fuel cells, and it may serve as a guideline for designing efficient HzOR electrocatalysts in the future.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

- 1 M. S. Dresselhaus and I. L. Thomas, *Nature*, 2001, **414**, 332–337.
- 2 V. H. Fragal, E. H. Fragal, T. Zhang, X. Huang, T. S. P. Cellet, G. M. Pereira, A. Jitianu, A. F. Rubira, R. Silva and T. Asefa, *Adv. Funct. Mater.*, 2019, **29**, 1808486.

- 29 G. Wang, J. Chen, P. Cai, J. Jia and Z. Wen, *J. Mater. Chem. A*, 2018, **6**, 17763–17770.
- 30 X. Yan, Y. Liu, J. Lan, Y. Yu, J. Murowchick, X. Yang and Z. Peng, *Mater. Chem. Front.*, 2018, **2**, 96–101.
- 31 L. Wang and H. Wang, Micro Nano Lett., 2018, 13, 138-142.
- 32 Y. Kuang, G. Feng, P. Li, Y. Bi, Y. Li and X. Sun, *Angew. Chem.*, *Int. Ed.*, 2016, **55**, 693–697.
- 33 G. Feng, Y. Kuang, P. Li, N. Han, M. Sun, G. Zhang and X. Sun, *Adv. Sci.*, 2017, 4, 1600179.
- 34 L. Zhou, M. Shao, C. Zhang, J. Zhao, S. He, D. Rao, M. Wei, D. G. Evans and X. Duan, *Adv. Mater.*, 2017, 29, 1604080.
- 35 J. Xie, H. Qu, F. Lei, X. Peng, W. Liu, L. Gao, P. Hao, G. Cui and B. Tang, *J. Mater. Chem. A*, 2018, **6**, 16121–16129.
- 36 Q. Wang and D. O'Hare, Chem. Rev., 2012, 112, 4124-4155.
- 37 J. Xie, X. Sun, N. Zhang, K. Xu, M. Zhou and Y. Xie, *Nano Energy*, 2013, 2, 65–74.
- 38 F. Song and X. Hu, Nat. Commun., 2014, 5, 4477.
- 39 M. Gong, Y. Li, H. Wang, Y. Liang, J. Z. Wu, J. Zhou, J. Wang, T. Regier, F. Wei and H. Dai, *J. Am. Chem. Soc.*, 2013, 135, 8452–8455.
- 40 X. Liu, X. Wang, X. Yuan, W. Dong and F. Huang, *J. Mater. Chem. A*, 2016, 4, 167–172.
- 41 J. Xie, L. Gao, S. Cao, W. Liu, F. Lei, P. Hao, X. Xia and B. Tang, *J. Mater. Chem. A*, 2019, 7, 13577–13584.
- 42 L. Martin, H. Martinez, D. Poinot, B. Pecquenard and F. Le Cras, J. Phys. Chem. C, 2013, 117, 4421-4430.

- 43 J. Xie, J. Xin, R. Wang, X. Zhang, F. Lei, H. Qu, P. Hao, G. Cui,
 B. Tang and Y. Xie, *Nano Energy*, 2018, 53, 74–82.
- 44 Y. Liu, C. Ma, Q. Zhang, W. Wang, P. Pan, L. Gu, D. Xu, J. Bao and Z. Dai, *Adv. Mater.*, 2019, **31**, 1900062.
- 45 L. Xu, Q. Jiang, Z. Xiao, X. Li, J. Huo, S. Wang and L. Dai, Angew. Chem., Int. Ed., 2016, 55, 5277-5281.
- 46 Y. Liu, Y. Ying, L. Fei, Y. Liu, Q. Hu, G. Zhang, S. Y. Pang,
 W. Lu, C. L. Mak, X. Luo, L. Zhou, M. Wei and H. Huang, *J. Am. Chem. Soc.*, 2019, 141, 8136–8145.
- 47 L. Li, L. Song, H. Guo, W. Xia, C. Jiang, B. Gao, C. Wu, T. Wang and J. He, *Nanoscale*, 2019, **11**, 901–907.
- 48 K. Akbar, J. H. Kim, Z. Lee, M. Kim, Y. Yi and S.-H. Chun, *NPG Asia Mater.*, 2017, **9**, e378.
- 49 H. Gao, Y. Wang, F. Xiao, C. B. Ching and H. Duan, *J. Phys. Chem. C*, 2012, **116**, 7719–7725.
- 50 X. Liu, Y. Li, N. Chen, D. Deng, X. Xing and Y. Wang, *Electrochim. Acta*, 2016, **213**, 730–739.
- 51 W. Wang, Y. Wang, S. Liu, M. Yahia, Y. Dong and Z. Lei, *Int. J. Hydrogen Energy*, 2019, **44**, 10637–10645.
- 52 X. Gao, C. Du, C. Zhang and W. Chen, *ChemElectroChem*, 2016, 3, 1266–1272.
- 53 J. Xie, W. Liu, X. Zhang, Y. Guo, L. Gao, F. Lei, B. Tang and Y. Xie, ACS Mater. Lett., 2019, 1, 103–110.
- 54 J. Xie, W. Liu, F. Lei, X. Zhang, H. Qu, L. Gao, P. Hao, B. Tang and Y. Xie, *Chem.–Eur. J.*, 2018, **24**, 18408–18412.
- 55 D. Merki, S. Fierro, H. Vrubel and X. Hu, *Chem. Sci.*, 2011, 2, 1262–1267.