Construction of surface lattice oxygen in metallic N–CuCoS$_{1.97}$ porous nanowire for wearable Zn–air battery

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Achieving high activity and stability oxygen evolution reaction (OER) catalysts to optimize the efficiency of metal–air battery, water splitting and other energy conversion devices, remains a formidable challenge. Herein, we demonstrate the metallic porous nanowires arrays with abundant defects via nitrogen and copper codoped CoS$_{1.97}$ nanowires (N–CuCoS$_{1.97}$ NWs). The N–CuCoS$_{1.97}$ NWs can serve as an excellent OER self-supported electrode with an overpotential of 280 mV (j = 10 mA cm$^{-2}$) and remarkable long-term stability. The X-ray absorption near-edge structure (XANES) and X-ray photoelectron spectrum (XPS) measurements confirmed the surface lattice oxygen created on the N–CuCoS$_{1.97}$ NWs during OER. Then, the density function theory (DFT) results evident that lattice oxygen constructed surface of N–CuCoS$_{1.97}$ NWs has more favorable OER energetic profiles and absorption for reaction intermediate. More importantly, the flexible and wearable Zn–air battery fabricated by the N–CuCoS$_{1.97}$ NWs shows excellent rechargeable and mechanical stability, which can be used in portable mobile device.

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1. Introduction  

Advanced technology is being developed to meet higher standards of energy conversion efficiency and lowered greenhouse gas emissions, but their commercial potential is contingent on developing highly boosting and stable catalysts [1–4]. Therefore, catalysts are the central components for those technologies, and largely dictate the ultimate their performance [5–8]. Although noble metals show superior catalytic performance, such as iridium (Ir) and ruthenium (Ru) with high active for OER, and platinum (Pt) with superior active for hydrogen evolution reaction (HER) and oxygen reduction reaction (ORR), their low abundance and high cost limit their large-scale applications [9–11]. Great efforts have been devoted to design new strategies catalysts with improved activity by enhancing electrical conductivity [12–15], introducing defects [16–20], creating nanointerface [21–26], and tuning electronic structure [27–31], etc. However, achieving high catalytic activity with cheap metal-based nanocatalysts still remains a formidable challenge. The transition metal sulfide has emerged as an interesting class of potential catalysts in electrocatalytic reactions for the ideal atomic arrangement and high electrical transport [32,33]. Generally, the electrocatalytic reactions take place on the active sites of the catalysts surface, namely only the active sites exposed on catalysts surface have activity [34–36]. Therefore, it is very important to enhance the exposed active sites content of catalysts. There are several ways to enhance the content of exposed active sites. One is the preparation of atomic ultrathin nanostructures, and another is the formation of porous structure [37–42]. Additionally, metal sulfide is not very stable in basic media and surface modification should be used to increase its corrosion resistance in alkaline solutions.

Herein, we report the nitrogen and copper codoped CoS$_{1.97}$ metallic porous nanowires arrays (N–CuCoS$_{1.97}$ NWs) with abundant defects confirmed by the high-resolution transmission electron microscopy (HRTEM), X-ray absorption fine structure spectroscopy (EXAFS) and electron spin resonance (ESR) measurements. Meanwhile, the X-ray absorption near-edge structure (XANES) and X-ray photoelectron spectrum (XPS) evidenced the construction of lattice oxygen on the surface of N–CuCoS$_{1.97}$ NWs in OER, on which excess active sites and metal–O bond further enhanced the stability of the N–CuCoS$_{1.97}$ NWs in basic media. The excellent OER...
performance of N–CuCoS$_{1.97}$ NWs was further confirmed by both experiment and DFT method. Additionally, the N–CuCoS$_{1.97}$ NWs based flexible Zn–air battery also shows superior rechargeable and mechanical capability. The wearable Zn–Air battery shows another application in wearable mobile devices, indicating the promising prospects of the N–CuCoS$_{1.97}$ NWs based wearable Zn–air battery.

2. Experimental

2.1. Chemicals and materials

Co(NO$_3$)$_2$·6H$_2$O (99.0%), Cu(NO$_3$)$_2$·6H$_2$O (99.0%), sulfur (99.0%), Nafion® (5 wt%) and N, N-dimethylformamide (DMF) were purchased from Aladdin. The de-ionized (DI) water was obtained from a Millipore Autopure system (18.2 MΩ, Millipore Ltd., USA). The 1.0 M KOH was used as the electrolytes in the electrochemical experiments. All the other materials were of analytical grade and without further purification.

2.2. Synthesis of Co-based precursor

A mixture of cobalt(II) nitrate hexahydrate (1.4553 g, 5.0 mmol), ammonium fluoride (0.3704 g, 10 mmol) and urea (0.5631 g, 9.4 mmol) was dissolved in distilled water (50 mL) and further stirring for 30 min. Then, the solution was transferred to a 100 mL Teflon-lined stainless-steel autoclave containing two carbon fiber paper (CFP 3 × 4 cm) and maintained at 120 °C for 6 h. After the reaction, the autoclave was cooled to room temperature naturally. The precipitate was rinsed with ethanol and distilled water for more than three times and dried under vacuum at 50 °C for 4 h.

2.3. Synthesis of CuCo-based precursor

The synthesis of CuCo precursor was the same as the above method except for adding copper(II) nitrate hexahydrate (0.4305 g, 1.7 mmol) and cobalt (II) nitrate hexahydrate (0.9691 g, 3.3 mmol) instead of cobalt(II) nitrate hexahydrate (1.4553 g, 5.0 mmol).

2.4. Synthesis of CoS$_{1.97}$ NWs and CuCoS$_{1.97}$ NWs

In a typical procedure, two-piece of the Co-based or CuCo-based precursor with the CFP (3 × 4 cm) and 300 mg sulfur powder were placed in two crucibles, which are 20 cm apart in the tube. Then the tube was heated to 380 °C with a rate of 10 °C min$^{-1}$ under the flowing N$_2$ atmosphere. After reacting at 380 °C for 3 h, the system was cooled to room temperature naturally under the flowing N$_2$ atmosphere.

2.5. Synthesis of N–CoS$_{1.97}$ NWs and N–CuCoS$_{1.97}$ NWs

Two pieces of the Co-based or CuCo-based precursor with the CFP (3 × 4 cm) and 300 mg sulfur powder were placed in two crucibles, which are 20 cm apart in the tube. Then the tube was heated to 380 °C with a rate of 10 °C min$^{-1}$ under the flowing NH$_3$ atmosphere. After reacting at 380 °C for 3 h, the system was cooled to room temperature naturally under the flowing NH$_3$ atmosphere.

2.6. Characterization

The morphologies of the samples were investigated using field-emission scanning electron microscopy (FESEM, Zeiss) at an acceleration voltage of 5 kV. All samples were coated with a thin layer of gold prior to FESEM observation. The chemical compositions were investigated by the energy dispersive X-ray spectroscopy (EDX). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were performed at an acceleration voltage of 200 kV with a JEOL JEM 2100 TEM. Sample compositions were determined by XPS (ESCALAB 5700, England). X-ray diffraction (XRD) experiments were conducted from 20° to 90° on a XPert Pro X-ray diffractometer with Cu Kα radiation (λ = 0.1542 nm) at the voltage of 40 kV and current of 40 mA. X-ray photoelectron spectroscopy (XPS) analyses were made with a VG ESCALAB 220i-XL device. All XPS spectra were corrected using C 1 s line at 284.6 eV. The absorption spectra of M (M = Co, Cu, S, N, and O) K-edge were collected in transmission mode using a Si (111) double-crystal monochromator at the BLW141 station of the Shanghai Synchrotron Radiation Facility (SSRF). The electrical transport property measurements were carried out on pressed pellets using a Keithley 4200-SCS semiconductor characterization system and four-point probe method. The temperature-dependent conductivity of the obtained nanocatalysts was measured through a four-terminal configuration. The NWs were scraped out on the CFP and prepared to film (1 mm thickness). Four silver wires were attached to the NWs film via silver paste, and then dried in air. The measurement was done on a Janis Research system and via Keithley 2600 semiconductor analysis.

2.7. Electrocatalytic research

Electrochemical measurements were carried out at room temperature using the catalysts arrays on the CFP as the working electrode directly connected to a CHI 760 E Electrochemical Workstation (CHI Instruments, Shanghai Chenhua Instrument Corp., China) in a conventional three-electrode system at a scan rate of 2 mV s$^{-1}$. The saturated HgHgO$_2$ (1.0 M KOH) was used as a reference electrode, and a Pt net was employed as an auxiliary electrode. The potentials were referenced to the RHE through RHE calibration, $E_{RHE} = E_{Hg/HgO} + 0.094 + 0.0591pH$. Also, a resistance test was made, and the IR compensation was applied by using the CHI software.

2.8. Calculation details

All DFT calculations were carried out within the periodic plane wave framework as implemented in Vienna ab initio simulation package (VASP) [43]. The electron-ion interaction was represented by the projector augmented wave (PAW) and the kinetic energy cut from plane wave was set as 400 eV. The geometry optimization was based on the exchange-correlation functional GGA-PBE with on-site Coulomb repulsion (PBE+U) [44,45]. To estimate the energetics of OER, the solvation energy due to the long-range electrostatic interaction was also computed by a periodic continuum solvation model with a smooth dielectric function suggested by Gyggi et al. [46–48]. The effective U-J terms ($U_{	ext{eff}}$) as determined by linear response theory were set as 3.5 eV for Co. The geometry convergence criterion was set as 0.06 eV/Å for the maximal component of force. The k-point mesh utilized was up to (2 × 2 × 1) in the Monkhorst–Pack scheme, which was verified to be accurate enough for these bulk systems. A rectangular unit cell of β–CoOOH/N–CuCoS$_{1.97}$ heterojunction model is fabricated with 5.51 Å × 5.51 Å were utilized for surface slabs. 2 × 2 × 1 K points were routinely utilized for energy and structural calculations. CoS$_{1.97}$ (100) slab includes 3 Co layers and 6 S layers parallel to (100) surface, where the bottom 1 Co layers and 2 S layers are fixed at bulk-truncated positions. As for β–CoOOH (104) surface, it consists of 4 Co layers and 8 O layers, where one Co or O atom is replaced by Cu and N to simulate the Cu and N dopants.
2.9. Fabrication of N–CuCoS$_{1.97}$ NWs based Zn–air battery

In a typical procedure, the home-made solid Zn–air battery were fabricated by using the N–CuCoS$_{1.97}$ NWs as cathode, zinc anode as anode, hydrogel polymer electrolyte as the solid electrolyte and nickel foam as the air collector [26,34].

3. Results and discussion

3.1. Characterization of the N–CuCoS$_{1.97}$ NWs

Fig. 1(a) shows X-ray diffraction (XRD) patterns of N–CuCoS$_{1.97}$, CuCoS$_{1.97}$, N–CoS$_{1.97}$ and CoS$_{1.97}$ NWs. The diffraction peaks of all samples have the similar cubic CoS$_{1.97}$ structure with a space group of P6$_3$ (JCPDS No. 83–573, $a=b=c=5.5385$ Å). Because of N doping into CoS$_{1.97}$ lattice, the XRD peaks of N–CuCoS$_{1.97}$ and N–CoS$_{1.97}$ NWs show the slightly higher shift compared with those of CoS$_{1.97}$ NWs. However, the CuCoS$_{1.97}$ and CoS$_{1.97}$ NWs show the similar XRD pattern due to similar ionic radius of Cu and Co [49]. Raman spectra of N–CuCoS$_{1.97}$, CuCoS$_{1.97}$, N–CoS$_{1.97}$ and CoS$_{1.97}$ NWs were also studied to confirm the structure change (Fig. S1). The scanning electron microscope (SEM) was used to evident the morphology of the NWs. CoS$_{1.97}$ NWs show solid nanowires array (Fig. 1b), similar morphology can be found in CuCoS$_{1.97}$ NWs (Fig. 1c). However, N–CoS$_{1.97}$ (Fig. 1d) and N–CuCoS$_{1.97}$ NWs (Fig. 1e) show a rougher surface with porous structure. Further, transmission electron microscopy (TEM) image (Fig. 1f) shows that the N–CuCoS$_{1.97}$ NWs have the micropore and uneven edge. High-resolution transmission electron microscopy (HRTEM) image of the N–CuCoS$_{1.97}$ NWs (Fig. 1g) shows clear lattice fringe spacing of 0.265 nm, corresponding to the interplanar distance of (100) for CoS$_{1.97}$. The corresponding Fast Fourier Transform (FFT) pattern reveals that the N–CuCoS$_{1.97}$ NWs are hexagonal single crystal with c-axis crystalline orientation (inset of Fig. 1g). Additionally, Fig. 1(h) shows an obvious lattice distortion of N–CuCoS$_{1.97}$ NWs. The corresponding elemental mapping of N–CuCoS$_{1.97}$ NWs illustrates the uniform distribution of Co, Cu, N and S in the NWs (Fig. 1i). Additionally, the porous structures of those as-obtained NWs were further confirmed by Brunner–Emmet–Teller (BET) and Barrett-Joyner-Halenda (BJH) (Figs. S2 & 3). The N–CuCoS$_{1.97}$ NWs (15.25 m$^2$ g$^{-1}$) exhibit 1.2, 1.6, and 2.1 times higher BET than N–CoS$_{1.97}$ (13.13 m$^2$ g$^{-1}$), CuCoS$_{1.97}$ (9.43 m$^2$ g$^{-1}$), and CoS$_{1.97}$ NWs (7.57 m$^2$ g$^{-1}$). The BJH pore volume analysis indicates that N–CuCoS$_{1.97}$ NWs (0.078 cm$^3$ g$^{-1}$) possess a larger pore volume than N–CoS$_{1.97}$ (0.06 cm$^3$ g$^{-1}$), CuCoS$_{1.97}$ (0.043 cm$^3$ g$^{-1}$) and CoS$_{1.97}$ NWs (0.034 cm$^3$ g$^{-1}$).

3.2. Surface structural properties of the N–CuCoS$_{1.97}$ NWs

The electronic structure of the catalysts was further analyzed by X-ray absorption fine structure spectroscopy (EXAFS), X-ray absorption near-edge structure (XANES), X-ray photoelectron spectrum
Fig. 2. (a) Temperature-dependent electrical resistivity of N–CuCoS\(_{1.97}\) NWs. EXAFS spectra in R-space of CoS\(_{1.97}\) and N–CuCoS\(_{1.97}\) NWs at (b) Co K-edge and (c) Cu K-edge. XANES spectra of CoS\(_{1.97}\) and N–CuCoS\(_{1.97}\) NWs at (d) S K-edge and (e) N K-edge. (f) ESR spectra of CoS\(_{1.97}\), CuCoS\(_{1.97}\), N–CoS\(_{1.97}\) and N–CuCoS\(_{1.97}\) NWs.

(XPS) and electron spin resonance (ESR) measurements. The 4-probe method result indicating CoS\(_{1.97}\) based NWs display a metallic property with temperature-dependent resistance from 25 to 250 K, but N–CuCoS\(_{1.97}\) NWs display the most superior electroconductivity with the lowest resistance [Figs. 2a & S4] [14–17]. XPS results of N–CuCoS\(_{1.97}\) NWs (Fig. S5) show that Co, Cu, N and S all exist. Furthermore, the EXAFS measurement was employed to characterize the fine structure. The Fourier Transforms (FTs) of the N–CuCoS\(_{1.97}\) NWs at the Co K-edge present three peaks in the range of 1.0–4.0 Å (Fig. 2b). The first one at 1.8 Å corresponds to Co–S/N pair, the second one in the range of 2.8–3.1 Å corresponds to Co–S pair, and the third one at 3.6 Å is due to the scattering pair of Co–Co/Cu. Moreover, the intensity of the Co–S pair in the N–CuCoS\(_{1.97}\) NWs is slightly weaker than that from the CoS\(_{1.97}\) NWs, attributed to the N-doping. But the Co–Co/Cu peaks from CoS\(_{1.97}\) NWs to N–CuCoS\(_{1.97}\) NWs show negligible change. The FTs image of the N–CuCoS\(_{1.97}\) NWs shows two peaks at 1.8 Å for Cu–S/N pair and 3.6 Å for Cu–Co/Cu pair at the Cu K-edge (Fig. 2c). The fitting results (Tables S1&2) confirm that the local atomic arrangement in the N–CuCoS\(_{1.97}\) NWs is indeed different from that in the CoS\(_{1.97}\) NWs with increasing the coordination number and intensifying the disordered local atomic structure. Moreover, the X-ray absorption near-edge structure (XANES) was used to study the valence bonds of the N–CuCoS\(_{1.97}\) NWs at S K-edge and N K-edge. The XANES of the N–CuCoS\(_{1.97}\) NWs and CoS\(_{1.97}\) NWs at S K-edge presents two obvious resonances at the same location of 2472
and 2483 eV, but there is a distinct difference in amplitude due to the N doped in the CuCoS\textsubscript{1.97} NWs (Fig. 2d) [50–52]. As shown in Fig. 2(e), the XANES of the N–CuCoS\textsubscript{1.97} NWs at N K-edge shows two resonances at 397.1 eV for N–O bond and 405.3 eV for N–Co/Cu bond. Additionally, ESR was employed to investigate the defects in N–CuCoS\textsubscript{1.97}, CuCoS\textsubscript{1.97}, N–CoS\textsubscript{1.97} and CoS\textsubscript{1.97} NWs [26,34]. As shown in Fig. 2(f), N–CuCoS\textsubscript{1.97} NWs show the strongest ESR signal than N–CoS\textsubscript{1.97}, CuCoS\textsubscript{1.97} and CoS\textsubscript{1.97} NWs, indicating N–CuCoS\textsubscript{1.97} NWs contain the most sulfide defects.

### 3.3. OER electrocatalytic activity of the N–CuCoS\textsubscript{1.97} NWs

The OER catalytic performances of N–CuCoS\textsubscript{1.97} NWs were also evaluated by linear scan voltamogram (LSV) in 1.0 M KOH [53–55]. CuCoS\textsubscript{1.97}, N–CoS\textsubscript{1.97}, CoS\textsubscript{1.97} NWs and commercial Ir/C (20\%) were all used as control. The N–CuCoS\textsubscript{1.97} NWs display an onset potential of 260 mV for OER, lower than those of the CuCoS\textsubscript{1.97} (265 mV), N–CoS\textsubscript{1.97} (280 mV) and CoS\textsubscript{1.97} NWs (290 mV) (Fig. 3a). The overpotential (\(\eta\)) at \(j = 10 \text{ mA cm}^{-2}\) for the N–CuCoS\textsubscript{1.97} NWs is 280 mV, also lower than those for the CuCoS\textsubscript{1.97} (290 mV), N–CuCoS\textsubscript{1.97} (306 mV) and CoS\textsubscript{1.97} (330 mV), and much smaller than that for Ir/C (20\%) (310 mV) (Fig. 5d). Fig. 3(b) shows the Tafel plots (log \(j–\eta\)) of different catalysts for OER. The Tafel slope of the N–CuCoS\textsubscript{1.97} NWs is 41 mV dec\textsuperscript{−1}, smaller than those of CuCoS\textsubscript{1.97} (70 mV dec\textsuperscript{−1}), N–CoS\textsubscript{1.97} (74 mV dec\textsuperscript{−1}) and CoS\textsubscript{1.97} NWs (81 mV dec\textsuperscript{−1}), indicating more rapid OER rates on N–CuCoS\textsubscript{1.97} NWs. Furthermore, the electrochemical double-layer capacitances (\(C_{dl}\)) of those catalysts were calculated (Fig. 3c). The \(C_{dl}\) of N–CuCoS\textsubscript{1.97} NWs (383 mF cm\textsuperscript{−2}) exhibits 1.8, 1.9, and 3.8 times higher than those of CuCoS\textsubscript{1.97} (214 mF cm\textsuperscript{−2}), N–CoS\textsubscript{1.97} (199 mF cm\textsuperscript{−2}) and CoS\textsubscript{1.97} NWs (101 mF cm\textsuperscript{−2}) (Fig. 5f). The electrochemical impedance spectroscopy (EIS) analysis of N–CuCoS\textsubscript{1.97}, CuCoS\textsubscript{1.97}, N–CoS\textsubscript{1.97} and CoS\textsubscript{1.97} NWs was also performed (Fig. 5a). The Nyquist plots reveal a remarkable decrease of the charge-transfer resistance (R\textsubscript{ct}) from 15 \(\Omega\) (CoS\textsubscript{1.97} NWs) to 2 \(\Omega\) (N–CuCoS\textsubscript{1.97} NWs), which can be attributed to the enhancement of electrical conductivity (Table S3). Additionally, the N–CuCoS\textsubscript{1.97} NWs also show the best ORR performance in those obtained catalysts (Fig. 5d).

The chronoamperometric response was utilized to evaluate the stability of N–CuCoS\textsubscript{1.97} NWs for OER at different potentials. As shown in Fig. 3(d), the different potentials were chosen to study the current response during the long-term measurement. At lower current densities of 10 and 50 mA cm\textsuperscript{−2}, N–CuCoS\textsubscript{1.97} NWs
display excellent stability with about 2% and 5% current densities decay after stability test. N–CuCoS$_{1.97}$ NWs still exhibit a stable current density response at higher current density of 100 mA cm$^{-2}$. N–CuCoS$_{1.97}$ NWs show an excellent activity and stability compared with recently reported OER catalysts (Table S4). As shown in Fig. S10, N–CuCoS$_{1.97}$ NWs show a high Faradaic efficiency (FE) of about 98.7%.

To determine the active sites of those catalysts for OER, the OER energetic profiles on those catalysts were calculated. The lattice oxygen constructed NWs heterojunction was constructed by finite strain theory to estimate the OER energetic profiles. The most matched interfaces are (100)$_{\text{N–CuCoS}_{1.97}}$//(104)$_{\beta–\text{CoOOH}}$ and (010)$_{\text{N–CuCoS}_{1.97}}$//(010)$_{\beta–\text{CoOOH}}$ with an interfacial strain of 5% according to the orientation relationship (OR) [56]. As shown in Fig. 3(e), lattice oxygen constructed N–CuCoS$_{1.97}$ NWs were fabricated ($\beta–\text{CoOOH}/\text{N–CuCoS}_{1.97}$ NWs). The DFT results show that the water oxidation on those NWs proceeded via following four proton-releasing steps as:

\begin{equation}
\text{H}_2\text{O} + \text{H}^+ + \text{e}^- \rightarrow \text{H}_2\text{O}^+ + \text{H}^+ + \text{H}_2\text{O} \quad (1)
\end{equation}

\begin{equation}
\text{H}_2\text{O} + \text{OH}^- + \text{H}^+ \rightarrow \text{H}_2\text{O}_2^- + \text{H}^+ \quad (2)
\end{equation}

\begin{equation}
\text{H}_2\text{O} + \text{O}^2+ + \text{H}^+ \rightarrow \text{HO}_2^- + \text{H}^+ \quad (3)
\end{equation}

\begin{equation}
\text{H}_2\text{O}_2^- + \text{O}^2+ + \text{H}^+ \rightarrow 2\text{H}_2\text{O} + \text{O}_2 + \text{H}^+ \quad (4)
\end{equation}

Due to the lattice oxygen covered surface, the OOH species could be formed and the O$_2$ molecule is generated more easily. Energetic profiles in Fig. 3(f) show that $\beta–\text{CoOOH}/\text{N–CuCoS}_{1.97}$ NWs have an OER overpotential of 290 mV with the rate-determining step of B, close to that of experimental value. The OER activity of $\beta–\text{CoOOH}/\text{N–CuCoS}_{1.97}$ NWs can be attributed to the electron transfer from the semiconductor CoOOH to the metallic N–CuCoS$_{1.97}$, making the surface oxide be more favorable for intermediates adsorption. Additionally, $\beta–\text{CoOOH}/\text{CuCoS}_{1.97}$ NWs show an OER overpotential of 500 mV. Meanwhile, the DFT results also show a better OER energetic profiles of $\beta–\text{CoOOH}/\text{CuCoS}_{1.97}$ (320 mV) and $\beta–\text{CoOOH}/\text{N–CoS}_{1.97}$ NWs (290 mV) (Fig. S11).

3.4. Structure of the N–CuCoS$_{1.97}$ NWs after OER

Moreover, some high-tech tests were used to confirm the formation of lattice oxygen on the surface of N–CuCoS$_{1.97}$ NWs. As shown in Fig. 4(a), the porous nanowires morphology of the
N–CuCoS$_{1.97}$ was maintained. Furthermore, the HRTEM (Fig. 4b) shows a thin CoOOH layer with a lattice spacing of 0.198 nm appeared on the surface of N–CuCoS$_{1.97}$ NWs after OER. The mapping images (Fig. 4c) also show homogeneous distribution of Cu, Co, N, S, and O elements around the whole N–CuCoS$_{1.97}$ NWs. The XRD pattern of N–CuCoS$_{1.97}$ NWs (Fig. S12) shows two additional peaks at 25° and 43°, attributed to the surface oxidation in OER. Additionally, the XPS was used to characterize the surface changes of N–CuCoS$_{1.97}$ NWs after OER. Fig. S13 shows the main oxidation state of Co decreased to 2+ in N–CuCoS$_{1.97}$ NWs after OER, disappeared S and N on the surface, and the oxidation state of Cu also increased. The XANES at 0 K-edge shows an obvious oxygen deficiency at 537.5 eV (Fig. 4d) and the formation of metal–O bond [57,58]. The EXAFS was further employed to investigate the fine structure of N–CuCoS$_{1.97}$ NWs after OER, showing that both Co K-edge (Fig. 4e) and Cu K-edge (Fig. 4f) display slight oxidation of the N–CuCoS$_{1.97}$ NWs. The EXAFS spectra of the N–CuCoS$_{1.97}$ NWs at Co K-edge show obvious changes at the range of 1 – 2.5 Å, indicating the change of coordination bond, valence and defects of Co in the N–CuCoS$_{1.97}$ NWs. Furthermore, the fitting results (Table S5) confirm that the atomic arrangement in the N–CuCoS$_{1.97}$ NWs is structurally more disordered.

3.5. Performance of the N–CuCoS$_{1.97}$ NWs based liquid Zn–air battery

The energy conversion performance of those catalysts was confirmed using homemade Zn–air battery as a model [59–64]. The battery was built using zinc plate as the anode, catalysts as the air–cathode, and 6.0 M KOH as the electrolyte. Fig. 5(a) shows the open-circuit voltage (OCV) of those catalysts fabricated Zn–air battery. N–CuCoS$_{1.97}$ NWs display an OCV of 1.46 V for 48 h better than those of CuCoS$_{1.97}$ (1.40 V), N–Co$_{0.97}$ (1.36 V) and CoS$_{1.97}$ NWs (1.25 V). The maximum power density of N–CuCoS$_{1.97}$ NWs is 68.6 mW cm$^{-2}$, also much better than those of CuCoS$_{1.97}$ (44.6 mW cm$^{-2}$), N–Co$_{0.97}$ (30.5 mW cm$^{-2}$) and CoS$_{1.97}$ NWs (23.6 mW cm$^{-2}$) (Fig. 5b). In addition, N–CuCoS$_{1.97}$ NWs show the best discharge and charge capacity in this work (Fig. 5c). The battery cycling test was further conducted to confirm the recharge ability of N–CuCoS$_{1.97}$ NWs. Meanwhile, the rechargeable property of the N–CuCoS$_{1.97}$ NWs fabricated Zn–air battery was measured. As shown in Fig. 5(d), Zn–air battery fabricated with N–CuCoS$_{1.97}$ NWs shows a considerably stable charge and discharge with the virtually negligible voltage fading for 70 h. Based on the excellent OER and ORR performance, the Zn–air battery built by N–CuCoS$_{1.97}$ NWs as air–cathode shows higher voltage and better rechargeable ability.

3.6. Performance of the N–CuCoS$_{1.97}$ NWs based solid Zn–air battery

Furthermore, the solid Zn–air batteries composed with N–CuCoS$_{1.97}$ NWs air–cathode, zinc anode, and polyvinyl alcohol (PVA) were developed to demonstrate potential applications in flexible engineering (the inset in Fig. 6a) [26,34,50,56]. N–CuCoS$_{1.97}$ NWs based solid Zn–Air battery displays good performance with an open circuit voltage (OCV) of ~1.36 V for 15 h (Fig. 6a). Additionally, the rechargeable performance of those solid batteries was also confirmed. As shown in Fig. 6(b), the discharge/charge cycles for solid battery can be maintained for 500 min at the current densities of 1 and 3 mA cm$^{-2}$. More importantly, the N–CuCoS$_{1.97}$ NWs based solid Zn–air batteries shows superior flexibility (Fig. 6c), and the Zn–air batteries also show unique wearable property to power the mobile devices (Fig. 6d).
Fig. 6. (a) The open-circuit voltage of N–CuCoS$_{1.97}$ NWs based solid Zn–Air battery. The insert is the scheme of fabrication the solid battery. (b) Battery cycling test at 1 and 3 mA cm$^{-2}$ of the solid battery. (c, d) Photos of flexible and wearable N–CuCoS$_{1.97}$ NWs based solid Zn–air battery.

4. Conclusions

In summary, we demonstrate a highly active transition metal sulfide named as N–CuCoS$_{1.97}$ NWs for efficient electrocatalytic reaction and energy conversion. The boosting activity can be attributed to intrinsic metallic and abundant defects, which can be confirmed by HRTEM, EXAFS, and ESR. Furthermore, construction of lattice oxygen in N–CuCoS$_{1.97}$ NWs can improve its stability in basic media and increase its activity for excess active sites during OER. Meanwhile, the DFT results also evident that lattice oxygen constructed surface of N–CuCoS$_{1.97}$ NWs has more favorable OER energetic profiles and absorption for reaction intermediate. More importantly, N–CuCoS$_{1.97}$ NWs fabricated Zn–air batteries not only show excellent rechargeable and mechanical stability, but also display an amazing performance in flexible and wearable devices, which enriched the commercial prospect of Zn–air battery.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.ecocom.2018.06.005.

References
