Synthesis and characterization of CuO/\(\text{Ni}_7\text{S}_6\) composites for application in supercapacitors

Ke Xue, Bo Liu, Huimin Feng, Lecheng Tian, Juan Ding, Maryum Ali, Jingfeng Liu, and Zhicai Xing

Copper oxide (CuO) is considered a promising material for pseudocapacitor electrodes in supercapacitors. In this study, binder-free CuO/\(\text{Ni}_7\text{S}_6\) composite electrode materials were prepared on nickel foam using a two-step electrodeposition method. The test results show that the CuO/\(\text{Ni}_7\text{S}_6\)-1:1–20 composite material has the best electrochemical performance. It displays an areal capacitance of 8644.3 mF cm\(^{-2}\) at a current density is 1 mA cm\(^{-2}\). The assembled CuO/\(\text{Ni}_7\text{S}_6\)-1:1–20|PVDF/KOH|CuO/\(\text{Ni}_7\text{S}_6\)-1:1–20 devices can reach a maximum energy density (\(E_D\)) and power density (\(P_D\)) of 112.5 \(\mu\)Wh cm\(^{-2}\) and 4200 \(\mu\)W cm\(^{-2}\) respectively while retaining 58.3% of their initial capacitance after 3000 charge/discharge cycles. Two devices connected in series can power an LED lamp for up to 15 minutes. The results demonstrate that CuO/\(\text{Ni}_7\text{S}_6\) materials have significant potential for application in supercapacitors.

1. Introduction

The development and storage of sustainable energy sources are crucial in addressing issues related to energy shortages. In recent years, significant efforts have been focused on developing environmentally friendly energy storage devices. Supercapacitors (SC) have attracted wide attention in recent years due to their advantageous features, such as long cycle life, fast charging speed, high power density, low cost, and eco-friendliness. They provide a promising direction for research on efficient environment-friendly energy storage devices.\(^1\)–\(^4\)

Despite the attention SCs have received in the field of energy storage, their energy density and voltage window still fall short of lithium-ion batteries, which limits their widespread applicability. Developing new materials with high specific capacitance is an important strategy to increase the energy density of supercapacitors, as it is mainly determined by potential and capacitance.\(^5\)–\(^8\)

Researchers have shown interest in utilizing transition metal oxides as an electrode material due to their wide range of redox reactions and excellent electrochemical properties, such as low impedance, high specific capacitance, and multiple active sites.\(^9\)–\(^10\) CuO (a p-type semiconductor) is considered an ideal supercapacitor electrode material due to its easy preparation, non-toxicity, environmental friendliness, low cost, and high theoretical pseudocapacitance (1800 F g\(^{-1}\)).\(^11\)–\(^12\) However, the inherent low conductivity of CuO is a major drawback that limits its practical specific capacitance and application. However, studies have shown that combining multiple materials with different components can increase the number of electrically active sites, improve the ion transfer efficiency, and achieve synergistic effects between different components, leading to effectively improving the defects in the performance of a single material.\(^13\)–\(^14\) In a study, graphene was coated on the surface of copper oxide using an impregnation method. This resulted in the formation of a stable electron transport path enabling the composite to have a specific capacity 2.4 times higher than that of the pristine CuO nanomaterials.\(^15\) Similarly, by growing NiCo-LDH nanosheets on CuO, the specific surface area and specific capacity of the composite are significantly enhanced.\(^16\) Thus, the selection of suitable composite materials is crucial to compensate for the inherent defects of the CuO-based electrode materials, leading to improved electrochemical performance. Transition metal sulfides are frequently employed as electrode materials in supercapacitors due to their excellent electrical conductivity, high energy density, and good
mechanical stability. Nickel sulfide is another important class of transition metal sulfide compound, with over ten crystalline phases such as \( \alpha \)-NiS, \( \beta \)-NiS, NiS\(_2\), Ni\(_3\)S\(_4\), Ni\(_5\)S\(_6\), Ni\(_7\)S\(_6\), Ni\(_9\)S\(_8\), etc.\(^{18,19}\) Although Ni\(_7\)S\(_6\) is a less explored supercapacitor material, due to its excellent performance in electrocatalysis and sensors,\(^{20,21}\) it is believed to have good potential in supercapacitor applications as well.

This study proposes a two-step electrodeposition method to grow CuO/Ni\(_7\)S\(_6\) nanocomposites directly on Ni foam as a binder-free electrode material. When tested in 1 M KOH and at 1 mA cm\(^{-2}\) current density, the prepared CuO/Ni\(_7\)S\(_6\) nanocomposites exhibited an areal-specific capacitance of 8644.3 mF cm\(^{-2}\). The assembled CuO/Ni\(_7\)S\(_6\)-1:1–20|PVDF/KOH|CuO/Ni\(_7\)S\(_6\)-1:1–20 all-solid-state devices could reach a maximum \( E_a \) and \( P_a \) of 112.5 \( \mu \)W h cm\(^{-2}\) and 4200 \( \mu \)W cm\(^{-2}\), respectively. Two of these devices connected in series can illuminate an LED for up to 15 min. The excellent properties exhibited by the CuO/Ni\(_7\)S\(_6\)-1:1–20 composites indicate their promising prospects as supercapacitor electrode materials.

2. Experimental

2.1. Reagents

The chemicals employed include copper acetate (Cu(CH\(_3\)COO)\(_2\)-H\(_2\)O), disodium EDTA (EDTA-2Na), nickel chloride (NiCl\(_2\)-6H\(_2\)O), potassium hydroxide (KOH), thiourea (CH\(_4\)N\(_2\)S), absolute ethyl alcohol (C\(_2\)H\(_5\)O) and nickel foam (NF). All the chemicals were of analytical grade.

2.2. Fabrication of CuO/Ni\(_7\)S\(_6\) composites

Before use, NF was washed in acetone and anhydrous ethanol for 15 min each to remove oxides and impurities from the NF surface. Cu(CH\(_3\)COO)\(_2\) (0.02 M) and EDTA-2Na (0.0025 M) were used as electrolytes. To prepare CuO, an electrochemical workstation (CHI 660E) with a saturated calomel electrode (SCE), rectangular graphite block, and Ni foam as the reference, counter, and working electrode, respectively, was used. A constant potential of –1.3 V for 40 min was applied. To prepare CuO/NF material, these dried samples were annealed at 350 \(^\circ\)C for 1 h.

Three beakers were prepared and numbered 1, 2, and 3. The concentration ratios of CH\(_4\)N\(_2\)S and NiCl\(_2\)-6H\(_2\)O in the beakers were set to C\(_S\):C\(_N\) = 3:1, C\(_S\):C\(_N\) = 1:1, and C\(_S\):C\(_N\) = 1:3, respectively. These prepared solutions were used as the electrolyte. A CuO substrate was employed as the working electrode, SCE as the reference electrode, and the rectangular graphite block as the counter electrode. The electrochemical deposition voltage and deposition time were set to –1 V and 5 min, respectively. The deposited samples were thoroughly washed and then dried to obtain the desired samples, named CuO/Ni\(_7\)S\(_6\)-1:1–5, CuO/Ni\(_7\)S\(_6\)-1:1–10 and CuO/Ni\(_7\)S\(_6\)-1:3–5, respectively.

In another experiment, the solution in beaker 2 was used as the electrolyte (C\(_S\):C\(_N\) = 1:1) for the electrochemical deposition at different times. The fixed deposition voltage remained unchanged at –1 V and the deposition time was set at 5 min, 10 min, 20 min, and 30 min. The deposited samples were washed and then dried overnight to obtain the desired samples, named CuO/Ni\(_7\)S\(_6\)-1:1–5, CuO/Ni\(_7\)S\(_6\)-1:1–10 and CuO/Ni\(_7\)S\(_6\)-1:3–5, respectively. The excellent properties exhibited by the CuO/Ni\(_7\)S\(_6\)-1:1–20 composites indicate their promising prospects as supercapacitor electrode materials.

2.3. Fabrication of the CuO/Ni\(_7\)S\(_6\)-1:1–20|PVDF/KOH|CuO/Ni\(_7\)S\(_6\)-1:1–20 SSC

In device assembly, the composite CuO/Ni\(_7\)S\(_6\)-1:1–20 with the best performance was used as the positive and negative electrode. PVDF/KOH gel was used as the electrolyte, and NKK cellulose paper was used as the diaphragm. The gel was applied to the active substance portion of the two electrodes, and cellulose paper was placed in the middle followed by wrapping of cling film to assemble a typical sandwich structure CuO/Ni\(_7\)S\(_6\)-1:1–20|PVDF/KOH|CuO/Ni\(_7\)S\(_6\)-1:1–20 solid-state supercapacitor device. The LED-lit device shows specifications of voltage: 1.8–2 V, a current of 20 mA, and brightness of 2000–3000 mcd. The power supply for charging the device is a DC-regulated power supply.

2.4. Characterization

The surface morphology and elemental composition of the CuO/Ni\(_7\)S\(_6\) composites were determined by field emission scanning electron microscopy (FE-SEM) and energy dispersive spectrometry (EDS). Phase composition and crystal information were observed by X-ray diffraction (XRD). X-ray photoelectron spectroscopy (XPS) was used to determine the surface’s elemental composition and the samples’ chemical state. Statistics of impedance, charging and discharging processes, and electrochemical reaction kinetics of CuO/Ni\(_7\)S\(_6\) composites were analyzed using electrochemical impedance spectroscopy (EIS), galvanostatic charge–discharge (GCD) and cyclic voltammetry (CV).
3. Results and discussion

3.1. Structural analysis of the CuO/Ni$_7$S$_6$ material

The microstructure and morphology of the CuO/Ni$_7$S$_6$ material were analyzed by using FE-SEM. A wheat-like pattern was observed due to the accumulation of CuO particles (shown in Fig. 2a and b). The wheat-like CuO provides a large specific surface area, which facilitates the coating of subsequent films. The FE-SEM images of the CuO/Ni$_7$S$_6$ composites are shown in Fig. 2c and d. From the figures, it can be observed that the composite has a rich open-space structure, which is favorable for the full contact between the active substance and the electrolyte, thus exposing more reactive sites.$^{22,23}$

XRD tests were used to determine the physical phase composition of the CuO material and the CuO/Ni$_7$S$_6$ composite. As observed in Fig. 3, a characteristic peak of Ni can be seen (JCPDS No. 04-0850), because of the nickel foam acting as a conductive collector. The diffraction peaks at 35.5°, 38.7°, 61.5° and 66.2° in the diffractogram correspond to the (111), (111), (113) and (311) crystal planes, respectively, and are consistent with the characteristic peaks of CuO (JCPDS No. 48-1548). The diffraction peaks at 33.0°, 36.8°, 48.5°, and 50.3° correspond to the (060), (062), (016), and (125) crystal planes, respectively, and match JCPDS No. 24-1021, confirming the presence of the Ni$_7$S$_6$ phase. The presence of the diffraction peaks of NiO may be due to the partial oxidation of Ni$_7$S$_6$ during the drying and milling process carried out on the sample.

The chemical state of CuO/Ni$_7$S$_6$ was analyzed by XPS. In the CuO spectrum (Fig. 4a), the peaks at 933.99 eV and 953.99 eV belong to the Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$ of Cu, respectively. In contrast, the peaks at 941.6 eV, 943.9 eV, and 962.3 eV correspond to the vibrational satellite peaks of Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$. In Fig. 4a, the Cu 2p spectrum of the CuO/Ni$_7$S$_6$ composites shows two main peaks at 933.8 eV and 953.8 eV, corresponding to Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$, respectively. The spin–orbit coupling potential between Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$ is 20 eV, which agrees with the previously reported literature and further confirms the presence of Cu$^{2+}$. The Cu 2p spectral region is accompanied by three satellite peaks at 941.1 eV, 943.6 eV, and 962.0 eV, affirming the presence of the CuO phase.$^{24,25}$ The Cu 2p binding energies of the CuO/Ni$_7$S$_6$ composites are lower than that of the CuO by 0.19 eV, indicating that the electron density on the surface of CuO in the composite is reduced.$^{26}$ The presence of two spin–orbit peaks in the Ni 2p spectrum (Fig. 4b) is attributed to Ni 2p$_{3/2}$ (Ni$^{2+}$: 874.2 eV, Ni$^{3+}$: 876.6 eV) and Ni 2p$_{1/2}$ (Ni$^{2+}$: 856.2 eV, Ni$^{3+}$: 857.9 eV). In addition, two vibrational satellite peaks belonging to Ni 2p were seen at 880.7 eV and 862.2 eV, respectively.$^{27,28}$ This result indicates that both Ni$^{2+}$ and Ni$^{3+}$ are present in Ni$_7$S$_6$. In the S 2p spectra (Fig. 4c), two peaks and a satellite peak (169.0 eV) of S 2p$_{3/2}$ (162.5 eV) and S 2p$_{1/2}$ (161.4 eV) can be observed.$^{29,30}$ To gather information about the chemical components and elemental distribution of the samples, EDS tests were conducted. As shown in Fig. 5, the test results indicate an even distribution of the elements Cu, O, Ni, and S throughout the samples. All the above characterizations performed support the successful preparation of CuO/Ni$_7$S$_6$ composites.

3.2. Electrochemical performance analysis

To investigate the effect of different concentration ratios of CH$_4$N$_2$S to NiCl$_2$·6H$_2$O on the electrochemical properties of the CuO/Ni$_7$S$_6$ composites. Composites with ratios of CuS : Ni = 3 : 1, 1 : 1, and 1 : 3 (named: CuO/Ni$_7$S$_6$:3:1–5, CuO/Ni$_7$S$_6$:1:1–5 and CuO/ Ni$_7$S$_6$:1:3–5, respectively) were prepared. The electrochemical performances of the three composites were evaluated in the three-electrode system with 1 M KOH as the electrolyte. Fig. 6a shows the CV curve of the CuO/Ni$_7$S$_6$ composites. It is observed that each curve exhibits a pair of redox peaks, which is attributed to the redox reactions occurring in the KOH solution$^{31-33}$:

$$\text{CuO} + \text{H}_2\text{O} \leftrightarrow \text{Cu(OH)}_2$$  \hspace{1cm} (1)

$$\text{Ni}_7\text{S}_6 + 7\text{OH}^- \leftrightarrow \text{Ni}_7\text{S}_6(\text{OH})_7 + 7\text{e}^-$$  \hspace{1cm} (2)
The integral area of the CuO/Ni_{7}S_{6}-1:1–5 sample curve is the largest. Considering that the area of the CV curve can roughly reflect the specific capacitance, it is evident that the specific capacitance of the composite is the highest when the concentration ratio of the raw materials is 1:1.34,35 Fig. 6b shows the GCD curve of the CuO/Ni_{7}S_{6} composite when the current density is 1 mA cm^{-2}. As a result of the redox reaction, each GCD plot shows a typical charge discharge plateau. It is observed that the CuO/Ni_{7}S_{6}-1:1–5 electrode has the longest discharge time, which translates to the largest areal capacitance. The GCD results are consistent with the CV test results. The Nyquist plots and equivalent circuit diagrams of the samples are shown in Fig. 6c. Nyquist plots reveal that the CuO/Ni_{7}S_{6}-1:1–5 electrode has the largest slope of the curve, suggesting smaller ion diffusion resistance, and higher electron transfer efficiency.36 The CuO/Ni_{7}S_{6}-1:1–5 electrode exhibits the smallest semicircular diameter in the high-frequency region, indicating the smallest charge transfer resistance and highest charge transfer rate between the electrode and the electrolyte interface. Based on the x-axis intercept, the R_s values of the three electrodes are close to each other, which can be attributed to the same test electrolyte. The areal capacitance of the sample was calculated based on the GCD curve and eqn (3) and the resulting areal capacitance curve is plotted in Fig. 6d.

$$\text{C}_a = \frac{I \times \Delta t}{S \times \Delta U}$$  \hspace{1cm} (3)

where $S$ is the electrode area $(\text{cm}^2)$, $I$ is the discharge current $(\text{A})$, $C_a$ is the areal capacitance $(\text{mF cm}^{-2})$, $\Delta U$ is the voltage window $(\text{V})$, and $\Delta t$ is the discharge time $(\text{s})$. At a current density of 1 mA cm^{-2}, the CuO/Ni_{7}S_{6}-1:1–5 $(3668.57 \text{ mF cm}^{-2})$ composite exhibits the highest areal capacitance compared with CuO/Ni_{7}S_{6}-3:1–5 $(3248.57 \text{ mF cm}^{-2})$ and CuO/Ni_{7}S_{6}-1:3–5 $(3210 \text{ mF cm}^{-2})$. The analysis provides the impact of the concentration ratio of CH_{4}N_{2}S and NiCl_{2}-6H_{2}O on the electrochemical performance of the CuO/Ni_{7}S_{6} composites. Choosing an appropriate concentration ratio is crucial for the production of electrode materials with outstanding performance.

To investigate the electrochemical properties of the CuO/Ni_{7}S_{6} composites at different deposition times, the CuO/Ni_{7}S_{6}-1:1–(5, 20, 30) composites were synthesized with deposition times of 5, 20, and 30 min. Subsequently, their electrochemical properties were tested in a three-electrode system with 1 M KOH electrolyte. Fig. 7a shows the CV curves of the three samples revealing distinct redox peaks. The CV curve area of the CuO/Ni_{7}S_{6}-1:1–20 sample is the largest indicating that the
composite obtained by depositing for 20 min has the largest specific capacitance and superior reactivity. Fig. 7b showcases the GCD curve of the sample when the current density is 1 mA cm\(^{-2}\). A clear charging and discharging plateau can be observed, affirming that the capacitance contribution is primarily associated with redox reactions. A comparison of the GCD curves of the three samples shows that the CuO/Ni\(_7\)S\(_6\)-1:1–20 electrode has the longest discharge time, lasting for 6043 s. The discharge time of the CuO/Ni\(_7\)S\(_6\)-1:1–30 composite is 3372 s. It can be noted that the electrochemical performance of the CuO/Ni\(_7\)S\(_6\)-1:1–30 composite decreases significantly with the extension of the deposition time. This is mainly due to the excessive Ni\(_7\)S\(_6\) hindering the full contact between the electrolyte and the active site, resulting in the deterioration of the material performance. A comparison of the EIS curves of the three samples (Fig. 7c) shows that the CuO/Ni\(_7\)S\(_6\)-1:1–20 composite has the smallest x-axis intercept, the smallest semicircle diameter in the high-frequency region, and a larger straight-line slope in the low-frequency region. This indicates that the electrode (CuO/Ni\(_7\)S\(_6\)-1:1–20) has the smallest resistance to \(R_s\) and ion diffusion. A line graph of the areal capacitance of the three samples calculated at a current density of 1 mA cm\(^{-2}\) is given in Fig. 7d. The maximum specific capacitance is observed at this current density due to the slower migration rate of electrolyte ions, allowing for enhanced penetration into the material’s interior to fully react with the active sites. The areal capacitance of the CuO/Ni\(_7\)S\(_6\)-1:1–20 composite is significantly higher than that of CuO/Ni\(_7\)S\(_6\)-1:1–5 and CuO/Ni\(_7\)S\(_6\)-1:1–30 at all current densities. These electrochemical tests emphasize the importance of proper deposition time for improving the electrochemical performance of the composites.

Fig. 8 shows the performance comparison between the composite material and CuO. Fig. 8a compares the CV curves of the two materials at 10 mV s\(^{-1}\). From the figure, it can be seen that the closed area of the CV curve of CuO/Ni\(_7\)S\(_6\)-1:1–20 is obviously larger than that of CuO, which indicates that the electrochemical performance of the electrode material has been improved by the composite Ni\(_7\)S\(_6\). Fig. 8b shows the comparison of the GCD test of the two materials, which shows that the composite material has a larger voltage window as well as discharge time. Subsequently, EIS tests were performed on both materials, as shown in Fig. 8c. Compared to CuO, the CuO/Ni\(_7\)S\(_6\)-1:1–20 electrode has a smaller semicircular diameter in the high-frequency region as well as a larger straight-line slope in the low-frequency region, suggesting that the composite electrode facilitates the rapid transfer of electrons and ions.

After analyzing the electrochemical properties of the synthesized materials with different sulfur-to-nickel concentration ratios and different deposition times, it was concluded that the synthesized CuO/Ni\(_7\)S\(_6\)-1:1–20 electrode showed the best electrochemical performance when \(C_S:C_{Ni} = 1:1\) and the deposition time was 20 min. It can be observed from the CV curve of the CuO/Ni\(_7\)S\(_6\)-1:1–20 electrodes at different scanning
rates (5–60 mV s\(^{-1}\)) (Fig. 9a) that the shape of the curve does not change with the increase of the scanning rate, indicating that the CuO/Ni\(_7\)S\(_6\)-1:1–20 electrodes exhibit good cycling stability. The REDOX peak is shown in the curve, and with the increase of the scanning rate, the cathode peak moves to a small potential, and the anode peak moves to a large potential. This change is attributed to the shortened reaction time between the electrode active substance and the electrolyte as the sweep rate increases, resulting in an incomplete redox reaction. Fig. 9b shows the GCD curves of the CuO/Ni\(_7\)S\(_6\)-1:1–20 electrode at various current densities. A smaller voltage window was selected for the GCD test compared to the voltage window for the CV test. This is due to the decrease in coulombic efficiency at low current densities. The improved symmetry of the curves confirms the reversible charging and discharging behavior. A clear charge/discharge plateau is observed, indicating conversion of Ni\(_7\)S\(_6\) to Ni\(_7\)S\(_6\)(OH)\(_7\). With increasing current density, the GCD curve remains relatively unchanged maintaining a symmetrical profile, indicating electrode stability.

Fig. 10 shows the corresponding values of areal capacitance at different current densities. It is observed that the areal capacitance value decreases as the current density increases.
because the high current density accelerates the migration rate of the electrolyte ions, preventing them from completing the redox reaction in time. The capacitance values of the device at various current densities were calculated to be 8644.3 mF cm$^{-2}$, 7437.3 mF cm$^{-2}$, 6595.7 mF cm$^{-2}$, 5257.1 mF cm$^{-2}$, 4523.0 mF cm$^{-2}$, and 3880.0 mF cm$^{-2}$. All the determined values are higher than the areal capacitances of recently reported electrode materials based on Ni$_3$S$_2$ and CuO. The results confirm the effective synergy between CuO and Ni$_7$S$_6$ and demonstrate the potential of the Ni$_7$S$_6$ composite in extending the application of CuO-based electrode materials.

Fig. 11 displays the charge/discharge process of the CuO/Ni$_7$S$_6$-1:1–20 electrode at a current density of 20 mA cm$^{-2}$ for 3000 cycles to test the stability of the CuO/Ni$_7$S$_6$-1:1–20 composite. The test results show a capacitance retention of 59.4% after 3000 cycles, and a Coulombic efficiency close to 100%. Initially, the capacitance decreased significantly from 0 to 500 cycles, probably due to the partial detachment of the surface of the CuO/Ni$_7$S$_6$-1:1–20 electrode material. The GCD curves of the last 5 laps were intercepted, and it was observed that the shape of the GCD curves was well maintained without obvious deformation.

3.3. Solid-state symmetric supercapacitors

After the electrochemical performance analysis of the materials, the CuO/Ni$_7$S$_6$-1:1–20 composite material, exhibiting the best electrochemical performance, was selected as the positive and negative electrode material for a supercapacitor. A CuO/Ni$_7$S$_6$-1:1–20|PVDF/KOH|CuO/Ni$_7$S$_6$-1:1–20 solid-state symmetric supercapacitor device was assembled, and their electrochemical performance was analyzed. Fig. 12a shows the CV curves of the CuO/Ni$_7$S$_6$-1:1–20|PVDF/KOH|CuO/Ni$_7$S$_6$-1:1–20 device at various voltage windows to identify the optimal potential range. When the potential window is extended to 0–1.5 V, the CV curves show obvious polarization. This polarization is attributed to the decomposition of water in the PVDF/KOH gel electrolyte at higher voltage values. Thus, it was determined that the maximum stable voltage window for the device is 0–1.4 V. Fig. 12b shows the GCD curve of the device.
under different voltage windows when the current density is 2 mA cm$^{-2}$. It can be observed that a typical charging and discharging platform emerges when the voltage window is set to 0–1.2 V. These results align with the CV curve results because the anode peak potential of the curve is not reached within a small voltage window of 0–1.1 V. As the voltage window increases, oxidation peaks begin to appear, leading to the formation of the charge–discharge platform.

Fig. 13a shows the CV curves of the CuO/Ni$_7$S$_6$-1:1–20|PVDF/KOH|CuO/Ni$_7$S$_6$-1:1–20 device at different scan rates. Characteristic redox peaks can be observed, and the shape of the curves remains almost unchanged as the scan rate changes, indicating good reversible Faraday properties of the device. The GCD curve of the CuO/Ni$_7$S$_6$-1:1–20|PVDF/KOH|CuO/Ni$_7$S$_6$-1:1–20 device reveals (Fig. 13b) significant platform characteristics and nonlinear characteristics in the curve. When the current...
density of the device is 1400 mW cm\(^{-2}\), the capacitance retention rate was 58.3% of the initial capacitance. The assembly of the CuO/Ni\(_7\)S\(_6\)-1:1–20/PVDF/KOH/CuO/Ni\(_7\)S\(_6\)-1:1–20 device is illustrated in the diagram. As shown in Fig. 14a, the capacitance retention rate was 58.3% of the initial capacitance. The assembly of the CuO/Ni\(_7\)S\(_6\)-1:1–20/PVDF/KOH/CuO/Ni\(_7\)S\(_6\)-1:1–20 device is illustrated in the diagram. As shown in Fig. 14b, the \(R_e\) value of the device increases from 1.4 \(\Omega\) to 3.5 \(\Omega\) after 3000 cycles. As depicted in Fig. 14c–f, connecting two devices in series to power the LED results in the lighting time reaching 15 min. This further substantiates that the prepared device has energy storage capability in the application.

Fig. 15 shows the Ragone of the CuO/Ni\(_7\)S\(_6\)-1:1–20/PVDF/KOH/CuO/Ni\(_7\)S\(_6\)-1:1–20 devices compared with previous reports of the power density and energy density.

Data availability
All relevant data are within the paper.

Conflicts of interest
There are no conflicts of interest to declare.

Acknowledgements
This work was financially supported by the Education Department of the Jilin Provincial People’s Government (Grant No. JJKH20240907KJ). This work was financially supported by 2023 Zhejiang Province “leading wild goose” research and development project (Grant No. 2023C01238), 2023 Zhejiang Province “spearhead” research and development project (Grant No. 2023C01133), and Jiaxing city key research and development plan project (Grant No. 2023BZ10002).

References


9 H. Xu, Y. Zhao and J. Zhao, Ammonia-induced construction of three-dimensional sea urchin-like Co(OH)2@CuO structure for oxygen evolution reaction and supercapacitor, *J. Alloys Compd.*, 2023, **960**, 170944.


38 A. Keshavarz, J. Tashkhourian and S. F. Nami-Ana, Designing an asymmetric supercapacitor based on Co(OH)$_2$@PANI nanocomposite synthesized via a facile hydrothermal method, *J. Energy Storage*, 2023, **73**, 108825.


