Controllable synthesis of spherical S@CoMn2O4 battery-type electrode material for hybrid supercapacitors

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Abstract

A novel spherical Co-Mn composite-CoMn$_2$O$_4$ was synthesized via a one-step solvothermal method, and S doping CoMn$_2$O$_4$ (S@CoMn$_2$O$_4$) battery-type electrode material was further obtained via a hydrothermal vulcanization. This ion exchange technique is mainly carried out on the surface of the material and will not destroy the morphology of the original oxide-MOF, so the obtained materials generally have a core-shell structure. The S@CoMn$_2$O$_4$ not only remains a spherical character, but also possesses a coarser surface and porous structure, which considerably increases the specific surface areas (SSA) and electrochemical active sites (EAS) for electrode materials, thus facilitating the charge transfer kinetics for ions and electrons. When the current density (CD) is 1 A g$^{-1}$, the specific capacity ($C_s$) of S@CoMn$_2$O$_4$ is 812 C g$^{-1}$. Moreover, S@CoMn$_2$O$_4$ has excellent electrochemical cycling performance, and the retention rate of $C_s$ for the S@CoMn$_2$O$_4$ reach 92.91% after 5000 cycles at 10 A g$^{-1}$. When the specific power ($P_s$) is 775 W kg$^{-1}$, the specific energy ($E_s$) for S@CoMn$_2$O$_4$/AC device reaches 44.36 Wh kg$^{-1}$.

1. Introduction

Supercapacitors (SCs) have been widely concerned for their advantages of high specific power and energy density, good cycle stability, fast charge and discharge, low cost, small footprint, high safety, environmental protection, flexible operation and high reliability [1–5]. SCs can be divided into three types according to the charge storage mechanism, namely electric double-layer capacitor (EDLC), pseudo capacitor (PC) and battery-type supercapacitor (BTS) [6]. In EDLC, energy is stored by accumulating electrostatic charges at the interface between the electrode and electrolyte [7–9]. In electrochemical test, the cyclic voltammetry (CV) curve presents a rectangular shape, and the galvanostatic charge-discharge (GCD) curve presents a triangular shape [10]. PC stores energy by a Faraday redox reaction on or near the surface of the electrode [11, 12]. In electrochemical tests, the CV curve shows a twisted rectangular shape, and the GCD curve shows a twisted triangular shape, which is similar to the EDLC electrode material [13]. BTS stores energy by a Faraday redox reaction in the bulk electrode material. In the electrochemical test, the CV curve exhibits an obvious redox peak, and the constant GCD curve exhibits an obvious platform.

In recent years, as a typical electrode material for BTS, bimetallic oxide has attracted much attention due to its simple synthesis, variable oxidation state, low cost, high electrochemical stability and high charge-discharge rate [14–18]. Malae et al. [19] summarized the electrochemical performance for nano-ferrites such as Fe$_3$O$_4$, NiFe$_2$O$_4$, MnFe$_2$O$_4$, CoFe$_2$O$_4$, CuFe$_2$O$_4$ and ZnFe$_2$O$_4$ electrode materials for SCs in aqueous electrolytes, and these materials show the specific capacity ($C_s$) between 137–517 F g$^{-1}$ at a current density (CD) of 1 A g$^{-1}$. Zhao et al. [20] reviewed 2D Co-based electrode materials (MCo$_2$O$_4$, M = Co, Fe, Cu, Ni, Zn, and Mn) for SCs, and these materials show the $C_s$ between 400–3294.3 F g$^{-1}$ at a CD of 1 A g$^{-1}$. Koudahi et al. [21] developed a spinel-type ZnNi$_2$O$_4$/NF electrode, and a $C_s$ of 235 C g$^{-1}$ was obtained at 1 A g$^{-1}$. Unfortunately, bimetallic oxides demonstrate poor electrical conductivity, however bimetallic sulfides possess larger SSA and more abundant EAS and show better electrochemical
performance [22–26]. So, one of the most common strategies is to convert bimetallic oxides into bimetallic sulfides. Yang et al. [27] developed a flower-like CoNi$_2$S$_4$ composite electrode material, and its $C_s$ showed 5.65 C cm$^{-2}$ at 10 mA cm$^{-2}$. The MnCo$_2$S$_4$ synthesized by Mola et al. shows a $C_s$ of 779 F g$^{-1}$ at a CD of 1 A g$^{-1}$ [28]. Xu et al. reported a Ti$_2$C$_2$-DA-NiMoS$_4$ heterostructure, and its specific capacity reached 1288 F g$^{-1}$ at 1 A g$^{-1}$. Heteroatom doping can not only greatly increase the specific surface areas (SSA) and electrochemical active sites (EAS) of materials, but also facilitate electron transport [29–31]. Hence, heteroatom doping is an effective means to ameliorate the electrochemical performance of materials. Among the different doping types, metal ion doping such as Mn$^{2+}$ [32], Fe$^{3+}$ [33], Cu$^{2+}$ [34] and Ni$^{2+}$ [35] is relatively common. Li et al. [32] developed a Mn$^{2+}$-doped CoSnO$_3$ (Mn@CoSnO) electrode, and the electrode shows a $C_s$ of 564 F g$^{-1}$, which is 3-fold than $C_s$ (191 F g$^{-1}$) of the undoped material-CoSnO$_3$. Moreover, the cycling stability of Mn@CoSnO is also greatly improved from 84.1% (CoSnO$_3$) to 104.7%. Repp et al. [33] prepared a Fe$^{3+}$ doped-Li$_4$Ti$_5$O$_{12}$ nanocomposite on reduced graphene oxide (RGO) for SCs electrode materials. Compared with rGO and Li$_4$Ti$_5$O$_{12}$/rGO electrodes, the composite electrode showed more excellent cycling performance and a higher $C_s$. Additionally, N, P, O or S elements are regarded as important dopants due to their lone pairs of electrons and entirely empty 3d orbitals, which can effectively regulate the local charge density between adjacent atoms to adjust the state of the surface charge and improve the conductivity of the material [35–38].

The aims of this paper are as follows: (1) a spherical Co-Mn composite -CoMn$_2$O$_4$ was firstly synthesized by one-step solvothermal method, and S@CoMn$_2$O$_4$ was further obtained from vulcanization reaction; (2) the morphology, structure and composition of CoMn$_2$O$_4$ and S@CoMn$_2$O$_4$ materials were characterized via scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray spectroscopy (EDS) techniques; (3) the electrochemical performance of the CoMn$_2$O$_4$ and S@CoMn$_2$O$_4$ materials was investigated using CV, GCD, electrochemical impedance spectroscopy (EIS); (4) the hybrid supercapacitor device was assembled with the positive electrode -S@CoMn$_2$O$_4$ and the negative electrode-active carbon (AC) to evaluate its practical application ability.

2. Experimental

2.1 Chemicals

Manganese (II) acetate tetrahydrate, Cobalt (II) acetate tetrahydrate, Ethylene glycol, KOH, Na$_2$S and other chemicals are all analytically pure (A.R.) and purchased from Macklin's Reagent (ShangHai, China).

2.2 Pretreatment of nickel foam (NF)

To get rid of the oxides and impurities on NF, the NF (1×1 cm$^2$) was respectively put into 3 mol L$^{-1}$ HCl and acetone for ultrasonic treatment for 15 min, then washed for several times using ethanol and ultrapure water, respectively.
2.3 Preparation of S@CoMn$_2$O$_4$

Mn(Ac)$_2$·4H$_2$O (2 mmol) and Co(Ac)$_2$·4H$_2$O (1 mmol) were successively added into 50 mL ethylene glycol and stirred to dissolve. The above solution and pretreated NF were then transferred to an autoclave (100 mL) and reacted at 160°C for 12 h. Finally, the obtained samples were dried for 6 h using vacuum drying technique (60°C) to obtain the CoMn$_2$O$_4$ precursors. The above precursors and 4 mmol of Na$_2$S were stirred in 50 mL ultrapure water for 6 hours, and placed in an autoclave (100 mL) and induced reaction for 10 h at 160°C. Finally, the sample was dried for 6 h in a vacuum drying oven (60°C) to obtain the target product.

2.4 Characterization of materials

The crystal structure of CoMn$_2$O$_4$ and S@CoMn$_2$O$_4$ was characterized by XRD (Bruker D8 ADVANCE). The chemical states of the surface elements of the S@CoMn$_2$O$_4$ were measured by XPS (Thermo Scientific K-Alpha). The morphology of the CoMn$_2$O$_4$ and S@CoMn$_2$O$_4$ samples was investigated by SEM (CaiSi Sigma 300) and TEM (JEOL-2100FS, Oxford Xmax 80T).

2.5 Electrochemical measurement

The CV, EIS and GCD of the CoMn$_2$O$_4$ and S@CoMn$_2$O$_4$ electrodes were carried out in a 1 M KOH electrolyte using a three-electrode system (the CoMn$_2$O$_4$ or S@CoMn$_2$O$_4$ - working electrode, Ag/AgCl - reference electrode, and platinum wire - counter electrode). The electrochemical performance of S@CoMn$_2$O$_4$ was tested in a two-electrode system (the S@CoMn$_2$O$_4$ - the positive electrode, AC - the negative electrode) with 1 M KOH electrolyte to determine its practical application ability.

3. Results and discussion

3.1 Characterization of S@CoMn$_2$O$_4$

Scheme 1. The schematic diagram of construction process for S@CoMn$_2$O$_4$ electrode.

The XRD patterns of S@CoMn$_2$O$_4$ is shown in Fig. 1. As shown in Fig. 1, the characteristic peaks of S@CoMn$_2$O$_4$ are similar to those of CoMn$_2$O$_4$, which corresponds to JCPDS No. 01-1126 card. The results not only indicate the existence of CoMn$_2$O$_4$, but also confirm that no new impurity phase was formed during the vulcanization process. However, compared with CoMn$_2$O$_4$, some characteristic peaks of S@CoMn$_2$O$_4$ appear a slight deviation, which indicated that the vulcanization process can induce lattice expansion of CoMn$_2$O$_4$, that is, sulfur doping composite has a slight effect on lattice parameters, but does not change the crystal structure [39, 40].

In addition, the components and valence states of S@CoMn$_2$O$_4$ were determined by XPS full and fine spectrum of elements (Fig. 2) and the existence of O, Mn, Co and S elements was proved. C elements (Fig.
2B) are mainly from adsorbed organic impurities. High resolution spectrum of O 1s fitting three peaks (O1, O2 and O3) is originated from H-O-H, M-O-H and M-O-M (M = Mn, Co) [41, 42]. The fine spectrum of Co 2p (Fig. 2D) depict a pair of spin orbit peaks and two satellite peaks (labeled “Sat.”). The Co 2p3/2 peak located at 781.4 eV and 777.5 eV and the fitting peaks of Co 2p1/2 at 797.5 eV and 793.2 eV both indicate the presence of Co3+ and Co2+ states (Fig. 2D), respectively [43, 44]. Three types of manganese species were observed in Mn 2p spectra using a Gaussian fitting method (Fig. 2E), which is attributed to the presence of mixed Mn2+, Mn3+ and Mn4+. The peaks of S@CoMn2O4 (Fig. 2E) at 653.1 eV and 640.8 eV are Mn2+, the peaks at 654.4 eV and 642.5 eV are Mn3+ and the peak at 645.1 eV is Mn4+ [45]. Figure 2F shows the high resolution spectrum of S 2p for S@CoMn2O4, and the peaks at 162.1 eV and 160.8 eV correspond to S 2p1/2 and S 2p3/2, respectively, which can be attributed to sulfur-metal (S-M) bonds. In addition, the peaks at 169.6 eV and 168.5 eV are consistent with high sulfur oxidation state (SOx n−) [46, 47].

The specific morphologies and structures of the CoMn2O4 and S@CoMn2O4 samples were tested by SEM (Fig. 3). Figures 3A and B are the SEM images of CoMn2O4, and Fig. 3C and D are the SEM images of S@CoMn2O4. From Fig. 3A and B, CoMn2O4 material is clearly a regular solid nanosphere with a smooth surface. From Figs. 3C and D, compared to CoMn2O4, the S@CoMn2O4 material also has a spherical structure, but its surface was relatively coarse and abundant small nanosheet and some defects on the surface of nanosphere were obviously observed. Interestingly, the S@CoMn2O4 maintains the spherical structure of the precursor (CoMn2O4) to form a special nanosheet@nanosphere core-shell structure. Such special core-shell structure can facilitate electron and ion transport.

The detailed topographic characteristics of S@CoMn2O4 was also obtained through TEM (Figures. 4A, B, C and D). From Fig. 4A, the S@CoMn2O4 shows an approximate nanosphere, and the surface of the sphere is relatively rough and covered by numerous nanosheets (Figs. 4A, B and C), which are consistent with SEM results. Additionally, according to the high-resolution TEM image of S@CoMn2O4, some distinct diffraction patterns can be observed, and the fringe spacing of 0.219 nm corresponds to the crystal plane (103).

Figure 5 shows The corresponding elemental mapping diagrams (Co (A), Mn (B) and S (C)) of the surface part of S@CoMn2O4 samples. The results show that there are also a large number of S elements in addition to the Co and Mn elements on the surface part of S@CoMn2O4 (Fig. 5A, B, C), indicating the successful synthesis of S@CoMn2O4. The chemical compositions of the surface part of S@CoMn2O4 were further evaluated through EDS tests. The results indicate that the atomic percent contents of three elements-Co, Mn and S for the CoMn2S4 (Fig. 5D) are 21.04%, 37.42% and 41.54%, respectively. In other words, the n(Co): n(Mn): n(S) for the surface part of S@CoMn2O4 were calculated to be 1 : 1.89 : 3.61 (~ 1 : 2 : 4), which indicates that the surface composition is approximately CoMn2S4.
3.2 Electrochemical properties of S@CoMn$_2$O$_4$ electrode in three-electrode system

In order to investigate the electrochemical properties of S@CoMn$_2$O$_4$, CV, GCD and EIS curves were tested with 1 M KOH electrolyte in a three-electrode system. Figure 6A is the CVs of S@CoMn$_2$O$_4$ at different scanning rates (5, 7, 9, 10, 20, 30, 50, 100 and 200 mV s$^{-1}$). From Fig. 6A, these CVs have a pair of obvious redox peaks, indicating that S@CoMn$_2$O$_4$ electrodes show obvious Faraday redox behavior. The peak currents increase with the increase of scanning rate, indicating the rapid electrochemical response capability for the S@CoMn$_2$O$_4$ electrodes [48]. As a scanning speed increases from 5 to 200 mV s$^{-1}$, the oxidation and reduction peaks of CVs shift to positive and negative potentials, respectively, indicating that the Faraday redox reaction is quasi-reversible and the transport and transfer for ions and electrons are very rapid [49]. The shape of CVs at different scanning rates remains relatively unchanged, indicating that the S@CoMn$_2$O$_4$ have stable performance and good rate capability. However, at high scanning rates ($\geq 10$ mV s$^{-1}$), the oxidation peaks gradually become less obvious. The redox peaks are attributed to the interaction between S@CoMn$_2$O$_4$ and electrolyte ions (OH$^-$). The following equations (1–3) describe the corresponding Faraday redox reactions among different oxidation states of S@CoMn$_2$O$_4$ [50].

\[
\text{CoMn}_2\text{S}_4 + 3\text{OH}^- = 2\text{MnS}_x\text{OH} + \text{CoS}_4 - 2x\text{OH} + 3e^- \quad (1)
\]
\[
\text{CoS}_4 - 2x\text{OH} + \text{OH}^- = \text{CoS}_4 - 2x\text{O} + \text{H}_2\text{O} + e^- \quad (2)
\]
\[
\text{MnS}_x\text{O} + \text{OH}^- = \text{MnS}_x\text{O} + \text{H}_2\text{O} + e^- \quad (3)
\]

Redox processes of redox couple (Co$^{2+}$/Co$^{3+}$ and Mn$^{2+}$/Mn$^{3+}$/Mn$^{4+}$) are involved in the entire Faraday process.

Figures. 6B and C are the GCDs of S@CoMn$_2$O$_4$ electrode. The oxyhydroxides (MnS$_x$OH and CoS$_4 - 2x$OH) appear in the reaction process, so the battery behavior is displayed in the charging and storage process. It involves a phase transformation and thus generates a constant potential during charging and discharging [49]. In addition, from a CD from 1 to 10 A g$^{-1}$, all GCDs show symmetry, reflecting the reversible property of the capacitors [51]. When the CD is varied from 1 to 10 A g$^{-1}$, the $C_s$ of S@CoMn$_2$O$_4$ are calculated to be 812, 767.8, 689.7, 639.2, 595, 553.2, 513.8, 476.8, 441.9 and 409 C g$^{-1}$, respectively.

The ion transport characteristics of the S@CoMn$_2$O$_4$ electrode was further tested using EIS (the frequency range: 0.01–100 kHz) (Fig. 6D). In the high-frequency region, the intercept of a curve on the x-axis represents the ohmic resistance ($R_s$) between the active materials and electrolytes. The diameter of the arc is expressed as the charge transfer resistance ($R_{ct}$). In the low-frequency region, the curve slope (Warburg diffusion element, W) corresponds to the diffusion capacity of the electrolyte on the electrode surface [49]. The $R_{ct}$ values of S@CoMn$_2$O$_4$ are calculated to be 0.29 $\Omega$, indicating that the S@CoMn$_2$O$_4$
The electrode has the smallest internal charge transfer resistance, which significantly improves the conductivity of the Faraday redox reaction. However, the linear slopes of S@CoMn$_2$O$_4$ is close 45°, indicating that all of them have easy ion diffusion and fast Faraday reaction rate [52]. Figure 6E shows the cycling stability for S@CoMn$_2$O$_4$ in a long cycle test. After 5000 cycles, the capacitance retention rates of S@CoMn$_2$O$_4$ are 92.91% at a CD of 10 A g$^{-1}$, respectively. These results show that S@CoMn$_2$O$_4$ is a promising electrode material. Table 1 lists the $C_s$ and cyclic stability of S@CoMn$_2$O$_4$ electrode compared with those of the reported CoMn$_2$O$_4$ correlated electrode materials [20, 53–58].

Table 1. The $C_s$ and cyclic stability of S@CoMn$_2$O$_4$ electrode compared with those of the reported CoMn$_2$O$_4$ correlated electrode materials

<table>
<thead>
<tr>
<th>Electrode materials</th>
<th>$C_s$ (C g$^{-1}$)</th>
<th>Cycling stability</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnCo$_2$S$_4$</td>
<td>311.6 (1 A g$^{-1}$)</td>
<td>3000 cycles 96.5% (2 A g$^{-1}$)</td>
<td>20</td>
</tr>
<tr>
<td>MnCo$_2$O$_4$/NiO</td>
<td>453.3 (1 A g$^{-1}$)</td>
<td>4000 cycles 91.89% (5 A g$^{-1}$)</td>
<td>53</td>
</tr>
<tr>
<td>MnCo$_2$O$_4$@MnCo$_2$S$_4$</td>
<td>773.3 (1 A g$^{-1}$)</td>
<td>-</td>
<td>54</td>
</tr>
<tr>
<td>Ag-Doped MnCo$_2$O$_4$</td>
<td>423.9 (1 A g$^{-1}$)</td>
<td>1000 cycles 93.7% (10 A g$^{-1}$)</td>
<td>55</td>
</tr>
<tr>
<td>MnCo$_2$O$_4$/graphene</td>
<td>201.2 (1 A g$^{-1}$)</td>
<td>5000 cycles 97.4% (10 A g$^{-1}$)</td>
<td>56</td>
</tr>
<tr>
<td>CoMn$_2$O$_4$</td>
<td>360.9 (1 A g$^{-1}$)</td>
<td>5000 cycles 87% (100 mV s$^{-1}$)</td>
<td>57</td>
</tr>
<tr>
<td>MnCo$_2$S$_4$</td>
<td>600 (1 A g$^{-1}$)</td>
<td>-</td>
<td>58</td>
</tr>
<tr>
<td>S@CoMn$_2$O$_4$</td>
<td>812 (1 A g$^{-1}$)</td>
<td>5000 cycles 92.91% (10 A g$^{-1}$)</td>
<td>This work</td>
</tr>
</tbody>
</table>

Figure 7A shows the comparison of CVs of CoMn$_2$O$_4$ and S@CoMn$_2$O$_4$ at 10 mV s$^{-1}$. From Fig. 7A, the CVs area enclosed by NF is almost to zero, indicating that NF does not participate in Faraday redox reaction and does not contribute at all to the $C_s$[59]. The results show that S@CoMn$_2$O$_4$ electrode shows a larger integral area and sharper redox peak compared with CoMn$_2$O$_4$ electrode, indicating that S@CoMn$_2$O$_4$ electrode shows more abundant active sites for Faraday redox reaction, which promotes charge storage and capacitance improvement. Figure 7B is the comparison of GCDs of CoMn$_2$O$_4$ and S@CoMn$_2$O$_4$ electrodes at 5 A g$^{-1}$. In Fig. 7B, the charge and discharge time of NF is almost zero, and the results are consistent with those of CVs. The charge and discharge times of S@CoMn$_2$O$_4$ electrodes increase in succession, indicating that the specific capacities increase in sequence. However, S@CoMn$_2$O$_4$ samples have higher $C_s$ and discharge time, which is related to higher conductivity and more EAS. The fluffy spherical structure not only achieves a higher SSA, but also enhances the ability of ion/electron rapid transfer at the interface between the electrode and electrolyte [59]. Figure 7C shows the relations diagrams of $C_s$ for CoMn$_2$O$_4$ and S@CoMn$_2$O$_4$ at different CDs. When the CDs are varied form 1 to 10 A g$^{-1}$, the $C_s$ of CoMn$_2$O$_4$ are calculated to be 221, 182.4, 157.8, 140, 125, 112.2, 104.3, 93.6, 83.7.
and 74 C g\(^{-1}\), respectively, which is well below the \(C_s\) of S@CoMn\(_2\)O\(_4\). These phenomena is mainly due to the following aspects: 1. The electrode materials were obtained via in-situ growth synthesis method, which avoids the addition of binders and additives that do not participate in redox reactions [60]; 2. The three-dimensional structure of NF provides channels for ion migration and accelerates charge transfer [59]; 3. The synergistic effect between Mn and Co enhances the \(C_s\) of electrode materials.

### 3.3 Electrochemical properties of S@CoMn\(_2\)O\(_4\) electrode in a two-electrode system

To further test the practical application capability of the materials, electrochemical tests were performed in 1M KOH electrolyte in a two-electrode system with the negative electrode (AC) and positive electrode (S@CoMn\(_2\)O\(_4\)). Prior to fabrication of the device, the mass load of S@CoMn\(_2\)O\(_4\) and AC materials is balanced and calculated according to the respective electrical chemical behavior of the anode and cathode materials in the two-electrode system [50]. According to the principle of charge balance (\(Q^+ = Q^-\)), the mass ratio for the anode and cathode materials is closely associated with the \(C_s\) and the voltage window of anode and cathode [61, 62]. By calculation, the mass of the S@CoMn\(_2\)O\(_4\) (anode) and AC (cathode) were calculated to be 2.5 and 3 mg, respectively. A serial CV tests were carried out to determine the optimal operating voltage window (Fig. 8A). The results show there are obvious polarization phenomena in the voltage window of 0–1.65 V. According to the principle of voltage window maximization, the working voltage window of S@CoMn\(_2\)O\(_4\) is determined to be 0–1.55 V.

In Fig. 8B, all CVs show an analogous shape with the increasing scanning sweep, indicating that the device has the ability of fast charge and discharge and good rate capability. By calculation, the \(C_s\) of the S@CoMn\(_2\)O\(_4\)//AC device (Fig. 8C) is 205.8, 191.4, 177.6, 167.5, 160.2, 153.65, 148.4, 144 and 139.5 C g\(^{-1}\) at CDs of 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5 and 5 A g\(^{-1}\), respectively. Figure 8D is the curve of \(C_s\) variation at different CDs. Figure 8E shows the Ragone plots revealing the \(E_s\) and \(P_s\) of the S@CoMn\(_2\)O\(_4\)//AC device. According to the formula (3 and 4), the \(E_s\) of CoMn\(_2\)S\(_4\)//AC are 44.36, 41.20, 38.23, 36.06, 34.49, 33.08, 31.95, 31 and 30.03 Wh kg\(^{-1}\) at the \(P_s\) of 775, 1162.5, 1550, 1937.5, 2325, 2712.5, 3100, 3487.5 and 3875 W kg\(^{-1}\). Figure 8F shows the Nyquist plots for S@CoMn\(_2\)O\(_4\)//AC devices at open circuit potential. The \(R_{ct}\) of S@CoMn\(_2\)O\(_4\)//AC devices in the high frequency region is 0.86 Ω, indicating that the \(R_{ct}\) for the S@CoMn\(_2\)O\(_4\)//AC devices are small, and the device has good conductivity and contact performance. At low frequencies, the higher slopes of S@CoMn\(_2\)O\(_4\)//AC devices indicate rapid ion migration between electrode and electrolyte. Its self-discharge characteristics were studied after charging for 20 min at 1.5 V, and the results are shown in Fig. 8G. The S@CoMn\(_2\)O\(_4\)//AC device exhibits rapid self-discharge within 1.9 h and gradually tends to be stable after several hours. After 25 h, the output voltage of S@CoMn\(_2\)O\(_4\)//AC device is stable at 0.19 V, showing that the S@CoMn\(_2\)O\(_4\)//AC device has low self-discharge performance [63]. In Fig. 8F, a red LED light can be lighted for more than 60 s by two devices in series, indicating that the S@CoMn\(_2\)O\(_4\) material possesses the practical application ability.
4. Conclusions

In summary, a novel electrode material- S@CoMn$_2$O$_4$ was prepared by in-situ growth method. Compared with CoMn$_2$O$_4$, the S@CoMn$_2$O$_4$ shows better electrochemical performance and cyclic stability, which is mainly attributed to the fact that S@CoMn$_2$O$_4$ has a higher SSA and abundant EAS. When a CD is 1 $\text{A g}^{-1}$, the $C_s$ of S@CoMn$_2$O$_4$ reaches 812 $\text{C g}^{-1}$. In addition, the S@CoMn$_2$O$_4$ electrode material shows excellent cycling feature and the retention rates of $C_s$ reaches 92.91% after 5000 cycles at 10 $\text{A g}^{-1}$. When the $P_s$ is 775 $\text{W kg}^{-1}$, the $E_s$ of S@CoMn$_2$O$_4$//AC device reaches 44.30 $\text{Wh kg}^{-1}$. Therefore, S@CoMn$_2$O$_4$//AC is a promising energy storage device.

Declarations

Acknowledgements

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Author contributions

Xinrong Lv, Xiaoqin Min and Xuhui Liu: Validation, Conceptualization, Methodology, Investigation, Writing - original draft. Changgui Yang: Methodology, Investigation. Jianyou Chen: Visualization, Software. Xiaoyun Lin: Conceptualization, Resources, Writing - review & editing, Project administration.

Conflicts of 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.

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**Scheme 1**

Scheme 1 is available in Supplementary Files section.

**Figures**
Figure 1

(A) XRD patterns of S@CoMn$_2$O$_4$. 
Figure 2

XPS spectra of C 1s (B), O 1s (C), Co 2p (D), Mn 2p (E) and S 2p (F) of S@CoMn$_2$O$_4$ (A, B, C, D, E and F).
Figure 3

SEM images of CoMn$_2$O$_4$ (A and B) and S@CoMn$_2$O$_4$ (C and D).
Figure 4

TEM images of S@CoMn$_2$O$_4$ (A, B and C) and high-resolution TEM image (D).
Figure 5

The corresponding elemental mapping (Co (A), Mn (B) and S (C)) and EDS (D) of the surface part of S@CoMn$_2$O$_4$ samples.
Figure 6

CVs of the S@CoMn$_2$O$_4$ (A) at different scan rates (5, 7, 9, 10, 20, 30, 50, 100 and 200 mV s$^{-1}$); GCDs of the S@CoMn$_2$O$_4$ (B, C); EIS spectra of the S@CoMn$_2$O$_4$ at open circuit voltages (D); Cyclic stability of S@CoMn$_2$O$_4$ at a CD of 10 A g$^{-1}$ (E).
Figure 7

(A) CVs of the NF, CoMn$_2$O$_4$ and S@CoMn$_2$O$_4$ at a scan rate of 10 mV s$^{-1}$; (B) GCDs of the NF, CoMn$_2$O$_4$ and S@CoMn$_2$O$_4$ at a CD of 5 A g$^{-1}$; (C) the corresponding $C_s$ values at different CDs of the CoMn$_2$O$_4$ and S@CoMn$_2$O$_4$. 
Figure 8

CV curves of S@CoMn$_2$O$_4$//AC (A) with different voltage windows at 5 mV s$^{-1}$; CVs of S@CoMn$_2$O$_4$//AC (B) at different scan rates (5, 8, 10, 20, 30, 50, 80, 100 and 200 mV s$^{-1}$); GCDs of S@CoMn$_2$O$_4$//AC (C) at different CDs (1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5 and 5 A g$^{-1}$); (D) the corresponding $C_s$ values at different CDs for S@CoMn$_2$O$_4$//AC; (E) Ragone plot of the S@CoMn$_2$O$_4$//AC; (F) Nyquist plots at open circuit potential of S@CoMn$_2$O$_4$//AC; (G) Self-discharge curves of the device after charging at 1.50 V for 15 min; (H) Picture of lighting a red LED light by two S@CoMn$_2$O$_4$//AC devices in series.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.
• GraphicalAbstract.png
• Scheme1.png