Supercapacitors have been widely recognized as a promising device for the storage of renewable energy. Herein, a facile electrochemical oxidation strategy is described to construct a nickel sulfide/oxide heterostructure which enhances the specific areal capacitance of Ni$_3$S$_2$ electrodeposited on nickel foam. The resulting heterostructure electrode exhibits high areal capacitance, 65 times that of the as-prepared Ni$_3$S$_2$ electrode (2035 mF cm$^{-2}$ vs. 31 mF cm$^{-2}$ at a current density of 8 mA cm$^{-2}$), while still maintaining great stability, showing no performance degradation after 5000 charge–discharge cycles. Its exceptional capacitance, advanced rate capability, and superior cycling stability are attributed to the transformed composition and unique nanostructure achieved during electrochemical oxidation, which can provide a large electrochemically active surface area, fast electron/electrolyte ion transport, and robust structural stability. Such a low-cost and facile strategy can be potentially applicable to prepare many other materials for supercapacitor applications.

Because of the increasing energy demand and depleting fossil fuels worldwide, a great deal of effort has been invested in developing novel materials for advanced energy storage devices, among which supercapacitors have attracted considerable attention because of their low cost, long cycling life, and high power density. Generally, two types of supercapacitors have been widely studied: electrochemical double-layer capacitors and pseudocapacitors. Benefiting from the fast and reversible surface redox reactions for charge storage, pseudocapacitors usually possess much higher energy density than electrochemical double-layer capacitors.

Taking into account the decisive role of electrode materials for supercapacitors, many researchers have focused on the rational design and synthesis of nonprecious, stable, and high-performance electrode materials for supercapacitor applications. Particularly, transition metal sulfides/oxides have attracted intense interest due to their high theoretical capacitance, environmental compatibility, low cost, and earth abundance. In general, there are two primary approaches to obtain pseudocapacitors with high performance. The first strategy is to optimize the electrode materials by varying the composition, such as mono- and heterometallic oxides and chalcogenides (e.g., NiS, NiO$_x$, Ni$_3$S$_2$, Co$_9$S$_8$, Co$_3$O$_4$, NiCo$_2$O$_4$, CoNi$_2$S$_4$, NiS, and NiCo$_2$S$_4$), which have been reported to have excellent capacitance. Another widely adopted approach is to tailor the structure of the electrode materials via nanoengineering to result in a high surface area. Following this strategy, many nanostructured materials, for instance electrode materials of hollow prisms, nanospheres, and nanowires, have been reported with improved capacitance relative to their corresponding bulk counterparts. Despite significant progress, designing a low-cost and facile process for fabricating high-performance pseudocapacitor electrodes is still challenging but highly desirable.

Herein, we describe an alternative in situ electrochemical oxidation (denoted as ECO) approach to construct a nickel sulfide/oxide heterostructure which enhances the specific areal capacitance of the Ni$_3$S$_2$/nickel foam (Ni$_3$S$_2$/NF) electrode. The resulting ECO-Ni$_3$S$_2$/NF exhibits a remarkably increased areal capacitance of 2035 mF cm$^{-2}$, which is 65 times that of the parent Ni$_3$S$_2$/NF at a current density of 8 mA cm$^{-2}$. Furthermore, the ECO-Ni$_3$S$_2$/NF also displays excellent cycling stability, retaining the initial specific capacitance even after 5000 charge–discharge cycles. Such an effective strategy is potentially applicable to produce many other electrode materials for multiple energy-related applications.

Potentiodynamic deposition was utilized to prepare Ni$_3$S$_2$ on nickel foam (see the ESI† for details). In sharp contrast to the smooth morphology of a pristine nickel foam (Fig. S1†), the entire surface of Ni$_3$S$_2$/NF was fully covered by nanoflake-like composites with no regular crystalline particles or aggregates (Fig. 1a and S2a†). Elemental mapping results of Ni$_3$S$_2$/NF (Fig. S2b†) confirmed the uniform coverage of the entire nickel foam with evenly distributed nickel and sulfur. The X-ray
A close inspection reveals the presence of a large amount of active sites. In order to probe the inner structure of Ni₃S₂/NF, cross-section SEM images of both electrodes were collected. Fig. 1c shows an even and intense layer of Ni₃S₂ still existed in close contact with the nickel foam. The elemental mapping images of ECO-Ni₃S₂/NF (Fig. S5f) showed that the S content in the inner layer was much higher than that in the outer layer, further confirming the formation of a nickel sulfide/oxide heterostructure on the surface during ECO. The XRD pattern of ECO-Ni₃S₂/NF was very similar to that of Ni₃S₂/NF, indicating the remaining Ni₃S₂ after ECO (Fig. S3†). The lack of peaks attributable to nickel oxides was probably due to the amorphous nature of the newly formed oxides. Inductively coupled plasma atomic emission spectroscopy analysis of Ni₃S₂/NF showed the deposited amount of Ni and S to be 4.62 and 1.68 mg cm⁻², respectively. After ECO, the S content decreased to 0.56 mg cm⁻², implying that nearly two thirds of the original Ni₃S₂ were oxidized during ECO.

In order to further probe the composition and valence state of each element in the electrodeposited samples, X-ray photoelectron spectroscopy (XPS) was conducted. The XPS survey spectra of Ni₃S₂/NF and ECO-Ni₃S₂/NF are included in Fig. S7,† displaying all the anticipated elements like Ni and S. The much higher intensity of the O 1s peak at 528 eV of ECO-Ni₃S₂/NF compared to that of Ni₃S₂/NF demonstrated the large degree of surface oxidation of the former during ECO (Fig. S7b†), in agreement with the above elemental mapping results (Fig. S5†).

The high-resolution Ni and S XPS spectra of these two samples are compared in Fig. 1e and f. Ni 2p spectra of both samples could be deconvoluted into two spin–orbit doublets, which were assigned to Ni 2p₃/2 and 2p₁/2, and two shakeup satellites (Fig. 1e). The high-resolution Ni 2p₃/2 spectrum was deconvoluted into three subpeaks at binding energies of 852.8, 854.6, and 860.9 eV (Fig. 1e), assignable to Ni²⁺ in Ni₃S₂, oxidized Ni species, and the Ni 2p₃/2 satellite peak of Ni₃S₂, respectively. Similarly, XPS fitting of the high-resolution S 2p spectra (Fig. 1f) resulted in a doublet at 161.8 and 163.2 eV, corresponding to S 2p₃/2 and 2p₁/2 peaks, respectively. The remaining sulfide peak from Ni₃S₂ in the S 2p spectrum of ECO-Ni₃S₂/NF corroborated the partial oxidation of Ni₃S₂ during the anodic potential cycling.

The electrochemical properties of Ni₃S₂/NF and ECO-Ni₃S₂/NF were investigated in a three-electrode configuration (see the ESI† for details). We first varied the numbers of potentialdynamic deposition cycling to optimize the capacitance performance of Ni₃S₂/NF and the corresponding ECO-Ni₃S₂/NF. As shown in Fig. S8† the best energy storage properties were achieved at 15 potential cycles. Hereafter, all the electrochemical studies were conducted under the optimal conditions unless noted otherwise. In virtue of electrodeposition, no conductive agents/binders were needed for the electrochemical studies. The cyclic voltammograms of Ni₃S₂/NF and ECO-Ni₃S₂/NF collected between 0 and 0.55 V vs. Ag/AgCl are shown in Fig. 2a. It clearly shows that ECO-Ni₃S₂/NF displays an apparent redox feature with anodic and cathodic peaks at 0.41 and 0.24 V vs. Ag/AgCl, respectively. The integrated area of the anodic peak is nearly equal to that of the cathodic peak, implying a good reversibility of the fast charge–discharge process of ECO-Ni₃S₂/NF. On the same scale of current density, it is difficult to define the redox features of Ni₃S₂/NF. The inset in Fig. 2a displays an expanded current region to well present the redox peaks of Ni₃S₂/NF, which exhibits anodic and cathodic peaks at 0.37 and 0.31 V vs. Ag/AgCl. Both of the redox features of ECO-

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**Fig. 1** (a and c) SEM and cross-section SEM images of Ni₃S₂/NF and (b and d) SEM and cross-section SEM images of ECO-Ni₃S₂/NF; high-resolution Ni 2p (e) and S 2p (f) spectra of Ni₃S₂/NF (blue) and ECO-Ni₃S₂/NF (red).
Ni$_3$S$_2$/NF and Ni$_3$S$_2$/NF correspond to faradaic process-based pseudocapacitance$^{37}$ and the former apparently demonstrates a much higher capacitance than the latter. In addition, the redox features of ECO-Ni$_3$S$_2$/NF were further examined in Fig. 2b with increasing scan rate from 5 to 100 mV s$^{-1}$. With the increase in scan rate, the well-defined redox peaks were still maintained while the respective current density increased accordingly. A similar trend was observed for Ni$_3$S$_2$/NF (Fig. S9$^t$). At higher scan rates, the anodic peak shifted positively while the cathodic peak moved to lower potential, likely due to the increasing voltage drop with increasing scan rates.

Next, the galvanostatic charge–discharge (GCD) measurements were carried out to confirm the improvement of capacitance after electrochemical oxidation. The areal capacitance of an electrode can be calculated from the GCD curve based on the equation $C = \frac{I \Delta t}{A \Delta V}$, where $C$ is the areal capacitance, $I$ is the discharge current, $\Delta t$ is the discharge time, $A$ is the electrode area and $\Delta V$ is the potential window. Fig. 3a shows the GCD curves of Ni$_3$S$_2$/NF and ECO-Ni$_3$S$_2$/NF at a current density of 20 mA cm$^{-2}$, wherein ECO-Ni$_3$S$_2$/NF exhibits a much longer discharge time. In fact, the calculated capacitance of ECO-Ni$_3$S$_2$/NF (1828 mF cm$^{-2}$) is 62 times that of Ni$_3$S$_2$/NF (29.6 mF cm$^{-2}$). Fig. 3b shows the GCD curves at varying current densities of 8, 12, 20, 28, 40, and 80 mV cm$^{-2}$. The resulting areal capacitances of ECO-Ni$_3$S$_2$/NF were 2035, 1996, 1828, 1744, 1635, and 1216 mF cm$^{-2}$, all substantially larger than those of the pristine Ni$_3$S$_2$/NF (Fig. S10$^t$). Although with increasing current density, a decrease in capacitance was observed for ECO-Ni$_3$S$_2$/NF, it still retained more than 1200 mF cm$^{-2}$ even at 80 mA cm$^{-2}$ (Fig. 3c).

In fact, over the entire range of current density (8 to 80 mA cm$^{-2}$), the areal capacitance of ECO-Ni$_3$S$_2$/NF remained at least 60 times higher than that of Ni$_3$S$_2$/NF (Table S1$^t$). It should be noted that the possible capacitance contribution from the oxidized nickel foam substrate was negligible (Fig. S11$^t$). Besides the improvement of capacitance of ECO-Ni$_3$S$_2$/NF compared to that of the parent Ni$_3$S$_2$/NF, the unique heterostructure of ECO-Ni$_3$S$_2$/NF has superior capacitance to many other nickel sulfides and nickel oxides.$^{20,38,39}$ More detailed comparison is listed in Table S2.$^t$ The coulombic efficiencies of Ni$_3$S$_2$/NF and ECO-Ni$_3$S$_2$/NF at different current densities are shown in Fig. S12.$^t$ With the increase in current density, the coulombic efficiencies of both ECO-Ni$_3$S$_2$/NF and Ni$_3$S$_2$/NF decreased; however ECO-Ni$_3$S$_2$/NF possessed an apparently higher coulombic efficiency than Ni$_3$S$_2$/NF at the same current density, indicating the excellent charge–discharge ability.

Encouraged by the high areal capacitance of ECO-Ni$_3$S$_2$/NF, subsequently we assessed its robustness via consecutive charge–discharge cycles. Fig. 3d shows its areal capacitance retention over 5000 cycles at a current density of 100 mA m$^{-2}$. Apparently, a very stable areal capacitance was maintained throughout the 5000 cycles. The nearly perfect overmatch of the initial GCD curve with the final one (Fig. 3d inset) clearly highlights the superior stability of ECO-Ni$_3$S$_2$/NF as a supercapacitor.

It is generally accepted that electrochemically active surface area (ECISA) is proportional to double layer capacitance measured in a non-faradaic region.$^{28}$ In order to shed some light on the factors responsible for the capacitance enhancement of
ECO-Ni$_3$S$_2$/NF compared to that of Ni$_3$S$_2$/NF, we collected their cyclic voltammograms between 0 and 0.1 V vs. Ag/AgCl at varying scan rates (Fig. S13†). Fig. 4a compares the cyclic voltammograms of ECO-Ni$_3$S$_2$/NF and Ni$_3$S$_2$/NF collected at 5 mV s$^{-1}$, wherein the former exhibited significantly larger current densities. The linear fitting of the current density at 0.05 V vs. Ag/AgCl over the scan rate resulted in an ECSA of ECO-Ni$_3$S$_2$/NF ~7 times that of Ni$_3$S$_2$/NF (Fig. 4b), probably due to the increased roughness after ECO. Such a high ECSA of ECO-Ni$_3$S$_2$/NF will be undoubtedly beneficial towards its large capacitance, even though the 60 times higher capacitance of ECO-Ni$_3$S$_2$/NF relative to that of Ni$_3$S$_2$/NF cannot be solely explained by the 7 times increase in the ECSA. We reasoned that the altered composition of the electrode material after electrochemical oxidation (nickel sulfide/oxide heterostructure) would also play an important role in contributing to the resulting high capacitance.

In summary, we reported that a facile electrochemical oxidation strategy was able to construct a nickel sulfide/oxide heterostructure which significantly enhances the areal capacitance of electrodeposited Ni$_3$S$_2$ on nickel foam. The resulting heterostructure electrode exhibited an areal capacitance 65 times that of the original Ni$_3$S$_2$/NF (2035 vs. 31 mF cm$^{-2}$ at a current density of 8 mA cm$^{-2}$) and also maintained great stability for 5000 charge–discharge cycles. Such an improved capacitance was likely attributed to the combined effects of the increased electrochemically active surface area and unique heterostructure. Such an electrochemical activation method is complementary to traditional structural engineering and constituent modulation through synthetic routes and hence it is potentially applicable to prepare various electroactive materials for supercapacitor applications.

Conflict of interest

The authors declare no competing financial interests.

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