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Flexible Additive-Free CC@TiO$_x$N$_y$@SnS$_2$ Nanocomposites with Excellent Stability and Superior Rate Capability for Lithium Ion Batteries

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A novel material consisting of metal oxide-nitride (TiO$_x$N$_y$, nanowires) and metal sulfide (SnS$_2$, nanosheets) is synthesized on a flexible carbon cloth substrate by two steps hydrothermal reaction. The as-synthesized carbon cloths/titanium oxynitride/tin disulfide (CC@TiO$_x$N$_y$@SnS$_2$) nanocomposites are tested directly as additive-free anode materials for lithium-ion batteries. The free-standing CC@TiO$_x$N$_y$@SnS$_2$ electrode displays an initial discharge capacity of 1082 mAh g$^{-1}$ at a current density of 1 C, with a coulombic efficiency of 74%. The reversible capacity as high as 612 mAh g$^{-1}$ can still be maintained after 100 charging/discharging cycles. Moreover, this material shows outstanding rate property with a high reversible discharge capacity of 419 mAh g$^{-1}$ at a current density of 5 C, which is higher than the theory capacity of graphite. Also, a stable high discharge capacity of 676 mAh g$^{-1}$ can be attained when the current density is switched back to 1 C. The high electrochemical performance can be attributed to the high electrical conductivity of the TiO$_x$N$_y$, facilitates the transport of electrons and lithium ions and the unique layer structure of SnS$_2$.

1. Introduction

Lithium-ion batteries (LIBs) bear with many superior properties, including high energy and power densities, long cycle life, and environmental benignity, and thus have been regarded as ideal power supplies for electric vehicles (EVs) and hybrid electric vehicles (HEVs). To fulfill the increasing demands for HEVs and EVs practicable applications, LIBs with higher energy, larger powder and longer cycle lifespan are highly required. Unfortunately, commercially used graphite carbon has struggled to meet these requirements because of its low theoretical capacity (~372 mAh g$^{-1}$).

To date, various materials have been developed as promising high performance anode electrodes of LIBs. Among them, tin sulfides (SnS$_2$) has received considerable attention due to its high theoretical capacity. SnS$_2$ has a layered Cdl$_2$-type structure, in which tin atoms are sandwiched two layers of sulfur atoms. Recent studies have shown that nanostructured SnS$_2$-base materials revealed that remarkably improved electrochemical properties as anode material for LIBs compared to their bulk counterparts, which primarily owns to their unique morphology, consist of a finite lateral sized and its well-defined layered structure. For example, acetylene black incorporated porous 3-dimensional (3D) SnS$_2$ nanoflowers show high cyclability and rate capability and deliver an average reversible capacity as high as 525 mAh g$^{-1}$ at a current density of 400 mA h/g over 70 cycles. Preferential c-Axis orientation of ultrathin SnS$_2$ nanoplates on graphene can maintain a charge capacity of 704 mAh g$^{-1}$ after 100 cycles at 0.6 C and deliver a charge capacity of 303 mAh g$^{-1}$ at 10 C. Lamellar sandwich SnS$_2$@PANI nanocomposites have a high initial reversible capacity (968.7 mAh g$^{-1}$), excellent cyclability (730.8 mAh g$^{-1}$ after 80 cycles), and an extraordinary rate capability (356 mAh g$^{-1}$ at the rate of 5A g$^{-1}$). Free-standing SnS$_2$@graphene nanocable network not only shows high specific capacity of 720 mAh g$^{-1}$ even after 350 cycles at a current density of 0.2 A g$^{-1}$, with over 93.5% capacity retention, but also exhibits a high-rate capability of 580 mAh g$^{-1}$ even at the current rate of 1 A g$^{-1}$. However, its major volume expansion during the charge–discharge process leads to a significant capacity loss and poor cycling stability, which greatly hinders its practical application in lithium-ion batteries. Thus, it is necessary to explore a useful method to improve the reversible capacity and lithium storage performance of SnS$_2$.

Carbon cloths (CC), a new kind of substrate, have been received large attention because their high conductivity, excellent mechanical flexibility and high strength. They have been utilized as substrate for the growth of electrode materials in order to serve as binder-free, enabling high capacity, good cycling stability and excellent rate performance for flexible LIBs. Also, titanium oxynitride (TiO$_x$N$_y$) has been reported to be a crucial factor in composite electrodes.
because they have the merit of high dispersion of the active material in a highly conductive matrix, which would curb the particles aggregation and dramatically boost the cycling performance of LIBs at high charge/discharge rates.\textsuperscript{26-29}

Herein, we develop a facile strategy to design and fabricate a unique hierarchical hybrid structure of carbon cloths supported TiO\textsubscript{x}N\textsubscript{y} and Sn\textsubscript{2} (denoted as CC@TiO\textsubscript{x}N\textsubscript{y}@Sn\textsubscript{2}) as flexible additive-free anode material for LIBs. With the compositional and structure advantages, the as-synthesized CC@TiO\textsubscript{x}N\textsubscript{y}@Sn\textsubscript{2} electrode display an initial discharge capacity of 1082 mAh g\textsuperscript{-1} at a current density of 1 C, the reversible capacity as high as 612 mAh g\textsuperscript{-1} can still be maintained after 100 charging/discharging cycles. Moreover, these materials show a high reversible discharge capacity of 419 mAh g\textsuperscript{-1} at a current density of 5 C, a stable high discharge capacity of 676 mAh g\textsuperscript{-1} can be attained when the current density is switched back to 1 C.

2. Experimental Method

2.1 Materials

Carbon cloth (flexible substrate), Titanium (IV) tetrachloride (TiCl\textsubscript{4}, 99%), concentrated hydrochloric acid (HCl, AR), tetrabutyl titanate [Ti(O\textsubscript{2}C\textsubscript{2}H\textsubscript{5})\textsubscript{4}, 98%], Tin chloride pentahydrate (SnCl\textsubscript{2}·5H\textsubscript{2}O, AR), L-cysteine (C\textsubscript{4}H\textsubscript{7}N\textsubscript{2}O\textsubscript{5}S, AR) and ethanol (C\textsubscript{2}H\textsubscript{5}OH, AR) were purchased from Chemical Reagents Factory and used without further purification.

2.2 Synthesis of CC@TiO\textsubscript{x}N\textsubscript{y}

TiO\textsubscript{2} nanowires were grown on a carbon cloth by hydrothermal method according to the previous report.\textsuperscript{30} In a typical procedure, a piece of carbon cloth with 2.5 cm × 4 cm was cleaned with deionized water, ethanol, sequentially for 30 minutes in an ultrasonic bath, respectively, and then dried at room temperature. The cleaned carbon cloth was immersed in 0.2 M aqueous titanium (IV) tetrachloride solution for two minutes and allowed to be dried by blowing in the compressed air. And then the blown-dried carbon cloth was heated on a hotplate at about 320 °C for few minutes, which generated nanoparticles on the surface of the carbon cloths. This process was repeated about four times to ensure uniformity. 20 mL of concentrated hydrogen chloride acid was diluted in 20 mL deionized water and then mixed with 1.2 mL of tetrabutyl titanate under stirring on a magnetic stirrer until a clear solution was obtained. The carbon cloth was then immersed in the clear solution and transferred to Teflon-lined stainless steel autoclave (50 mL). The sealed autoclave was heated in an electric oven at 160 °C for 330 minutes and cooled down to room temperature. The carbon cloths with TiO\textsubscript{2} samples was washed thoroughly with deionized water several times and dried in air. To obtain the TiN nanowires, the synthesized TiO\textsubscript{2} was calcined in NH\textsubscript{3} gas at a temperature of 700 °C at a heating rate of 5 °C min\textsuperscript{-1} for 60 minutes.

2.3 Synthesis of CC@TiO\textsubscript{x}N\textsubscript{y}@Sn\textsubscript{2} nanocomposites

Sn\textsubscript{2} nanosheets were decorated on the TiN nanowires by hydrothermal method. A piece of carbon cloth covered uniformly with TiN nanowires was immersed in a solution of Tin(IV) chloride pentahydrate (SnCl\textsubscript{2}·5H\textsubscript{2}O, 0.14 g) and L-cysteine (0.77 g), then transferred into a Teflon-lined stainless steel autoclave (50 mL), and hydrothermally treated in an airflow electric oven at 160 °C for 240 minutes and cooled down to room temperature. A greenish-black CC@TiO\textsubscript{x}N\textsubscript{y}@Sn\textsubscript{2} film was collected, washed with distilled water and dried for subsequent experiments.

2.4 Synthesis of CC@SnS\textsubscript{2} and SnS\textsubscript{2}

Tin(IV) chloride pentahydrate (SnCl\textsubscript{2}·5H\textsubscript{2}O, 0.14 g) and L-cysteine (0.77 g) were dissolved in water. A piece of clean carbon cloth was immersed into the solution, transferred into a Teflon-lined stainless steel autoclave. The sealed autoclave was heated in an electric oven at 160 °C for 240 minutes and cooled down to room temperature. A green carbon cloth covered with SnS\textsubscript{2} (CC@SnS\textsubscript{2}) was collected, washed with water and dried in 60 °C. The preparation process of pristine SnS\textsubscript{2} nanosheets was similar to CC@SnS\textsubscript{2}, except for adding carbon cloth.

2.5 Material Characterization

The phase, morphology, structure and composition of the as-synthesized samples were characterized by X-ray diffraction (XRD, Bruker, D8 ADVANCE, Cu Kα radiation), field-emission scanning electron microscopy (FE-SEM, JSM-6330F), transmission electron microscopy (TEM, JEM2010-HR, 200 KV), X-ray Photoelectron Spectroscopy (XPS, ESCALab250, Thermo VG) and Raman spectrometer (FT-IR, Nicolet 330).

2.6 Electrochemical Measurement

The electrochemical properties of the samples were tested using CR2032-type coin cells. For pristine SnS\textsubscript{2} nanosheets, the working electrode was composed of active material, carbon black (Super-P-Li), and polyvinylidene fluoride (PVDF) at a weight ratio of 80:10:10. The electrode slurry was coated onto Cu foil and then dried under vacuum at 100 °C over night. For other composition, the working electrodes were prepared by cutting the carbon cloth covered uniformly with samples into smaller square pieces with area of 0.64 cm\textsuperscript{2}. Both the carbon cloth with loading samples and bare carbon cloth were weighed in a high-precision analytical balance (Sartorius, max weight 5100 mg, d=0.001 mg). The mass loading of the active material was 1~2 mg cm\textsuperscript{-2}. The 2032 Coin cells were assembled in an argon-filled glove box (Mikrouna (China) Co., Ltd., the moisture and oxygen concentrations below 1.0 ppm) using a pure lithium foil as the counter and reference electrode, 1 M LiPF\textsubscript{6} in a mixture of ethylene carbonate/dimethyl carbonate (1:1, V/V) as electrolyte, and a microporous membrane (Celgard 2400) as the separator. The galvanostatic charge-discharge measurements were tested at different current densities in the voltage range of 0.01-3 V using a Neware battery testing system. Cyclic voltamogram (CV) measurements and electrochemical impedance spectroscopy (EIS) measurements were performed with an electrochemical workstation (CHI 760D) at room temperature.

3. Results and Discussion

TiO\textsubscript{x}N\textsubscript{y} and SnS\textsubscript{2} nanocomposites were grown on carbon cloth by two steps hydrothermal reaction. Firstly, TiN nanowires
were obtained by growing TiO$_2$ nanowires on a flexible carbon cloth substrate, followed by further thermal treatment in NH$_3$ atmosphere. X-ray diffraction (XRD) data confirmed that the TiN nanowires are cubic phase (Fig. S1). In Fig. 1a, SEM image shows that the surface of carbon cloth is uniformly covered with TiN nanowires. The SEM images with a high magnification (Fig. 1b) displays that the TiN nanowires have diameters in a typical range between 100 and 200 nm and lengths about 1.5 μm. The as-prepared carbon cloth supported TiN nanowires were then immersed in a solution containing SnCl$_2$, L-cysteine, and hydrothermal reaction heated at 160 °C for 240 minutes to form the final products CC@Ti$_x$N$_y$@Sn$_z$. The XRD spectra of the CC@Ti$_x$N$_y$@Sn$_z$ nanocomposites (Fig. S2) shows that the reflections from TiO$_2$, TiN, SnS$_2$ and carbon textile can be clearly discerned, which match with the PDF patterns of JCPDS card no. 65-0965 (TiN) and JCPDS card no. 23-0677 (SnS$_2$), justifying the formation of the CC@Ti$_x$N$_y$@Sn$_z$ nanocomposites. SEM images collected from the CC@Ti$_x$N$_y$@Sn$_z$ nanocomposites are shown in Fig. 1. In Fig. 1c, the surface of the carbon textile also becomes rough, when compared with the bare TiN nanowires (Fig. 1b). The higher magnification SEM image in Fig. 1d reveals that the SnS$_2$ nanosheets with lateral size of about 300-400 nm are uniformly coated on the TiN nanowires substrate.

The structure of the as-synthesized CC@Ti$_x$N$_y$@Sn$_z$ can be seen clearly in the TEM image in Fig. 2a. The selected-area electron diffraction (SAED) patterns demonstrate that the CC@Ti$_x$N$_y$@Sn$_z$ nanocomposites are polycrystalline in nature (Fig. 2a inset). Well-resolved lattice fringes of 0.31 nm corresponding to the (100) planes of the hexagonal SnS$_2$ (JCPDS card no. 23-0677) are observed in the nanocomposites (Fig. 2b and 2c), consistent with the layered structure of the SnS$_2$. Additionally, energy dispersive spectroscopy (EDS) elemental mapping collected from the part of Fig. 2a show that the Sn and S signals are strongly detected, while the Ti, O, N signals are detected to be sparingly distributed in the nanosheets (Fig. 2d-i). The EDS data reveal that the Ti$_x$N$_y$@Sn$_z$ nanocomposites have the Ti:O:N:Sn:S ratio of 10:15:9:41:25.

For comparison, carbon cloth covered with SnS$_2$ nanosheets (CC@SnS$_2$) was also prepared according to the preparation of CC@Ti$_x$N$_y$@Sn$_z$ without the absence of TiN nanowires. All of the XRD peaks can be assigned to layered structure SnS$_2$ and carbon cloth (Fig. S3) and SEM image certified that the carbon cloth covered by uniform SnS$_2$ nanosheets (Fig. S4). Also, the pristine SnS$_2$ samples were synthesized without carbon cloth. The XRD pattern can be assigned to layered structure SnS$_2$ without other impurity phase (Fig. S3). The SEM image (Fig. S5) illustrates that the pristine SnS$_2$ has uniform nanosheets morphology.

The full Raman spectra of the CC@Ti$_x$N$_y$@Sn$_z$ nanocomposites are shown in Fig. S6. The enlarge spectrum of the high wavelength region displayed in Fig. 3a shows Raman shift of 146, 441 and 638 cm$^{-1}$ corresponds to the characteristic Raman peaks of TiO$_2$. The D and G peaks of the carbon cloth was distorted and some new peaks emanates around 1400-1500 cm$^{-1}$, which are attributed to the C=N stretching bond, resulted from the reaction of reduced N and carbon cloth. Such C=N bond has been proven to be have high electrical conducti-
vity, which may enhance the electrical conductivity of the fabricated CT@TiO$_2$N$_x$@SnS$_2$ nanocomposites.\textsuperscript{36}

Furthermore, X-ray photoelectron spectroscopy (XPS) studies were carried out to determine the change of surface chemical composition and oxidation state of the CC@TiO$_2$N$_x$@SnS$_2$ nanocomposites. To get the insight study about the oxidation states, the XPS experiment was also performed for the TiN for comparison. Fig. 4a shows the XPS survey spectra of the TiN nanowires and the CC@TiO$_2$N$_x$@SnS$_2$ nanocomposites. The XPS spectra of the CC@TiO$_2$N$_x$@SnS$_2$ nanocomposites consists of mainly the Sn, S, Ti, O, N and C oxidation states; while the no trace of Sn and S peaks can be observed in the TiN spectra. The Ti 2p core-level spectra of the two samples can be seen in Fig. 4b. Multiple peaks are evolved in the Ti 2p spectra of the C@SnS nanocomposites, which are assigned to be Ti-N, Ti-O-N and Ti-0,\textsuperscript{37} but the Ti-N peak was absent in the Ti 2p spectra of the CC@TiO$_2$N$_x$@SnS$_2$ nanocomposites, confirming the formation of the oxynitride.\textsuperscript{30, 39} Similar phenomenon can also be observed in the N 1s core-level spectra (Fig. 4c). The N 1s spectrum of the TiN presents a doublet at around 396 and 397 eV, corresponding to the Ti-N and Ti-O-N peaks, respectively; while the Ti-N peak is also not present in the CC@TiO$_2$N$_x$@SnS$_2$ nanocomposites, which also affirms that the oxynitride was formed.\textsuperscript{30, 41} These results reveal that the surfaces of the CC@TiO$_2$N$_x$@SnS$_2$ nanocomposites are composed of Ti-O and Ti-O chemical states. An additional peak at binding energy of about 164.5 eV was observed in the S 2p peaks of the CC@TiO$_2$N$_x$@SnS$_2$ nanocomposites, which is quite different from the common S 2p spectra reported for SnS$_2$ in other literatures.\textsuperscript{37-41} This additional peak can be attributed to sulfoxoyanion from the sulfite, suggesting the nanocomposite surface is functionalized by some sulfoxyl groups, which have been also reported to possess good electrical conductivity.\textsuperscript{44}

Next, we investigate the electrochemical properties of the CC@TiO$_2$N$_x$@SnS$_2$ nanocomposites as anode material for LIBs.

Figure 5a shows the 1st, 3rd cycles CV curves of the CC@TiO$_2$N$_x$@SnS$_2$ nanocomposites between 0.01 and 3.0 V at a scan rate of 0.1 mV/s. (b) The 1st, 2nd and 100th charge-discharge voltage curves of CC@TiO$_2$N$_x$@SnS$_2$ at a current density of 1 C. (c) Cyclic performance of CC@TiO$_2$N$_x$@SnS$_2$, CC@TiN, CC@SnS and SnS$_2$ electrode at a current density of 1 C. (d) Rate capability of CC@TiO$_2$N$_x$@SnS$_2$, CC@TiN, CC@SnS, and SnS$_2$ electrode at various current rates from 1 to 20 C.

![Figure 4](image1.png)

**Fig. 4.** XPS Characterization of the TiN nanowires and CC@TiO$_2$N$_x$@SnS$_2$ nanocomposites: (a) XPS survey spectrum. (b) Ti 2p core-level spectrum. (c) N 1s core-level spectrum. (d) S 2p core-level spectrum.
percentage of the TiO$_x$N$_y$ in CC@TiO$_x$N$_y$@SnS$_2$ is 44 % and SnS$_2$ is 56 %. Thus, the theoretical capacity of CC@TiO$_x$N$_y$@SnS$_2$ can be calculated as follows: $C_{\text{theoretical}} = C\left(\text{TiO}_x\text{N}_y\right) \times (\% \text{ mass of TiO}_x\text{N}_y) + C\left(\text{SnS}_2\right) \times (\% \text{ mass of SnS}_2) = 335 \times 44 \% + 645 \times 56 \% = 508.6 \text{ mAh g}^{-1}$. From the second cycle onward, the cycle performance at a current density of 1 C is shown in Fig. 5c. The CC@TiO$_x$N$_y$@SnS$_2$ electrode exhibits excellent capacity retention even prolonging cycle numbers. Apart from the first cycle with a large irreversible capacity, the following up cycles own a coulombic efficiency of about 98% (Fig. S8), a reversible capacity as high as 612 mAh g$^{-1}$ can still be maintained after 100 charging/discharging cycles, which is higher than its theoretical capacity (508.6 mAh g$^{-1}$). Such capacity is remarkably compared to the previous reports in cycling stability of SnS$_2$-based electrodes. As shown in Fig. 5d, the average discharge capacities of CC@TiN, CC@SnS$_2$, and pristine SnS$_2$ nanosheets, are also showed in Fig. 5c. Under the same test conditions, the CC@TiN, CC@SnS$_2$, and pristine SnS$_2$ nanosheets exhibit much faster capacity fading, after 100 charging/discharging cycles, the discharge capacity are 301, 480 and 270 mAh g$^{-1}$, respectively. The pristine SnS$_2$ nanosheets electrode shows the worst cycle performance. Interestingly, the discharge capacity of the CC@TiO$_x$N$_y$@SnS$_2$ electrode is higher than the addition of individual CC@TiN, CC@SnS$_2$, and SnS$_2$ electrode, which is even closer to the theoretical capacity of SnS$_2$ (645 mAh g$^{-1}$). After 100 charging/discharging cycles, SEM image of the CC@Ti@SnS$_2$ electrode studies reveals that the SnS$_2$ nanosheets still firmly adhere to the surface of the TiO$_x$N$_y$ nanowires (Fig. S9), indicating that the CC@TiO$_x$N$_y$@SnS$_2$ composites exhibit excellent chemical stability.

Considering the rate capacity is an important factor for the output powder. The rate capacity of the CC@TiO$_x$N$_y$@SnS$_2$, CC@TiN, CC@SnS$_2$, and SnS$_2$ electrode were carried out by charging/discharging at current density ranging from 1 C to 20 C. As shown in Fig. 5d, the average discharge capacities of CC@TiO$_x$N$_y$@SnS$_2$ electrode are maintained at 685, 601, 498, 417, 351, 284 and 219 mAh g$^{-1}$ from 1 C to 20 C, respectively. When the current density is switched back to 1 C, a stable high discharge capacity of 676 mAh g$^{-1}$ can be attained. By contrast, the discharge capacities of CC@TiN, CC@SnS$_2$, and SnS$_2$ electrode drop dramatically with increasing the current density. When compared with CC@SnS$_2$ and SnS$_2$ electrode, the CC@Ti@SnS$_2$ electrode shows higher reversible capacity and better cycling stability. These results clearly demonstrate that the TiO$_x$N$_y$ play an important role in improving the rate performance of SnS$_2$.

The attractive electrochemical performance of the CC@TiO$_x$N$_y$@SnS$_2$ electrode might be attributed to the unique structural features in several aspects. First, the flexible carbon cloths substrate, which provides strong mechanical support, acts as a conducting material and current collector. Second, the high electrical conductivity of the TiO$_x$N$_y$ facilitates the transport of electrons and lithium ions. The link of SnS$_2$ nano-

![Fig. 6 Nyquist plots of the fresh battery and after 100 charging/discharging cycles of CC@TiO$_x$N$_y$@SnS$_2$ electrode at a current density of 1 C.](image-url)

sheets and the current collector provides intimate adhesion, ensuring that the active material does not come off from the current collector, and also stimulate electrons transfer between SnS$_2$ nanosheets and the substrate. Third, the large surface area of the 2D SnS$_2$ nanosheets with layered structure enhances rapid diffusion of lithium ions. Moreover, the SnS$_2$ nanosheets anchor on the TiO$_x$N$_y$ nanowires can allow the electrolyte to penetrate entirely, holding each SnS$_2$ nanosheet not only surrounded by the electrolyte solution but also contact with the carbon cloth current collector. This is a key feature to high rate capacity. Thus, the above characteristics work together, giving the electrode excellent lithium storage properties.

To deeply understand the electrochemical performances, the electrochemical impedance spectroscopy (EIS) was conducted at room temperature. Fig. 6 shows the Nyquist plots of the fresh and after 100 cycles CC@TiO$_x$N$_y$@SnS$_2$ electrode. Each plot consists of a semicircle in the medium-high frequency region, which is ascribed to the charge transfer or electrochemical reaction resistance, and a sloped line in the low frequency region, which is related to the diffusion of lithium ion. The Nyquist plots exhibit that the diameter of the semicircle for after 100 cycles electrode in the medium-high frequency region is smaller than the fresh electrode, indicating lower charge transfer impedances for after 100 cycles electrode. This phenomenon has been commonly observed for metal oxide LIBs electrodes, and herein could be due to the reduction of the nanocomposite into their corresponding metals during the irreversible reactions.

4. Conclusions

In summary, the novel material CC@TiO$_x$N$_y$@SnS$_2$ nanocomposites were synthesized by two step hydrothermal method. Investigation on the lithium storage performance indicates that the CC@TiO$_x$N$_y$@SnS$_2$ electrode displays an initial discharge capacity of 1082 mAh g$^{-1}$ at a current density of 1 C, with a coulombic efficiency of 74 %. The reversible capacity as high as 612 mAh g$^{-1}$ can still be maintained after 100 cycles charging/discharging. Even at a high current density of 5 C, the electrode shows a high reversible discharge capacity.
of 419 mAh g⁻¹. The excellent electrochemical performances suggest that CC@TiO₂Nₓ@Sn₂ can be feasible alternative electrode materials for the next generation lithium ion batteries. Also, this approach can also be extended for the development of other diverse inorganic electrode materials.

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References

Graphical Abstract

Free-standing CC@TiO$_x$N$_y$@SnS$_2$ nanocomposites were synthesized via two steps hydrothermal process. The flexible additive-free CC@TiO$_x$N$_y$@SnS$_2$ electrode possesses high lithium storage capacity, outstanding cycling stability and excellent rate performance.