



Cabbage-like CoO/Ti₃C₂ with high cycling stability in lithium-ion storage

Dajun Wu^{a,1,*}, Xinyue Zhang^{a,1}, Xuan Wan^a, Heng Zhang^a, Zhicheng Wang^a, Shi Tao^a, Bin Qian^a, Shaohui Xu^{b,*}, Paul K. Chu^c

^a Jiangsu Laboratory of Advanced Functional Materials, School of Electronic and Information Engineering, Changshu Institute of Technology, Changshu 215500 China

^b Key Laboratory of Polar Materials and Devices, Ministry of Education, and School of Physics and Electronic Science, East China Normal University, 500 Dongchuan Road, Minhang District, Shanghai 200241 China

^c Department of Physics, Department of Materials Science and Engineering, and Department of Biomedical Engineering, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, China

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ABSTRACT

Cobalt monoxide (CoO) has attracted much attention due to its high theoretical capacity and long cycling life in lithium-ion batteries (LIBs). However, the intrinsic CoO anode has poor conductivity and experiences large volume changes during cycling. The use of the proper carbide materials and morphological modification can overcome some of the barriers. In this work, few-layer Ti₃C₂ is used to fabricate the cabbage-like CoO/Ti₃C₂ composite by a one-step hydrothermal process, and the electrochemical properties of samples are evaluated systematically. The composite has a cabbage roll structure with a diameter of 2–7 μm assembled on folded nanosheets with a lateral dimension of 1–2 μm. The interlayer spacing is 0.1–0.5 μm and the Ti₃C₂ mass ratio is less than 9%. The cabbage-like CoO/Ti₃C₂ electrode shows a high original specific capacity of 980.5 mAh g⁻¹ at 0.5 C. After 1000 cycles, the reversible discharging capacity is still 598.1 mAh g⁻¹ besides a good capacity retention ratio of 93.2%. Compared with CoO and CoO/rGO, the cabbage-like CoO/Ti₃C₂ has a faster ion transport rate and robust skeleton, leading to excellent cycling stability. The simple fabrication strategy and materials with outstanding cycling stability have large potential in the development of next-generation LIBs.

1. Introduction

Transition metal oxides (TMOs) [1] such as MnO₂ [2], NiO [3], Fe₂O₃ [4], and CoO [5] have high theoretical specific capacities of 600–1200 mAh g⁻¹ as anode materials in lithium-ion batteries (LIBs). In particular, CoO has garnered significant attention due to its high theoretical capacity, cost-effectiveness, and environmental friendliness [6–8]. However, the low conductivity and the structural instability of CoO cause serious capacity decay during cycling [9]. In this respect, nanoscale cobalt monoxide with the proper morphology and composition shows good results in energy storage and conversion applications. Although efforts have also been made to improve the properties by preventing aggregation of CoO-based materials, it is still challenging to further improve the energy density and produce CoO with a high capacity for anodes in LIBs. Techniques like nano-crystallization [10,11], doping [12,13], and compositing [14–16] are typically employed to enhance the specific capacity and cycling stability of CoO. For instance,

Wan et al. [14] have fabricated layered mesoporous CoO/reduced graphene oxide (CoO/RGO), and the lithium-ion battery composed of CoO/RGO and an aqueous electrolyte shows a high discharge capacity of 2189.4 mAh g⁻¹ at 100 mA g⁻¹. Yang et al. [5] have prepared ZnO/CoO nanoclusters immobilized on N-doped 3D reduced graphene oxide by a solvothermal and freeze-drying method, and the capacity of CoO_{1.2}/ZnO_{0.6}-NrGO (6.78) is 600 mA h g⁻¹ at 2.0 A g⁻¹ after 1000 cycles. A bionic “flos albiziae” like CoO/SiO₂ heterostructure anode prepared on copper foam has a high reversible capacity of 1251 mAh g⁻¹ after 250 cycles at 500 mA g⁻¹ [17]. In order to improve the electrochemical properties, CoO-based composites comprising carbonaceous materials, metal oxide, carbide, and so on have been proposed for anodes in LIBs.

Two-dimensional (2D) titanium carbide such as Ti₃C₂, a type of MXene transition metal carbide, has been explored as an anode in LIBs due to its unique layered structure, excellent hydrophilicity, good conductivity, and favorable Li⁺ intercalation [18]. However, there are four major limitations of 2D MXene electrodes, including self-stacking, low

* Corresponding authors.

E-mail addresses: 201700028@cslg.edu.cn (D. Wu), 050522137@cslg.edu.cn (X. Zhang), 050523142@cslg.edu.cn (X. Wan), wangzc@cslg.edu.cn (Z. Wang), taoshi@cslg.edu.cn (S. Tao), njqb@cslg.edu.cn (B. Qian), shxu@ee.ecnu.edu.cn (S. Xu), paul.chu@cityu.edu.hk (P.K. Chu).

¹ The two co-first authors contributed equally to the work.

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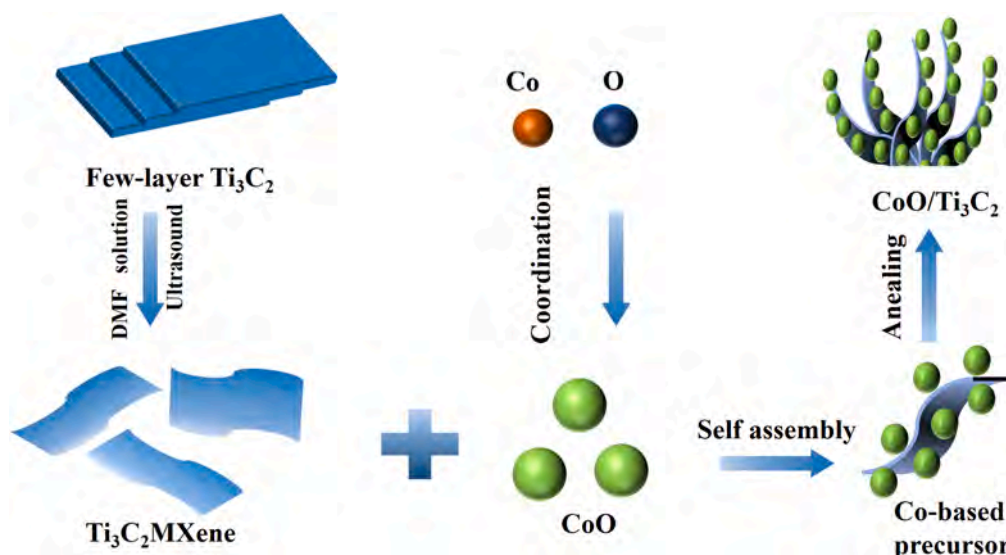


Fig. 1. Schematic illustration of the synthesis of cabbage-like CoO/Ti₃C₂.

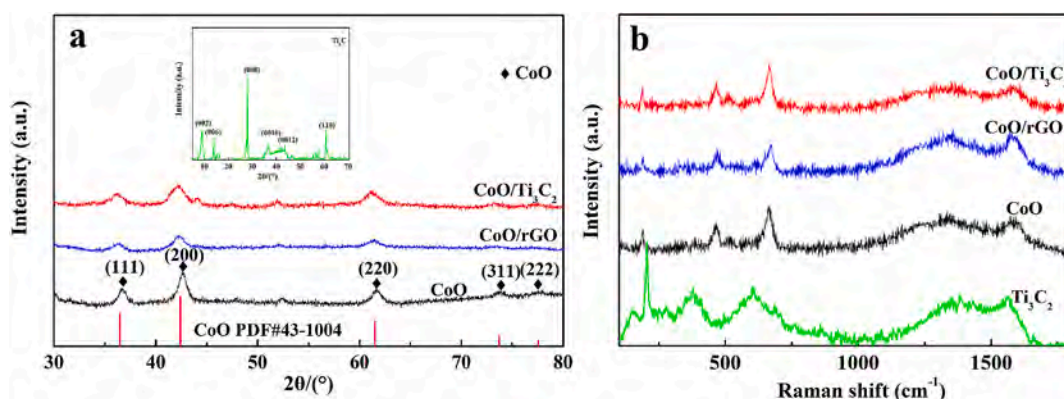


Fig. 2. (a) XRD patterns and (b) Raman scattering spectra of Ti₃C₂, CoO, CoO/rGO, and CoO/Ti₃C₂.

specific surface area, and disturbance of Li⁺ diffusion by surface terminations [19]. To overcome these hurdles plaguing hierarchical Ti₃C₂-based composites, heteroatom doping and coatings (sulfide, hydroxide, carbon, etc.) have been proposed, for example, Ti₃C₂@Si@N [20], SnO₂/Ti₃C₂T_x [21], TiO₂/Ti₃C₂ [22], Ti₃C₂/VN@C [23], Ti₃C₂/NiFe-LDH [24], SiO₂/Ti₃C₂ [25], SnS/Ti₃C₂ [26], and Ni-MOF/Ti₃C₂ [27]. Furthermore, Ti₃C₂ and cobalt oxide nanostructures had been researched, such as CoO/Ti₃C₂ [28], Ti₃C₂@CoO/ZnO [29], Co-MOF/Ti₃C₂T_x [30], Co₃O₄/Ti₃C₂T_x [31], and Ti₃C₂T_x/CoNi-MOF [32]. For instance, Zhu et al. [28] have used a hydrothermal technique to introduce CoO nanoparticles to increase the surface areas of Ti₃C₂ and prevent the aggregation of Ti₃C₂. Compared to CoO or Ti₃C₂ alone, CoO/Ti₃C₂ has a larger initial discharge capacity of 1389 mAh g⁻¹ with a Coulombic efficiency of 61 % at 100 mA g⁻¹. After 100 cycles, the reversible capacity remains at 313 mAh g⁻¹. Tang et al. [29] have anchored CoO/ZnO nanodots onto Ti₃C₂ to address self-stacking and increase the surface area, resulting in a specific capacity of 627 mAh g⁻¹ at a high current density of 1 A g⁻¹ for 300 cycles.

Most of these studies have primarily focused on enhancing the electrochemical properties by depositing CoO coatings on Ti₃C₂. Virtually, precise control of the morphology of CoO/Ti₃C₂ is crucial to the surface area and cycling characteristics [33]. To the best of our knowledge, the use of few-layer Ti₃C₂ as a conductive agent to control morphology of CoO-based composites are still scarcely reported. Herein, the cabbage-like CoO/Ti₃C₂ composite is prepared by a hydrothermal

process and annealing. The cabbage (2–5 μm) structure consists of few-layer Ti₃C₂ nanosheets and CoO nanoparticles (20–30 nm) with an interlayer spacing of 0.5–1 μm. The few-layer Ti₃C₂ nanosheets envelop the CoO nanoparticles to reduce direct contact with the electrolyte and improve the Coulombic efficiency and cycling stability. Compared to CoO and CoO/rGO, CoO/Ti₃C₂ has better Li-ion storage properties and stability as anodes in LIBs. This simple and scalable technique has large potential in the development of advanced CoO-based anodes in LIBs.

2. Experimental details

2.1. Chemicals and materials

All the chemical reagents were analytical grade and used without purification. Cobalt nitrate (Co(NO₃)₂·6H₂O), ammonium fluoride (NH₄F), urea (CO(NH₂)₂), and sodium dodecyl benzene sulfonate (SDBS) powder were purchased from Aladdin Reagents and few-layer Ti₃C₂ MXene, reduced graphene oxide (rGO) and the other reagents were obtained from Sinopharm Chemical Reagents Co. Ltd. Deionized water (18 MΩ) was used in the experiments.

2.2. Synthesis of CoO/Ti₃C₂

The cabbage-like CoO/Ti₃C₂ composite was prepared hydrothermally. In brief, 0.58 g of Co(NO₃)₂·6H₂O, 0.07 g of NH₄F, 0.24 g of CO

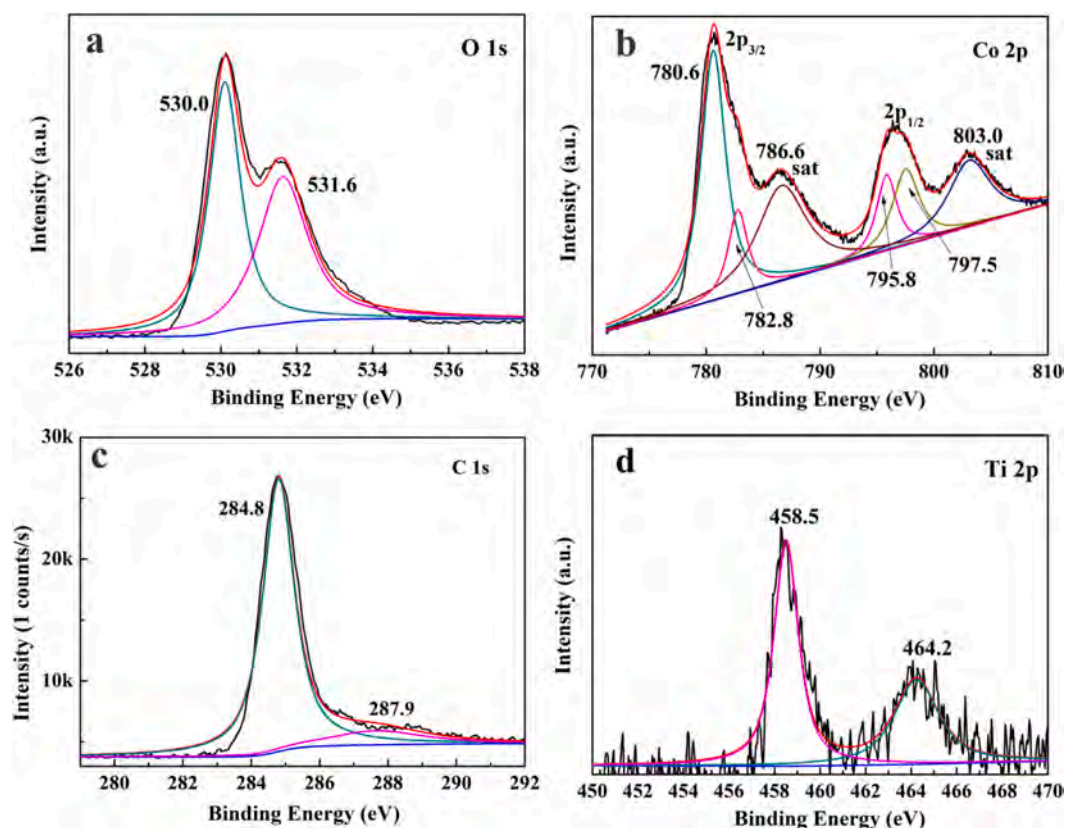


Fig. 3. XPS spectra of CoO/Ti₃C₂: (a) O 1s, (b) Co 2p, (c) C 1s, and (d) Ti 2p.

(NH₂)₂, and 0.20 g of SDBS powder were added to 35 ml of deionized water and stirred for half an hour until the solution turned pink. The solution was transferred to a 50 ml Teflon-lined stainless-steel autoclave containing 2.8 ml of the few-layer Ti₃C₂ dispersion (5 mg/ml). The sealed autoclave was heated to 120 °C for 8 h and after cooling to room temperature, the product was centrifuged with deionized water and ethanol until the pH was 7, followed by vacuum-drying for 10 h at 80 °C to produce the precursor. The precursor was then calcined at 500 °C for 2 h under argon to produce CoO with the layered structure. For comparison, the same procedure was adopted for the synthesis of CoO in the absence of Ti₃C₂ and CoO/rGO with 5 drops of the GO dispersion (5 mg/ml).

2.3. Assembly of LIBs and electrochemical assessment

The lithium-ion battery was assembled in a 2032-type button cell in an argon-filled glove box. A mixture of CoO/Ti₃C₂ (or CoO, CoO/rGO) powder, acetylene black, and polyvinylidene difluoride (PVDF) in *N*-methyl pyrrolidone (NMP) was mixed with a weight ratio of 8:1:1. After stirring for 4 h, the slurry was placed on a Cu foil and dried overnight at 60 °C in a vacuum oven. The counter electrode was a bare Li-metal foil. The electrolyte was 1 M LiPF₆ in diethyl carbonate (DEC)/ethylene carbonate (EC) (volume ratio 1:1), and a Celgard 2300 membrane was the separator. The LAND CT2001A system was used to conduct galvanostatic charging-discharging (GCD). The CHI760E (Chenhua, Shanghai) electrochemical workstation was employed for cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). To enhance the wettability of the cell components and achieve a stable potential, the cells were aged for 12 h before the charging-discharging measurement. CV and GCD were carried out in the potential window between 0.01 and 3.00 V (vs. Li/Li⁺) at room temperature. EIS was conducted at the open circuit potential (OCP) with an amplitude of 5 mV in the frequency range between 10⁵ and 10⁻² Hz.

3. Results and discussion

The cabbage-like CoO/Ti₃C₂ is prepared by a hydrothermal process and annealing as illustrated in Fig. 1. Cobalt nitrate, ammonium fluoride, urea, and SDBS are added to deionized water during synthesis, and the SDBS template controls the product morphology and crystal formation [40]. As shown by our previous experiments, few-layer Ti₃C₂ nanosheets have many oxygen-containing surface groups thus producing superior dispersive properties and adsorption in the aqueous solution. The few-layer Ti₃C₂ nanosheets effectively absorb Co ions during crystal nucleation and growth of the CoO precursor. Afterward, the precursor is calcined under argon atmosphere, carbonized, and crystallized to produce the final product of cabbage-like CoO/Ti₃C₂.

The structure and phase of CoO, CoO/rGO, and CoO/Ti₃C₂ are characterized by X-ray diffraction (XRD). As shown in Fig. 2a, the peaks at 36.6°, 42.5°, 61.5°, 73.7°, and 77.6° correspond to the (1 1 1), (2 0 0), (2 2 0), (3 1 1), and (2 2 2) planes of CoO (JCPDS 431004) [17]. But the concentration of rGO, Ti₃C₂ is less than 5 %, so it cannot be detected by XRD. The Ti₃C₂ sample exhibits typical diffraction peaks with the (0 0 2) plane, which are the same as the reported works [22].

Raman scattering is performed to analyze the structure of CoO, CoO/rGO, and CoO/Ti₃C₂. As shown in Fig. 2b, the peaks at 192 cm⁻¹ and 600 cm⁻¹ correspond to the F_{2g} vibrational mode of CoO, while those at 440 cm⁻¹ and 680 cm⁻¹ are the F_g and A_{1g} modes of CoO, respectively [14]. Four peaks are observed below 1000 cm⁻¹ from CoO/Ti₃C₂ and CoO/rGO [28] showing the CoO phase. The two broad peaks between 1200 and 1800 cm⁻¹ are the D- and G-peaks of graphitic carbon. Compared with the pure CoO and CoO/rGO, the intensities of the D-peak at 1300 cm⁻¹ and G-peak at 1570 cm⁻¹ of CoO/Ti₃C₂ increase because of the insertion of CoO between the layers of Ti₃C₂ and more exposed C on the surface, which are consistent with the XRD results. These surface defect sites provide more active sites for electron storage.

Fig. 3 shows that CoO/Ti₃C₂ contains O, Co, C, and Ti consistent with

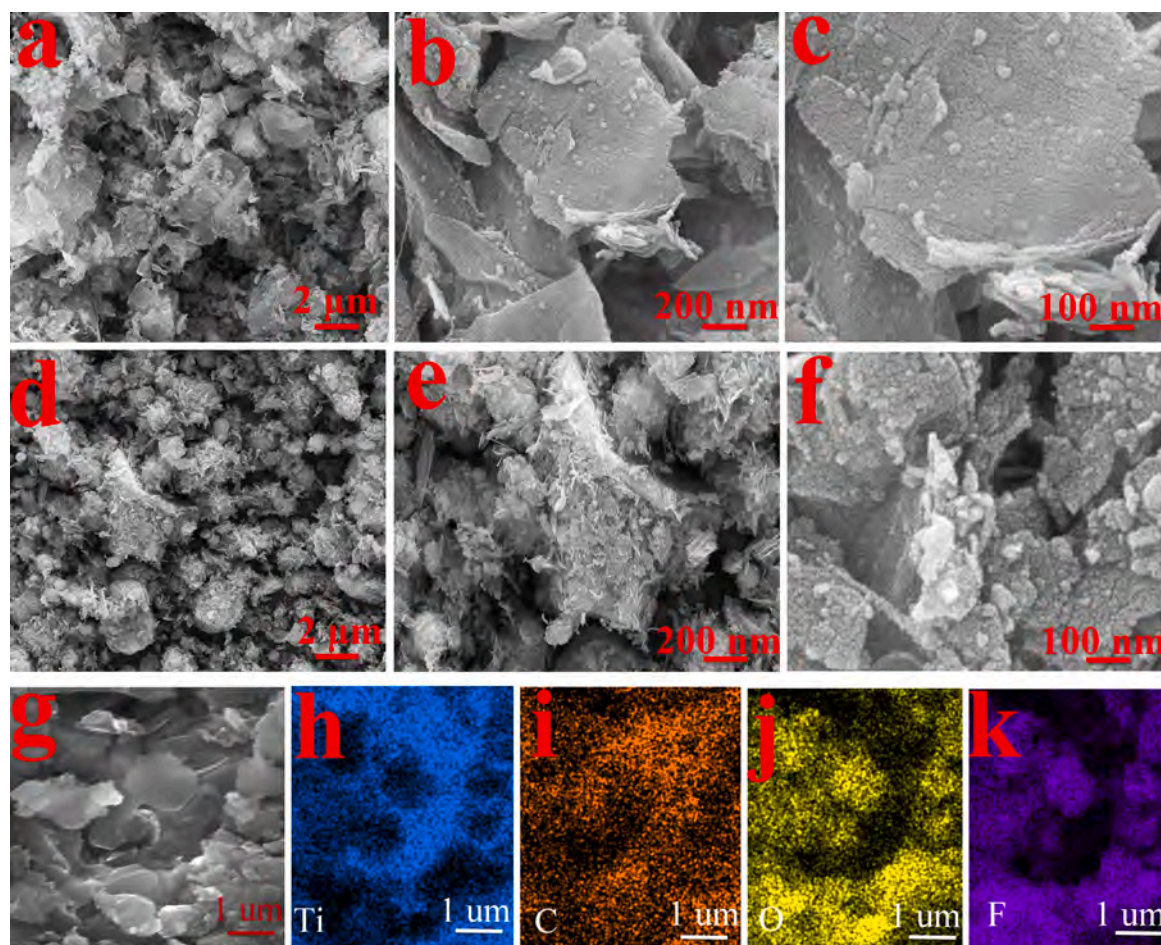


Fig. 4. SEM images of (a–c) CoO and (d–f) CoO/rGO; (g–k) SEM image and elemental maps of Ti₃C₂.

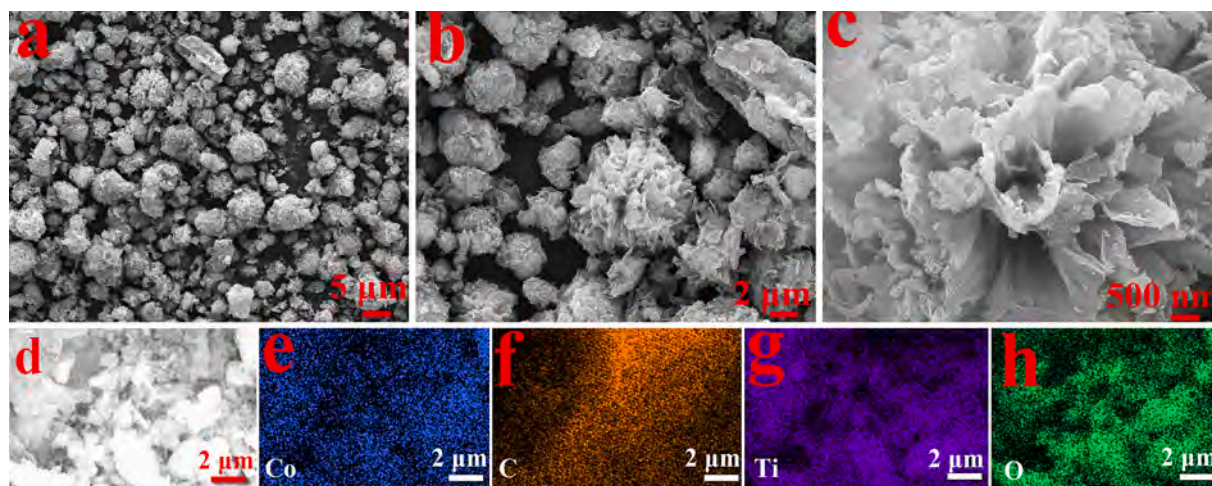


Fig. 5. SEM images of (a–c) CoO/Ti₃C₂ and (d–h) SEM image elemental maps of CoO/Ti₃C₂.

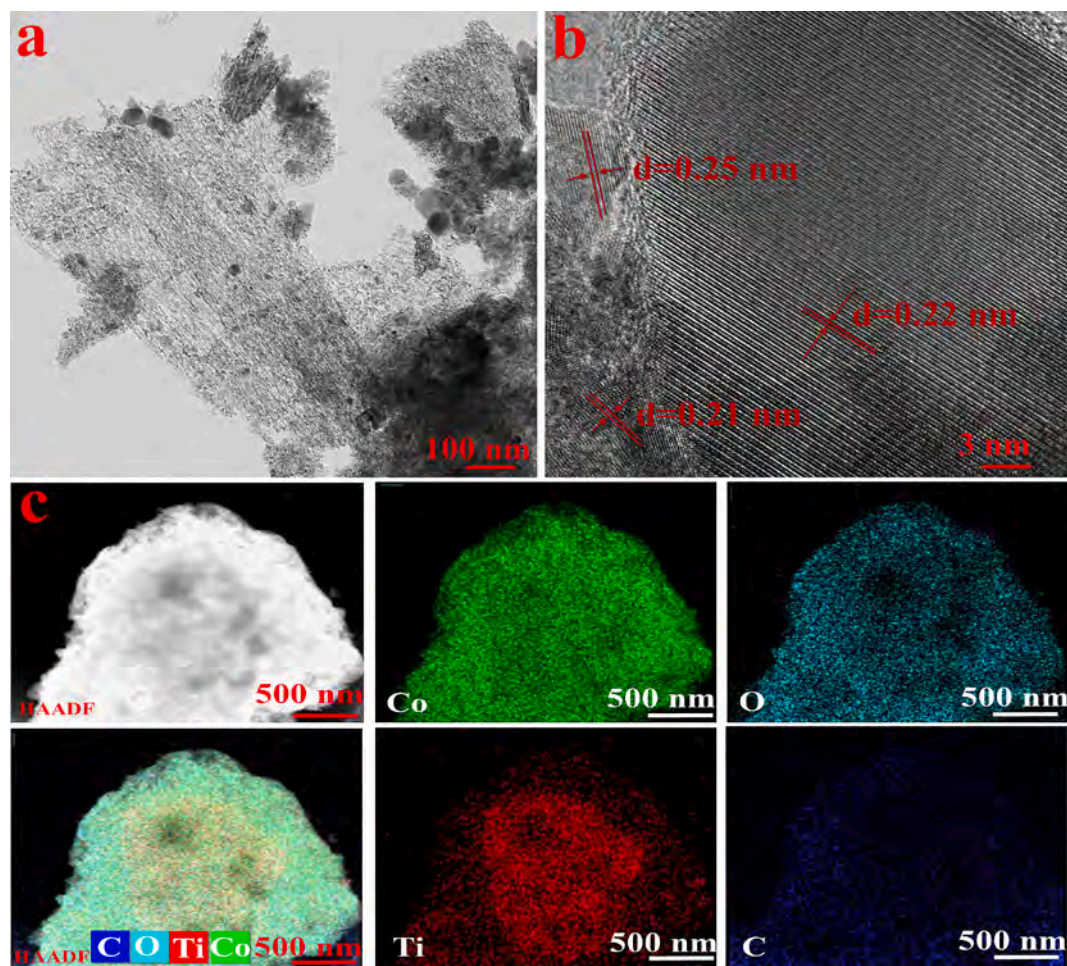


Fig. 6. (a–b) TEM and HR-TEM images of CoO/Ti₃C₂; (c) HAADF image of CoO/Ti₃C₂ and EDS elemental maps of Co, O, Ti, C.

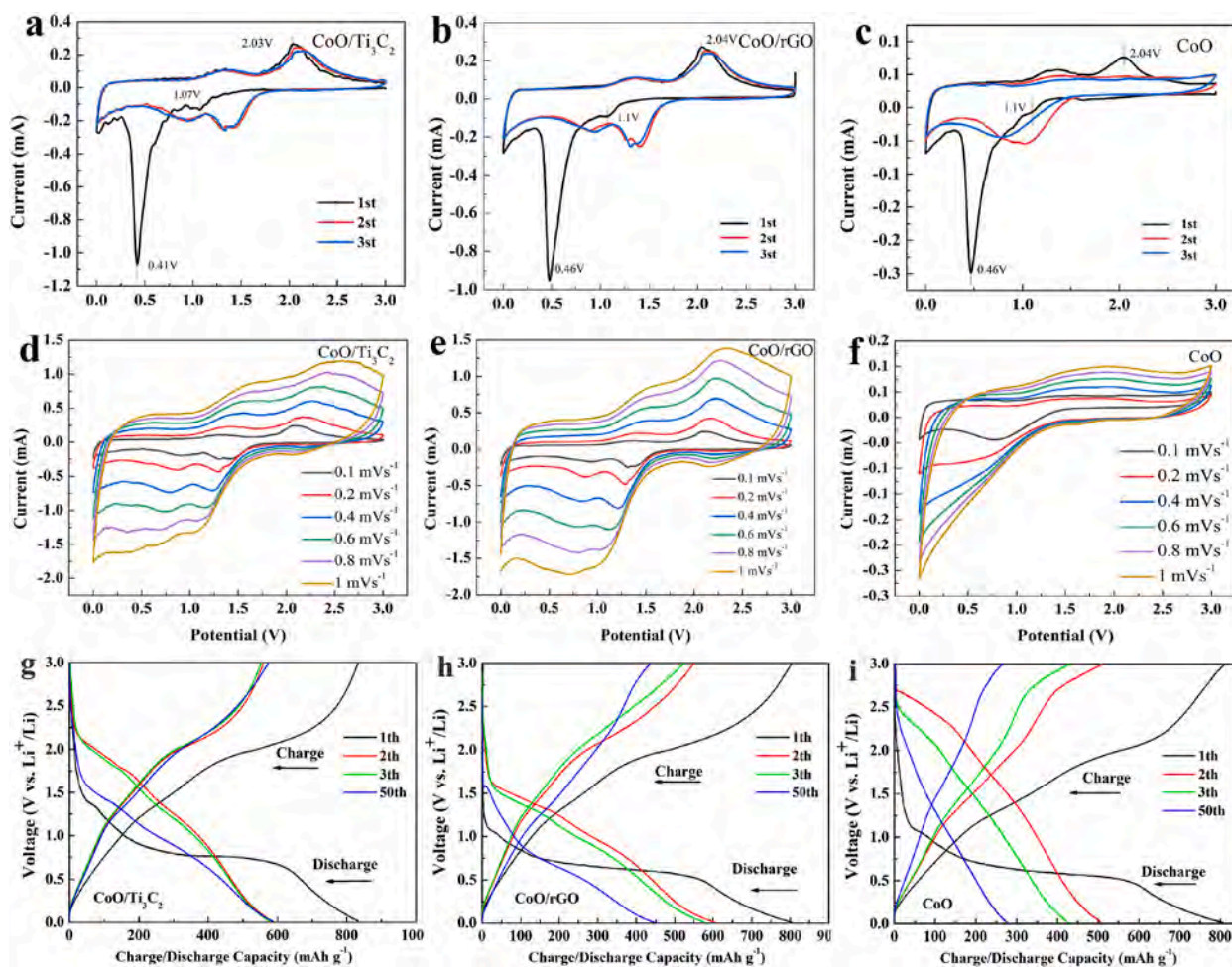


Fig. 7. 1st, 2nd, and 3rd cycles CV curves of (a) CoO/Ti₃C₂, (b) CoO/rGO, and (c) CoO at a scanning rate of 0.1 mV s⁻¹; CV curves of (d) CoO/Ti₃C₂, (e) CoO/rGO, and (f) CoO at scanning rates of 0.1, 0.2, 0.4, 0.8 and 1 mV s⁻¹; Charging and discharging curves of the first 3rd and 50th cycles of (g) CoO/Ti₃C₂, (h) CoO/rGO and (i) CoO.

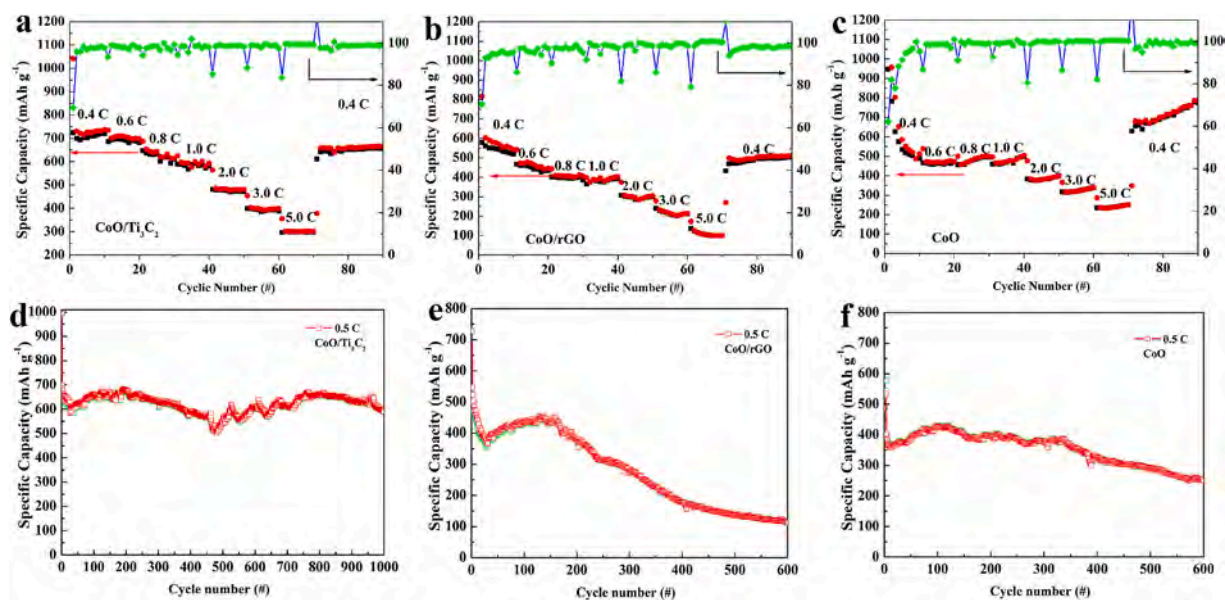


Fig. 8. Rate curves of (a) CoO/Ti₃C₂, (b) CoO/rGO, and (c) CoO; Cycling curves of (a) CoO/Ti₃C₂, (b) CoO/rGO, and (c) CoO.

Table 1
Comparison of the specific capacities of Co-based electrodes.

Materials	Specific capacity	Current Densities	After cycles	Retention ratios	References
CoO@CC	145 mAhg ⁻¹	0.1 A g ⁻¹	500	86.4 %	[11]
CoO@PAN	72.8 mAhg ⁻¹	10 C	1000	96.1 %	[15]
CoO/SnO ₂	1251 mAhg ⁻¹	0.5 A g ⁻¹	250	120 %	[17]
CoO/Ti ₃ C ₂	324 mAhg ⁻¹	0.1 A g ⁻¹	100	99 %	[28]
CoO/rGO	1167 mAhg ⁻¹	5 A g ⁻¹	40	76 %	[14]
Co@MXene/CNF	422.8 mAhg ⁻¹	1 A g ⁻¹	500	99 %	[39]
Ti ₃ C ₂ @CoO/ZnO	327 mAhg ⁻¹	1 A g ⁻¹	300	120 %	[29]
CoO @TiO ₂ /C	1136 mAhg ⁻¹	0.5 A g ⁻¹	200	110 %	[16]
Cabbage-like CoO/Ti₃C₂	598.1 mAhg⁻¹	0.5 C	1000	93.2 %	This work

XRD and Raman scattering. The O 1s peaks of CoO/Ti₃C₂ at 531.6 and 530.0 eV stem from Co-O in CoO. For the quantitative calculation of the mass ratio of Ti to Co element in CoO/Ti₃C₂, we integrated the XPS pattern area for each element, showing the mass ratio of Ti to Co element is 1:8. Fig. 3b shows that the Co 2p spectrum of CoO/Ti₃C₂ has two main peaks at 780.6 and 797.5 eV with a spin orbital splitting energy of 16.9 eV [8,12]. Likewise, the Co 2p_{3/2} peaks at 780.6 eV are characteristic of Co³⁺, while the two shake-up satellite peaks at 786.6 and 803.0 eV indicate spinel cobaltite. Generally, the satellite peak at 786.6 eV is ascribed to Co²⁺ and that at 803.0 eV shows Co³⁺. Hence, CoO/Ti₃C₂ is composed of Co^{2+/3+} on the surface. The C 1s spectrum can be deconvoluted into three peaks at 287.9 and 284.8 eV associated with C-OO and C sp² (Fig. 3c), respectively. Deconvolution of Ti 2p^{1/2} and Ti 2p^{3/2} shows two peaks corresponding to Ti-C at (464.2 eV) and Ti-O (at 458.5 eV) (Fig. 3d) [25]. These results reveal more surface defects, which are expected to improve the surface area and electrochemical properties. As we know that ICP-OES is a simple and rapid method in element analysis. The ICP-OES result (Ti of 24.5 mg/L and Co of 196 mg/L) suggests that the Ti to Co element mass ratio of CoO/Ti₃C₂ is also about 1:8, and then mole ratio of Ti to Co is about 3:20, indicating the Ti₃C₂ percentage of the total is ~ 9 %, which are consist with the results of XPS.

As shown in Figs. 4–5, the SEM images reveal that the flake-shape CoO is composed of nanoparticles with a length of 0.5 ~ 1 μm (Fig. 4a–c). In CoO/rGO, the CoO nanoparticles are uniformly coated on the surface of rGO (Fig. 4d–f) to improve the surface area and conductivity. Fig. 4g–k disclose the few-layer structure of Ti₃C₂ MXene with a length of 1 ~ 2 μm. Energy-dispersive X-ray spectroscopy (EDS) mapping shows uniform elemental distributions of Ti/C/O/F on Ti₃C₂. The oxygen-containing surface groups of Ti₃C₂ MXene produce superior dispersive properties and adsorption in the aqueous solution. Compared to CoO and CoO/rGO, CoO/Ti₃C₂ has a cabbage-like structure (Fig. 5a–c). The cabbage structure (2–5 μm) consists of few-layer Ti₃C₂ nanosheets and CoO nanoparticles (20–30 nm) with an interlayer spacing of 0.5–1 μm. EDS mapping provides evidence that Co, C, Ti, and O are well dispersed on CoO/Ti₃C₂ (Fig. 5d–h).

The TEM and HR-TEM images of CoO/Ti₃C₂ are depicted in Fig. 6a–b. The CoO/Ti₃C₂ nanobelts are composed of numerous nanoflakes with a length of ~1 μm and a width of 200 nm. The cabbage-like structure contains nanobelts with a micro-wrinkle structure for efficient support and more active surface sites. The CoO nanoparticles are incorporated uniformly into the few-layer Ti₃C₂ nanoflakes. As shown by the HR-TEM image of CoO/Ti₃C₂ (Fig. 6b), the inter-planar distances, d, are 0.24 nm and 0.21 nm, corresponding to the (2 2 0) and (2 0 0) planes of CoO [34]. The lattice stripe spacing of 0.22 nm aligns precisely

with the (1 0 4) crystal plane of Ti₃C₂ [35], thus affirming the successful synthesis of CoO/Ti₃C₂.

To determine the electrochemical properties, CV is conducted between 0.01 and 3.00 V at a scanning rate of 0.1 mV/s (in Fig. 7a–c). In the first cycle, two cathodic peaks are observed, a sharp one at 0.41 ~ 0.46 V and a small one at 1.07 ~ 1.01 V, which are related to Co²⁺ to Co, formation of SEI (solid electrolyte interphase), and irreversible electrolyte decomposition. The two broad peaks at 1.25 V and 2.04 V arise from metallic Co to Co²⁺ as well as Co²⁺ to Co³⁺ during anodic oxidation, respectively. The other cycles almost overlap. The cathodic peak, which moves to 1.0 V, is associated with the formation of the Li_xCoO phase, demonstrating the good reversible capability and high stability of CoO/Ti₃C₂. In the subsequent cycles, compared with other electrodes, the CV curves of CoO/Ti₃C₂ are more stable, indicating that the redox reactions taking place on the anode are reversible. CoO/Ti₃C₂ has smaller and different redox values of 0.38 and 0.63 V, indicating that CoO/Ti₃C₂ has high reversible capacity and good stability. Fig. 7d–f show the CV curves of CoO/Ti₃C₂, CoO/rGO, and CoO anodes at different scanning rates from 0.1 to 1 mV/s. Compared with other electrodes, the CV curves of CoO/Ti₃C₂ do not change significantly as the scanning rates increase [36] consequently demonstrating good reversibility.

The 3rd and 5th CV cycles of CoO/Ti₃C₂, CoO/rGO, and CoO are shown in Fig. 7g–i. The first GCD curve exhibits a noticeable plateau at 0.8 V (CoO/Ti₃C₂), 0.7 V (CoO/rGO), and 1.25 V (CoO), respectively, due to the solid electrolyte interphase (SEI) layer and interactions of CoO and Li⁺ [37,38]. The initial discharging capacities of CoO/Ti₃C₂, CoO/rGO, and CoO are 840.1 mAh g⁻¹, 798.3 mAh g⁻¹, and 802.4 mAh g⁻¹, respectively. After 50 cycles, the reversible capacities of CoO/Ti₃C₂, CoO/rGO, and CoO are 590.8 mAh g⁻¹, 447.6 mAh g⁻¹ and 270.4 mAh g⁻¹, respectively. The results confirm that the synergistic effects of CoO nanoparticles and few-layer Ti₃C₂ MXene improve the specific capacity and rates.

Fig. 8a–c show the rates of CoO/Ti₃C₂, CoO/rGO and CoO. The cabbage-like CoO/Ti₃C₂ achieves a substantial capacity of 724.5 mAh g⁻¹ at 0.4 C. When the rate of discharge changes from 0.4 to 5.0 C, the rechargeable capacities of the cabbage-like CoO/Ti₃C₂ nanocomposite are 724.5, 705.4, 651.2, 603.3, 481.9, 400.7, and 300.6 mAh g⁻¹. Hence, CoO/Ti₃C₂ shows enhanced Li-ion diffusion and electron transfer, leading to rate capabilities and reaction kinetics.

The enhanced Li⁺ storage capacity can be attributed to the synergetic effects between CoO and few-layer Ti₃C₂. Fig. 8d–f show the cycling results at 0.5 C. After 1,000 cycles, the discharging capacity of the cabbage-like CoO/Ti₃C₂ electrode is still 598.1 mAhg⁻¹ in addition to good capacity retention ratios of 93.2 % at 0.5 C, which are better than those of CoO/rGO (140.1 mAhg⁻¹, 28.2 %) and CoO (260.2 mAhg⁻¹, 68.4 %) after 600 cycles. The cycling properties of CoO/Ti₃C₂ are better than those of other CoO-based materials reported in the literature, including CoO/Ti₃C₂ [28], CoO/rGO [14], and Co@MXene/CNF [39], as shown in Table 1. The inverse cycle curves of CoO/Ti₃C₂ indicate faster ion transfer and the conductive network enhances the cycling stability of Co-based materials.

To check the morphology of the active materials after the cycling test, we disassemble the electrode of CoO/Ti₃C₂ after 1000 cycles in Fig. 9a–b. The structure of the CoO/Ti₃C₂ are robust enough to retain the structural integrity and order, and the CoO/Ti₃C₂ composites are intact, keeping the original morphology and construct. Fig. 9c–d shows the Nyquist plots of the cabbage-like CoO/Ti₃C₂, CoO/rGO, and CoO electrodes revealing a semicircle in the mid-to-high frequency region representing the charge transfer resistance and a sloping line in the low-frequency region [41–43]. The R_{ct} values of CoO/Ti₃C₂, CoO/rGO, and CoO are 85.3 Ω, 155.2 Ω, and 1.0 k Ω, respectively, indicating that Ti₃C₂ reduces the charge transfer impedance of CoO. The XRD of CoO/Ti₃C₂ electrode after 1000 cycles in Fig. 9e, revealing the structure of the CoO/Ti₃C₂ retain the original structure supporting the well stability cycles. All in all, the excellent electrochemical properties of CoO/Ti₃C₂

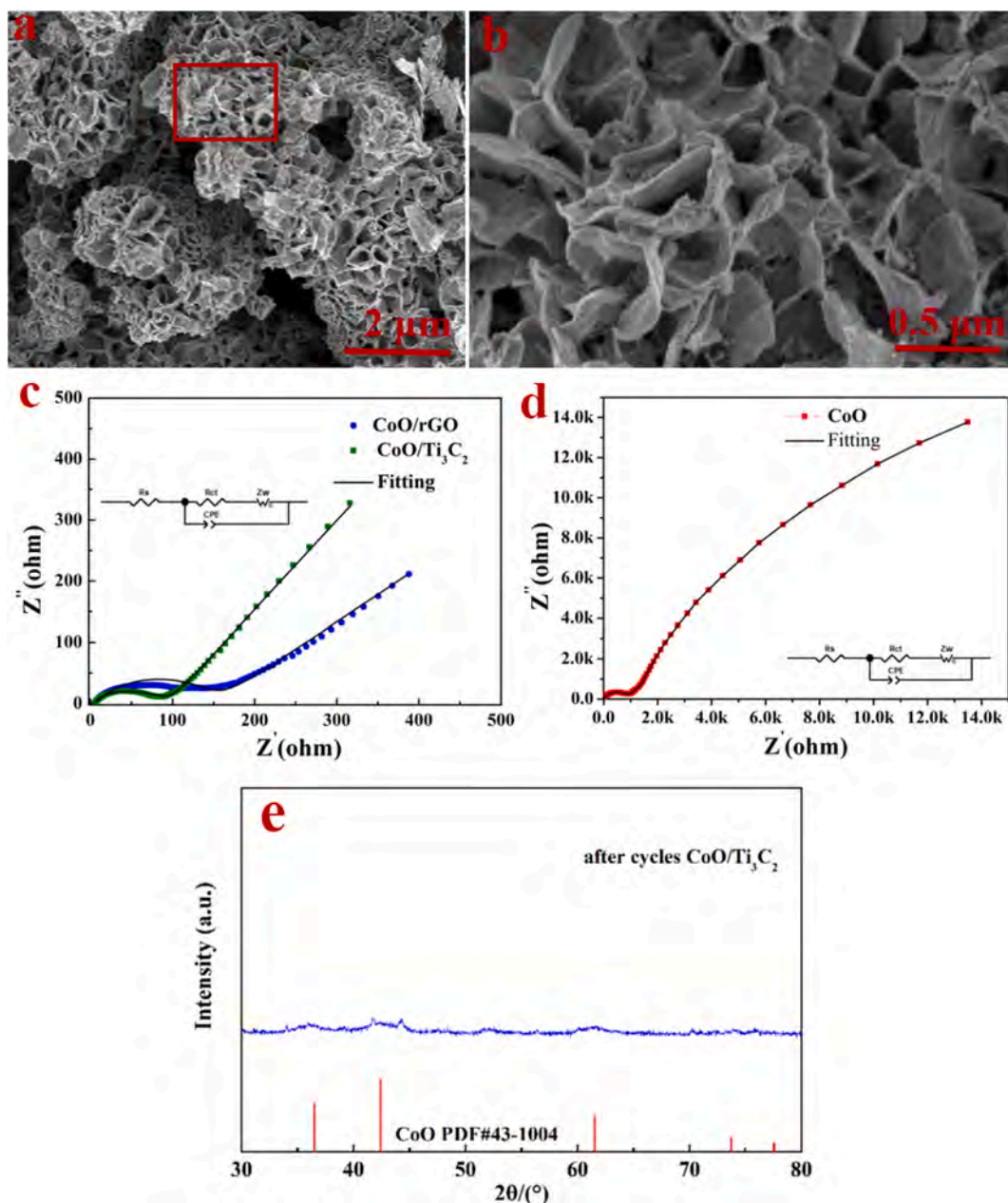


Fig. 9. (a–b) The morphology of the CoO/Ti₃C₂ after 1000 cycles; electrochemical impedance spectra with the fitting: (c) CoO/Ti₃C₂, CoO/rGO and CoO (d); (e) XRD of CoO/Ti₃C₂ after cycles.

stem from the incorporation of CoO nanoparticles into few-layer Ti₃C₂, consequently shortening the lithium transfer paths and improving the rate capability and cycling performance [44–46].

4. Conclusion

The cabbage-like CoO/Ti₃C₂ electrode is synthesized by a hydrothermal method and annealing process. The CoO/Ti₃C₂ as an anode has a higher specific capacity of 840.1 mAhg⁻¹ at 0.5 C than that of CoO/rGO (798.3 mAhg⁻¹ at 0.5C) and CoO (802.4 mAhg⁻¹ at 0.5 C) in LIBs. Moreover, the reversible capacity of CoO/Ti₃C₂ is still 598.1 mAhg⁻¹ after 1000 cycles, whereas the specific capacity of CoO/rGO (CoO) is lower at 140.1 mAhg⁻¹ (260.2 mAhg⁻¹) after 600 cycles. The excellent electrochemical characteristics arise from the larger surface area and shorter ion/electron transfer paths. The results indicate the large potential of CoO/Ti₃C₂ as anodes in next-generation LIBs.

CRediT authorship contribution statement

Dajun Wu: Writing – review & editing, Supervision, Resources, Project administration. **Xinyue Zhang:** Writing – original draft, Investigation, Data curation. **Xuan Wan:** Investigation, Formal analysis. **Heng Zhang:** Methodology. **Zhicheng Wang:** Software. **Shi Tao:** Visualization, Software. **Bin Qian:** Validation, Data curation. **Shaohui Xu:** Methodology, Investigation, Data curation. **Paul K. Chu:** Writing – review & editing, Visualization, Funding acquisition.

Declaration of competing 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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References

- X. Wang, R. Wang, Q. Kang, L. Yan, T. Ma, D. Li, Y. Xu, H. Ge, Construction of Cu-doped Co₃O₄/rGO composites with a typical buffer structure for high-performance lithium storage, *Colloid Surf. A* 656 (2023) 130325.
- X. Yuan, Z. Ma, S. Jian, H. Ma, Y. Lai, S. Deng, X. Tian, C. Wong, F. Xia, Y. Dong, Mesoporous nitrogen-doped carbon MnO₂ multichannel nanotubes with high performance for Li-ion batteries, *Nano Energy* 97 (2022) 107235.
- X. Du, Y. Ma, W. Zhang, M. Zhang, K. Su, Z. Li, The collaborative effect of Ni₃S₂-NiO heterojunction and porous carbon network modified lithium-sulfur battery separator for effectively inhibiting polysulfides shuttle, *J. Power Sources* 623 (2024) 235414.
- R. Li, A.R. Kamali, Clean preparation of Fe₂SiO₄ coated Fe₂O₃ integrated with graphene for Li-ion storage application, *Colloid Surf. A* 656 (2023) 130275.
- Z. Yan, Z. Sun, K. Yue, A. Li, L. Qian, CoO/ZnO nanoclusters immobilized on N-doped 3D reduced graphene oxide for enhancing lithium storage capacity, *J. Alloys Compd.* 836 (2020) 155443.
- Y. Li, X. Xiao, L. Zhang, B. Yan, H. Tao, X. Yang, Co@CoO core-shell cross-linked framework modified 3D Cu for dendrite-free lithium anode, *Chem. Eng. J.* 491 (2024) 151922.
- Y. Jiang, M. Du, P. Geng, B. Sun, R. Zhu, H. Pang, CoO/MoO₃@nitrogen-doped carbon hollow heterostructures for efficient polysulfide immobilization and enhanced ion transport in Lithium-Sulfur batteries, *J. Colloid Interface Sci.* 664 (2024) 617–625.
- X. Li, Q. Chu, M. Song, C. Chen, Y. Li, X. Tian, Y. Cui, D. Zhao, Porous CoO/Co₃O₄ nanoribbons as a superior performance anode material for lithium-ion batteries, *Appl. Surf. Sci.* 618 (2023) 156658.
- W. Kim, D. Shin, B. Seo, S. Chae, H. Cho, E. Jo, W. Choi, Precisely tunable synthesis of binder-free cobalt oxide-based Li-ion battery anode using scalable electrothermal waves, *ACS Nano* 16 (2022) 17313–17325.
- H. Chen, S. Zhang, S. Wu, K. Wang, C. Chen, Y. Chen, W. Chu, Z. Chen, H. Li, H. Liu, Design and synthesis of cellulose nanofiber-derived CoO/Co/C two-dimensional nanosheet toward enhanced and stable lithium storage, *J. Colloids Interfaces Sci.* 625 (2022) 915–924.
- L. Chen, G. Chen, W. Tang, H. Wang, F. Chen, X. Liu, R. Ma, A robust and lithiophilic three-dimension framework of CoO nanorod arrays on carbon cloth for cycling-stable lithium metal anodes, *Mater. Today Energy* 18 (2020) 100520.
- W. Wang, H. Wan, W. Cai, Y. Fang, Z. Fan, Y. Zhu, Y. Qian, The free-standing N-CoO matrix towards optimizing dual-electrodes for high-performance Li-O₂ batteries, *Chem. Eng. J.* 461 (2023) 142004.
- Y. Kim, C. Kim, S. Kim, Y. Kang, D. Lee, G. Park, Fabrication of heteroatom-doped cobalt oxide yolk-shell microsphere using recycled solution from waste materials and their excellent electrochemical properties as an anode material for lithium-ion batteries, *Rare Met.* 43 (2024) 4934–4947.
- W. Ban, J. Guo, W.H. Lai, Y.X. Wang, M. Liu, H.K. Liu, J.Z. Wang, S.L. Chou, S. X. Dou, Layered mesoporous CoO/reduced graphene oxide with strong interfacial coupling as a high-performance anode for lithium-ion batteries, *J. Alloys Compd.* 843 (2020) 156050.
- X. Xiao, H. Chen, J. Tang, L. Wang, CoO@PAN core-shell structure composite as protective layer for stabilizing lithium metal batteries, *J. Mater. Sci. Mater. Electron.* 34 (2023) 1–13.
- Y.F. Yuan, W.C. Zhao, L. Chen, G.S. Cai, S.Y. Guo, CoO hierarchical mesoporous nanospheres@TiO₂@C for high-performance lithium-ion storage, *Appl. Surf. Sci.* 556 (2021) 149810.
- S. Hou, M.N. Liao, Y.Y. Guo, T.Z. Liu, L.K. Wang, J. Li, C. Mei, W.P. Fu, L.Z. Zhao, SiO₂ nanoparticles modulating the “flos albiziae” like CoO by the synergistic effect with enhanced lithium storage, *Appl. Surf. Sci.* 530 (2020) 147223.
- E. Gibertini, F. Lissandrello, L. Bertoli, P. Viviani, L. Magagnin, All-inkjet-printed Ti₃C₂ MXene capacitor for textile energy storage, *Coatings* 13 (2023) 230.
- D. Seo, M.R. Kim, J.K. Song, E. Kim, J. Koo, K.C. Kim, H. Han, Y. Lee, C.W. Ahn, Hollow Ti₃C₂ MXene/carbon nanofibers as an advanced anode material for lithium-ion batteries, *ChemElectroChem* 9 (2022) 8.
- W.Y. Zhang, H.F. Shi, D.H. Wang, J.S. Wang, Z.H. Xiong, C.D. Wang, Y.S. Gu, Z. M. Bai, Q.J. Liang, X.Q. Yan, Three-dimensional Ti₃C₂ MXene@silicon@nitrogen-doped carbon foam for high performance self-standing lithium-ion battery anodes, *J. Electroanal. Chem.* 921 (2022) 116664.
- H. Liu, X. Zhang, Y. Zhu, B. Cao, Q. Zhu, P. Zhang, B. Xu, F. Wu, R. Chen, Electrostatic self-assembly of 0D-2D SnO₂ quantum dots/Ti₃C₂T_x MXene hybrids as anode for lithium-ion batteries, *Nano-Micro Lett.* 11 (2019) 65.
- Y. Jia, J. Liu, L. Shang, Layered structure 2D MXene/TiO₂ composites as high-performance anodes for lithium-ion batteries, *Ionics* 29 (2023) 531–537.
- G.P. Nunna, R. Pitcheri, B.A. Al-Asbah, S. Sangaraju, B. Khan, K.T. Jo, Ti₃C₂ MXene nanosheets/vanadium nitride@carbon composite electrodes for high-performance lithium-ion batteries, *Int. J. Energy Res.* 2023 (2023) 8091900.
- C.Y. Li, D.D. Zhang, J. Cao, P.F. Yu, M. Okhawilal, J. Yi, J.Q. Qin, X.Y. Zhang, Ti₃C₂ MXene-encapsulated NiFe-LDH hybrid anode for high-performance lithium-ion batteries and capacitors, *ACS Appl. Energy Mater.* 4 (2021) 7821–7828.
- J.Q. Liu, S.C. Song, D.C. Zuo, C. Yan, Z.J. He, Y.J. Li, J.C. Zheng, Synthesis and characterization of SiO₂/Ti₃C₂ anode materials for lithium-ion batteries via different methods, *Ionics* 26 (2020) 5325–5331.
- R.C. Wang, Q.L. Pan, Y.H. Luo, C. Yan, Z.J. He, J. Mao, K.H. Dai, X.W. Wu, J. C. Zheng, SnS particles anchored on Ti₃C₂ nanosheets as high-performance anodes for lithium-ion batteries, *J. Alloys Compd.* 893 (2022) 162089.
- S. Zheng, H. Zhou, H. Xue, P. Braunstein, H. Pang, Pillared-layer Ni-MOF nanosheets anchored on Ti₃C₂ MXene for enhanced electrochemical energy storage, *J. Colloid Interface Sci.* 614 (2022) 130–137.
- X. Li, J. Zhu, Y. Fang, W. Lv, F. Wang, Y. Liu, H. Liu, Hydrothermal preparation of CoO/Ti₃C₂ composite material for lithium-ion batteries with enhanced electrochemical performance, *J. Electroanal. Chem.* 817 (2018) 1–8.
- H. Tang, M. Jiang, E. Ren, Y. Zhang, X. Lai, C. Cui, S. Jiang, M. Zhou, Q. Qin, R. Guo, Integrate electrical conductivity and Li⁺ ion mobility into hierarchical heterostructure Ti₃C₂@CoO/ZnO composites toward high-performance lithium ion storage, *Energy* 212 (2020) 118696.
- Y. Ren, Q. Zhai, B. Wang, L. Hu, Y. Ma, Y. Dai, S. Tang, X. Meng, Synergistic adsorption-electrocatalysis of 2D/2D heterostructure toward high performance Li-S batteries, *Chem. Eng. J.* 439 (2022) 135535.
- X. Bu, F. Ma, Q. Wu, H. Wu, Y. Yuan, L. Hu, C. Han, X. Wang, W. Liu, X. Li, Metal-organic frameworks-derived Co₃O₄/Ti₃C₂T_x MXene nanocomposites for high performance ethanol sensing, *Sens. Actuators B-Chem.* 369 (2022) 132232.
- C.F. Du, Q. Song, Q. Liang, X. Zhao, J. Wang, R. Zhi, Y. Wang, H. Yu, The passive effect of MXene on electrocatalysis: a case of Ti₃C₂T_x/CoNi-MOF nanosheets for oxygen evolution reaction, *ChemNanoMat* 7 (2021) 539–544.
- N. Kitchamsetti, J.S. Cho, A roadmap of recent advances in MXene@MOF hybrids, its derived composites: synthesis, properties, and their utilization as an electrode for supercapacitors, rechargeable batteries and electrocatalysis, *J. Energy Storage* 80 (2024) 110293.
- M. Cui, X. Chen, Z. Wang, S. Tao, D. Wu, B. Qian, L. Wang, P.K. Chu, Fan-shape Mn-doped CoO/C microspheres for high lithium-ion storage capacity, *J. Alloy. Compd.* 903 (2022) 163980.
- P.F. Yan, L. Ji, X.P. Liu, Q.H. Guan, J.L. Guo, Y.L. Shen, H.J. Zhang, W.F. Wei, X. W. Cui, Q. Xu, 2D amorphous-MoO₃·x@Ti₃C₂-MXene non-van der Waals heterostructures as anode materials for lithium-ion batteries, *Nano Energy* 86 (2021) 106139.
- L. Li, G.X. Jiang, C.H. An, Z.J. Xie, Y.J. Wang, L.F. Jiao, H.T. Yuan, Hierarchical Ti₃C₂@TiO₂ MXene hybrids with tunable interlayer distance for highly durable lithium-ion batteries, *Nanoscale* 12 (2020) 10369–10379.
- X. Li, C. Wen, H. Li, G. Sun, In situ decoration of nanosized metal oxide on highly conductive MXene nanosheets as efficient catalyst for Li-O₂ battery, *J. Energy Chem.* 47 (2020) 272–280.
- J. Liu, J. Wu, C. Zhou, P. Zhang, G. Shouzhi, S. Li, Y. Yang, K. Li, L. Chen, M. Wang, Single-phase ZnCo₂O₄ derived ZnO-CoO mesoporous microspheres encapsulated by nitrogen-doped carbon shell as anode for high-performance lithium-ion batteries, *J. Alloy. Compd.* 825 (2020) 153951.
- Y. Chen, J. Cheng, A. Wang, C. Liu, H. Yan, Y. Qiu, Z. Wang, P.K. Chu, Y. Luo, The enhanced performance of Li-ion batteries based on Co-MOF/MXene composites, *Inorg. Chem. Commun.* 159 (2024) 111793.
- C. Ma, J. Dong, Y. Zhao, J. Li, H. Chen, Dual-template synthesis of novel pomegranate-like hollow carbon nanoparticles with improved electrochemical performance for Li-ion batteries, *Carbon* 110 (2016) 180–188.
- Z.Y. Huang, Y.F. Yuan, Z.C. Lin, J.J. Lin, S.B. Li, S.Y. Guo, Y.Z. Huang, W.W. Yan, Fluorinated WO₃ nanoneedle clusters in-situ grown in mesoporous hollow carbon nanospheres as advanced anode for lithium-ion batteries, *J. Alloy. Compd.* 969 (2023) 172458.
- J.F. Wang, Y.F. Yuan, Z.C. Lin, J.J. Lin, S.B. Li, Y.Z. Huang, S.Y. Guo, W.W. Yan, Boosting lithium storage performance of Co-Sn double hydroxide nanocubes in-situ grown in mesoporous hollow carbon nanospheres, *Electrochim. Acta* 465 (2023) 142971.
- J.H. Li, Z.S. Xiong, Y.J. Wu, H. Li, X.Y. Liu, H.J. Peng, Y.Y. Zheng, Q. Zhang, Q. B. Liu, Iron (Fe, Ni, Co)-based transition metal compounds for lithium-sulfur batteries: mechanism, progress and prospects, *J. Energy Chem.* 73 (2022) 513–532.
- J.H. Li, Z.Y. Wang, K.X. Shi, Y.J. Wu, W.Z. Huang, Y.G. Min, Q.B. Liu, Z.X. Liang, Nanoreactors encapsulating built-in electric field as a “bridge” for Li-S batteries: directional migration and rapid conversion of polysulfides, *Adv. Energy Mater.* 14 (2024) 2303546.
- J.H. Li, F.Y. Li, J.J. Pan, J.D. Pan, J.Y. Liao, H. Li, H.F. Dong, K.X. Shi, Q.B. Liu, Hollow Co₃S₄ nanocubes interconnected with carbon nanotubes as nanoreactors to accelerate polysulfide conversion for high-performance lithium-sulfur batteries, *Ind. Eng. Chem. Res.* 62 (2023) 4364–4372.
- Q.B. Liu, Y.J. Wu, D. Li, Y.Q. Peng, X.Y. Liu, B.Q. Li, J.Q. Huang, H.J. Peng, Dilute alloying to implant activation centers in nitride electrocatalysts for lithium-sulfur batteries, *Adv. Mater.* 35 (2023) 2209233.