2D titanium carbide and transition metal oxides hybrid electrodes for Li-ion storage

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The combination of nanomaterials with complementary properties in a well-designed architecture is an attractive strategy to develop multi-functional, high-performance materials for applications in energy conversion and storage, catalysis, electronic devices, and more. Herein, we propose three different methods: alternating filtration, spray coating, and in-situ wet chemistry synthesis, to achieve the hybridization of two-dimensional (2D) Ti3C2Tx MXene and transition metal oxides (TMOs), such as Co3O4 and NiCo2O4. The resulting flexible free-standing hybrid films were free of binders, conductive additives, or current collectors. When used directly as anodes for Li-ion batteries, these hybrid films successfully combined the metallic conductivity of Ti3C2Tx and high capacity of TMOs, showing excellent electrochemical performance for Li-ion storage. High reversible capacities over 1200 mA h g\(^{-1}\) were achieved by the MXene/TMO hybrid film electrodes fabricated by all three methods. All films also exhibited impressive long cycling stabilities and excellent rate performances. In particular, the spray-coated Ti3C2Tx/NiCo2O4 hybrid film electrode achieved high reversible capacities of 1330, and 650 and 350 mA h g\(^{-1}\) at 0.1, 5 and 10 C, respectively, along with no capacity decay over hundreds of cycles. This work demonstrates that the hybridization of MXenes, a large family of 2D transition metal carbides/nitrides, and TMOs has a significant potential for energy storage, and is promising for expansion into other applications.

1. Introduction

With the ever-increasing need for higher energy density in applications ranging from portable devices to emerging electric vehicles, tremendous efforts have been made to develop alternative, high-performance, electrode materials for the next-generation rechargeable lithium-ion batteries (LIBs). Among various strategies, combining distinct materials in a well-designed architecture, also called hybridization, is an attractive one [1–6]. This approach not only can fully utilize the merits of each component, but can also lead to unique nanostructures with impressive properties. For example, the hybridization of graphene and transition metal oxides (TMOs) combines the high electrical conductivity of graphene and the high Li-ion-storage capability of TMOs. Furthermore, the confinement of TMO nanoparticles between graphene layers prevents their cracking during charge-discharge cycling [7–9]. These facets endow graphene/TMO hybrids with a high capacity, high power, and excellent cycling stability when employed as an electrode material for LIBs, performing much better than separate components [1,7–9]. So far, numerous high-performance LIB electrode materials have been produced by this method, including the hybridization of carbonaceous materials and transition metal oxides/dichalcogenides [10–13], conducting polymers and TMOs [14,15], carbon and nanoscale silicon [16–18], and others.

In 2011, a family of two-dimensional (2D) transition metal carbides and nitrides, named MXenes, was discovered and tested as anode materials for LIBs [19–23]. MXenes are produced by selectively etching the A group element layers from their parent MAX phases or other layered ceramics [24–26]. They have a formula of M\(_{n+1}\)X\(_n\)\(\text{Ti}_x\), where M is an early transition metal, X is C and/or N, n=1, 2 or 3, and T\(_x\) refers to surface functional groups, such as –O, –OH, and –F [27,28]. MXenes combine metallic conductivity, hydrophilic surfaces, and a superior capacity for reversible intercalation of cations (e.g. Li\(^+\), Na\(^+\), K\(^+\), Mg\(^{2+}\), etc.), which, in turn, renders them promising as electrode materials for supercapacitors and LIBs [29–32].

When the MAX phases are etched, the resulting material is comprised of multilayer flakes, whose potential for cation intercalation...
is limited [22,24]. However, we have shown that upon delamination – which results in large quantities of ~1-nm-thick 2D flakes with lateral sizes up to several micrometers – these flakes can be readily assembled into flexible films with much better electrochemical performance as compared to their multi-layer counterparts [22,33]. For example, capacities of 400–600 mA h g\(^{-1}\) were achieved by MXene-based LIB anodes, which also delivered excellent cycling stability and superior rate performance due to their structural stability and high electrical conductivity [22,23,33]. However, compared to many other LIB anode materials, such as silicon [34] and TMOs [35,36], the capacities delivered by MXenes are relatively moderate. For instance, the theoretical capacities of multi-layer and delaminated Ti\(_3\)C\(_2\)T\(_x\), the most studied MXene to date, are just 268 and 536 mA h g\(^{-1}\), respectively [37], which are significantly smaller than those of silicon (~4200 mA h g\(^{-1}\)) [34], Co\(_3\)O\(_4\) (890 mA h g\(^{-1}\)) [38], or NiCo\(_2\)O\(_4\) (898 mA h g\(^{-1}\)) [39].

Among the many TMOs available, cobalt oxide (Co\(_3\)O\(_4\)) has received special attention because of its low cost, low toxicity, good chemical stability and high theoretical capacity (890 mA h g\(^{-1}\)) [40,41]. But its low electronic conductivity, rapid capacity loss and poor capacity retention have hampered its practical use in LIBs. Numerous efforts have been devoted to the hybridization of Co\(_3\)O\(_4\) with C-based materials to improve its electrochemical performance [10,38,41]. Compared with Co\(_3\)O\(_4\), the ternary NiCo\(_2\)O\(_4\) comprises two different cations and exhibits higher electrical conductivity and electrochemical activity [12,42–44].

The goal of this work is to determine if a combination of MXenes, which have metallic conductivity but a moderate lithium storage capacity, and TMOs with high capacities but poor conductivities, can result in improved electrochemical performance. Several groups have reported on the synthesis and characterization of MXene/TMO hybrids; in most cases, the hybrids were prepared by the partial oxidation of MXenes, in which the surface TMOs (e.g. TiO\(_2\) and Nb\(_2\)O\(_5\)) came from the oxidation of their parent carbides (e.g. Ti\(_3\)C\(_2\)Ti\(_2\)C\(_2\) and Nb\(_6\)C\(_2\)Ti\(_2\)C\(_2\)), leaving the residual MXenes at their core [45–49]. This partial oxidation led to a much improved energy storage performance compared to pristine MXenes, benefiting from the high capacities of TMOs. However, the MXenes’ electrical conductivity decreased due to their oxidation, resulting in limited rate performances.

In-situ growth of TMO nanoparticles on conductive frameworks, such as graphene, is among the most attractive methods of preparing TMO-containing hybrids for electrochemical energy storage and other applications [9,12,38]. This is because the in-situ growth method offers a more uniform distribution of TMO nanoparticles in the conductive frameworks and stronger interaction in the final hybrids compared to those prepared by random mixing methods or layer-by-layer assembly, improving the electrochemical performance. Recently, Zhang et al. reported on the in-situ formation of iron oxide on Ti\(_3\)C\(_2\)T\(_x\) by a liquid-phase precipitation reaction followed by high-temperature sintering, and demonstrated its efficient phosphate sequestration for water purification [50]. Using a similar method, Tang et al. successfully synthesized the Ti\(_3\)C\(_2\)T\(_x\)/MoO\(_3\) hybrids, which showed improved capacitive performance compared to pure Ti\(_3\)C\(_2\)T\(_x\) particles [51]. To date, all the MXene/TMO hybrids were prepared using multi-layer MXenes. This limited the location of the TMO particles to the outer surfaces of the multilayer MXene flakes, hindering the full utilization of each component’s merits.

Herein, we report on free-standing, flexible, and conductive MXene/TMO hybrid films fabricated by combining delaminated Ti\(_3\)C\(_2\)T\(_x\) MXene flakes with planar nanoparticles of Co\(_3\)O\(_4\) and NiCo\(_2\)O\(_4\). Three different methods, including alternating vacuum-assisted filtration (Fig. 1a), layer-by-layer spray coating (Fig. 1a), and an in-situ wet chemistry synthesis (Fig. 1b), were employed. These as-fabricated hybrid films exhibited excellent performance for Li-ion storage, including high capacities, impressive rate capabilities, and long cycling stabilities.

2. Experimental section

2.1. Preparation of delaminated Ti\(_3\)C\(_2\)T\(_x\) colloidal solution

First, 1.98g of lithium fluoride (LiF) (Alfa Aesar, 98.5%) was added to a 20 mL of 9.0 M HCl (Fisher, technical grade) aqueous solution. The mixture was stirred for 5 min to dissolve the salt. Then, 2g of Ti\(_3\)AlC\(_2\) powder – the synthesis of which is described elsewhere [32] – was added into the mixture over the course of 10 min to avoid overheating of the solution as a result of the reaction’s exothermic nature. The reaction mixture was kept at 35 °C for 24 h while stirring, after which the solid residue was washed with distilled water, centrifuged (3500 rpm), and decanted until the pH of the supernatant reached approximately 6. The final powder, with a small amount of water, was filtered through a polyvinylidene fluoride filter (0.45 μm pore size) and dried in air to obtain multi-layer Ti\(_3\)C\(_2\)T\(_x\) powder.

The as-produced Ti\(_3\)C\(_2\)T\(_x\) powder was dispersed in deaerated water with a weight ratio of Ti\(_3\)C\(_2\)T\(_x\):water of 1:20. The suspension was sonicated in an ultrasonic bath (Branson 2510, 120 W) for 1 h under bubbling Ar. After that, the suspension was centrifuged at 3500 rpm for 1 h and the supernatant fluid – comprised of a colloidal solution of delaminated Ti\(_3\)C\(_2\)T\(_x\) flakes with a concentration of ~1.0 mg mL\(^{-1}\) – was collected.

2.2. Synthesis of Co\(_3\)O\(_4\) and NiCo\(_2\)O\(_4\) nanoflakes

First, CoCl\(_2\)-6H\(_2\)O (98%, Sigma-Aldrich), AlCl\(_3\)-6H\(_2\)O (99%, Sigma-Aldrich) and urea (98%, Sigma-Aldrich) were dissolved in 50 mL of deionized water with [Co\(^{2+}\)]+[Al\(^{3+}\)]=0.15 mol L\(^{-1}\); a molar ratio of n(Co):n(Al)=2:1 and [urea]=3.0 mol L\(^{-1}\). The as-obtained solution was maintained at 100 °C under continuous magnetic stirring for 12 h in a 100 mL beaker under ambient atmosphere. Then, the prepared suspension was kept at 94 °C for another 12 h without stirring. The CoAl layered double hydroxide (LDH) flakes were obtained after the product was filtered, washed and dried in an oven at 90 °C overnight. The NiCoAl LDHs were prepared through a similar process with [Ni\(^{2+}\)]+[Co\(^{2+}\)]+[Al\(^{3+}\)]=0.15 mol L\(^{-1}\); n(Ni):n(Co):n(Al)=1:2:1 and [urea]=3.0 mol L\(^{-1}\).

One gram of the CoAl LDHs was dispersed in a 6 mol L\(^{-1}\) KOH (99%, Sigma-Aldrich) aqueous solution at 90 °C for 3 h to remove the Al. Cobalt hydroxide (Co(OH)\(_2\)) flakes were obtained after the product was washed with distilled water, centrifuged (3500 rpm), and decanted until the pH of the supernatant was ~8. Then, the Co(OH)\(_2\) flakes were transformed into Co\(_3\)O\(_4\) nanoflakes by heating them in air at 650 °C for 1 h. The NiCo\(_2\)O\(_4\) nanoflakes were prepared using a similar method from NiCoAl LDHs.

2.3. Preparation of sandwich-like Ti\(_3\)C\(_2\)T\(_x\)/Co\(_3\)O\(_4\) hybrid films

A 1 mg mL\(^{-1}\) Co\(_3\)O\(_4\) dispersion was prepared by directly dispersing Co\(_3\)O\(_4\) nanoflakes in deaerated water followed by sonication in an ultrasonic bath (Branson 2510, 120 W) for 1 h. Sandwich-like Ti\(_3\)C\(_2\)T\(_x\)/Co\(_3\)O\(_4\) hybrid films were prepared using an alternating filtration method. More specifically, a 1 mL delaminated Ti\(_3\)C\(_2\)T\(_x\) dispersion was filtered through a polypropylene membrane (3501 Coated PP, Celgard LLC, Charlotte, NC) to yield a thin Ti\(_3\)C\(_2\)T\(_x\) layer. Then, 1 mL Co\(_3\)O\(_4\) dispersion was filtered on top of the latter. The process was repeated to form films with alternating Ti\(_3\)C\(_2\)T\(_x\) and Co\(_3\)O\(_4\) layers. These films were then dried in air at room temperature and peeled off from the polypropylene membrane, yielding a free-standing sandwich-like hybrid film with a mass ratio of m(Co\(_3\)O\(_4\))/m(Ti\(_3\)C\(_2\)T\(_x\))=1, where m is the mass, which is henceforth referred to as H-1.0. Hybrid films of m(Co\(_3\)O\(_4\))/m(Ti\(_3\)C\(_2\)T\(_x\))=0.5, 2.0, and 4.0, which are henceforth referred to as H-0.5, H-2.0, and H-4.0, respectively, were also prepared by a...
similar method. The total mass of all the four films, \( m(Ti_3C_2Tx)+m(Co_2O_4) \), was 15.0 mg. The film densities were calculated by mass/(area-thickness), where the film thicknesses were determined by scanning electron microscopy (SEM).

### 2.4. Preparation of Ti3C2Tx/NiCo2O4 hybrid films by spray coating

First a 1 mg mL\(^{-1}\) NiCo2O4 dispersion was prepared by directly dispersing the NiCo2O4 nanoflakes in deaerated water followed by sonication in an ultrasonic bath (Branson 2510, 120 W) for 1 h. The delaminated Ti3C2Tx solution and NiCo2O4 dispersion were sprayed alternatively onto polypropylene membranes (3501 Coated PP, Celgard LLC, Charlotte, NC) with an area of 3 × 4 cm\(^2\) by two airbrushes (Master Airbrush Model G-233, USA). The nozzle size was 0.5 mm, and the operating pressure was 80 psi. The airbrushes were moved steadily at roughly 15 cm s\(^{-1}\) in all directions to obtain a homogeneous film. An air gun (Master heat gun Model HG-201A, USA) was used to dry the film after each layer of deposition. The hybrid film was peeled off from the polypropylene membrane; the mass of the final films was \( \approx 15 \) mg.

### 2.5. Preparation of Ti3C2Tx/NiCo2O4 hybrid films by an in-situ growth method

First, Co(NO3)\(_2\)-6H\(_2\)O (98%, Sigma-Aldrich), Ni(NO3)\(_2\)-6H\(_2\)O (98%, Sigma-Aldrich) and urea (98%, Sigma-Aldrich) were dissolved in 15 mL of a delaminated Ti3C2Tx solution with \[\text{[Co}^{2+}]\text{+[Ni}^{2+}]\] = 0.03 mol L\(^{-1}\), n(Co):n(Ni)=2:1 and [urea]=0.6 mol L\(^{-1}\). The as-obtained solution was maintained at 90 °C under continuous magnetic stirring for 3 h in a 20 mL glass bottle under ambient atmosphere. Then, the prepared suspension was kept at 90 °C for another 3 h without stirring. The product was washed with distilled water and centrifuged (3500 rpm) to collect the sediments. This process was repeated three times to remove the residual Co and Ni-containing salts. After that, the final sediments were re-dispersed in 20 mL deaerated water by sonication in an ultrasonic bath (Branson 2510, 120 W) for 1 h. The dispersion was then filtered through a polypropylene membrane (3501 Coated PP, Celgard LLC, Charlotte, NC) and was peeled off from the membrane after drying in air to yield a free-standing film. This film was annealed at 400 °C in Ar for 1 h, yielding a flexible Ti3C2Tx/NiCo2O4 hybrid film. The mass ratio of Ti3C2Tx to NiCo2O4 used for the in-situ growth process.

### 2.6. Material characterization

The samples’ morphologies were characterized using a SEM (Zeiss Supra 50VP, Germany) and a transmission electron microscope (TEM) (JEOL JEM-2100, Japan) using an accelerating voltage of 200 kV. Samples for the latter were prepared by dropping several drops of the colloidal suspension or sample dispersion in water onto a copper grid and drying in air. The X-ray diffraction (XRD) patterns were recorded by a powder diffractometer (Rigaku Smart-Lab, Japan) with Cu Kα radiation at a step scan of 0.02° and with a dwelling time of 0.5 s. Energy dispersive X-ray spectroscopy (EDX) analysis was conducted using an energy dispersive X-ray spectrometer (Oxford EDS, with INCA software). The sheet resistances of the films were measured using a 4-point probe instrument (ResTest v1, Jandel Engineering, UK). Each film was measured at five positions near the middle of the film. Averaged values were reported.

### 2.7. Electrochemical measurement

The Li-ion storage performance was evaluated in standard coin-type cells (CR-2016, MTI, Richmond, CA, USA). The free-standing hybrid films were cut into pieces and directly used as working electrodes. Lithium metal foil was used as the counter and reference electrodes; a polypropylene membrane (3501 Coated PP, Celgard LLC, Charlotte, NC) was used as a separator. Lithium hexafluorophosphate solution in ethylene carbonate and diethyl carbonate (1.0 M LiPF\(_6\) in EC/DEC=50/50 (v/v)) was used as the electrolyte.

The coin cells were tested in galvanostatic mode within the 0.01–3.0 V voltage range with respect to Li/Li\(^+\), using a battery cycler (Arbin BT-2143-11U, College Station, TX, USA). The loadings of the working electrodes were 1.0–2.0 mg cm\(^{-2}\). The capacities were calculated based on the mass of the entire working electrodes. In all cases, 1 C equals 320 mA g\(^{-1}\).

### 3. Results and discussion

#### 3.1. Sandwich-like Ti3C2Tx/Co3O4 hybrid films by alternating filtration method

Herein, ~1-nm-thick flakes of Ti3C2Tx [28,32], which provide superior conductivity, ensure mechanical integrity and flexibility, as well as some Li-ion storage capacity, were used for the hybridization
with Co$_3$O$_4$. The Co$_3$O$_4$ flakes were synthesized from their parent CoAl LDH to achieve a stable, 2D porous flake morphology. The LDHs are a class of 2D nanostructured brucite-like – i.e., Mg(OH)$_2$ – anionic clays composed of multiple positively charged layers with charge-balancing anions within their interlayer domains [52,53]. Synthesis details can be found in the Supporting information. In short, CoAl LDHs were synthesized by a urea-assisted co-precipitation process, with flakes of 3–5 µm in lateral size and 100–200 nm in thickness (Figs. S1 and S2). Al cations were selectively etched out by treating the CoAl LDH flakes in a 6.0 M KOH aqueous solution at 90 °C for 3 h, leaving cobalt hydroxide (Co(OH)$_2$) nanoflakes (Figs. S2b and S3). The latter were heated in air to 650 °C for 1 h to convert them to porous Co$_3$O$_4$ nanoflakes (Fig. S2c). XRD patterns of the CoAl LDHs, Co(OH)$_2$ and Co$_3$O$_4$ are shown in Fig. S2d confirming the structural transformations. The purpose for the selective removal of Al from the LDH precursor was to create vacancies in the oxide flakes, which in turn should facilitate electrolyte ion diffusion and improve their electrochemical performance [54]. Delamination of the hydroxide flakes was observed...
as evidenced by their significantly reduced thickness (Fig. S2a and b). This can be probably attributed to the removal of Al cations resulting in the loss of positive charges for the LDH layers together with the loss of charge-balancing interlayer anions, which, in turn, weakened the interactions between LDH layers and led to their delamination upon sonication [54]. As a result, the thickness of the resulting Co3O4 flakes was reduced from 100 to 200 nm for the LDH precursor to ~10 nm (Fig. S2c).

TEM image in Fig. 2a shows the typical morphology of the Ti3C2Tx flakes, which are 1–3 µm in lateral size. At 2–5 µm, the lateral size of the Co3O4 flakes is larger (Fig. 2b). The SEM image shown in Fig. 2b also highlights their porous morphology.

Free-standing, sandwich-like Ti3C2Tx/Co3O4 hybrid films with different mass ratios of Co3O4 to Ti3C2Tx were fabricated by an alternating vacuum-assisted filtration method (Fig. 2c, upper). The details can be found in the Supporting information. While all films exhibited excellent flexibility, the ones with higher MXene concentrations (H-0.5, H-1.0, and H-2.0) were easily wrapped around a 5 mm diameter glass rod with no observable mechanical damage (Fig. 2c, lower). The flexibility decreased with increasing of the Co3O4 content.

We also tried to filter a mixed Co3O4 and Ti3C2Tx dispersion, but could not obtain a free-standing and flexible Ti3C2Tx/Co3O4 hybrid film with a randomly mixed structure even when m(Co3O4)/m(Ti3C2Tx) =1.0, as the films broke apart after drying. Cross-sectional SEM image (Fig. S4a) shows that a good alignment and compact stacking in the pure Ti3C2Tx film, without Co3O4. Alternating layers of Ti3C2Tx and Co3O4 with a good flake alignment were observed for high concentration of MXene, e.g., H-0.5 and H-1.0 (Figs. 2d and S4b). However, the films became disordered (Fig. S4c and d) with increasing Co3O4 concentrations (e.g., H-2.0 and H-4.0). XRD peaks of both Ti3C2Tx and Co3O4 were observed in the hybrid films (Fig. 2e). The intensity of the Ti3C2Tx peaks decreased with content. Moreover, the Ti3C2Tx (006) peak at ~18° disappeared and the (002) peak became broader for lower concentration of MXene (H-4.0), showing decreased flake alignment due to increasing Co3O4 content [52], in agreement with the SEM images discussed above.

The addition of Co3O4 to Ti3C2Tx leads to a decrease in the film electrical conductivity from its initial value of 1300 S cm−1. However, even the films with the lowest Ti3C2Tx content (H-4.0) had a conductivity of 26 S cm−1, which is nevertheless comparable to that of solution-processed graphene films [55,56]. The film densities ranged from 1.2 g cm−3 for H-4.0 and 3.3 g cm−3 for H-0.5; both values less than the 3.8 g cm−3 for pure Ti3C2Tx films, suggesting the presence of pores that are expected to improve electrolyte access to the electrode. Because of their good mechanical flexibility and high electrical conductivity, the hybrid films were used directly as LIB anodes; no current collectors, conductive additives, or binders were used. This makes the measured capacity values even more impressive. All the hybrid films with different Co3O4 contents exhibited redox peaks – at ~1.1 and 2.2 V – in their cyclic voltammogram (CV) curves, similar to those for pure Co3O4 electrodes (Figs. 3a and S5a). In contrast, no obvious redox peaks can be found in the CV curves of pure Ti3C2Tx electrode (Fig. S6a), in good agreement of previous reports [19,21,22,57]. These redox peaks correspond well to the plateaus in the charge-discharge curves shown in Figs. 3b and S5b. The charge-discharge plateaus for H-0.5 were not as obvious as the other hybrid films. This was probably due to the large amount of Ti3C2Tx facilitating fast electron and ion transfer and leading to pseudocapacitive behaviour (Fig. 3b).

Cycling profiles of the hybrid films at 1 C are shown in Fig. 3c, in comparison with those of pure Ti3C2Tx and Co3O4 electrodes. At ~30 mA h g−1, the discharge capacities of the pure Ti3C2Tx films, were...
much lower than our previous report [22] (Fig. 3c). This is because of the compact stacking of Ti$_3$C$_2$T$_x$ flakes here limited the diffusion of electrolyte ions into the MXene film electrode (Fig. S6b). The addition of Co$_3$O$_4$ nanoflakes significantly increased the capacity (Fig. 3c and S4), not only because of their contributions to the overall capacity, but also because they resulted in a more open structure. All of the four hybrid films delivered higher capacities compared to pure Co$_3$O$_4$ or MXene electrode (Fig. 3c), proving the synergistic effects resulting from combining the highly-conductive Ti$_3$C$_2$T$_x$ flakes with the high-capacity Co$_3$O$_4$. At a current density of 1 C, the H-0.5 film showed a reversible capacity around 430 mA h g$^{-1}$ over 100 cycles; the values for the H-4.0 films were ~650 mA h g$^{-1}$. Furthermore, the synergistic effects also resulted in the increase of first-cycle reversibility from 60.1% for H-0.5 to 91.8% for H-4.0. The latter are significantly larger than those of pure Ti$_3$C$_2$T$_x$ (52.9%) or Co$_3$O$_4$ (67.9%) electrodes (Fig. 3c). The reason for this state of affairs is not entirely clear at this time.

The effect of cycling on the discharge capacities is shown in Fig. 3c. In most cases, the capacities increased with increasing cycles. This effect has been observed previously in our MXene work – and confirmed here for the pure Ti$_3$C$_2$T$_x$ films (Fig. S6) and has been attributed to the exposure of a large number of electrochemically active sites with cycling [57–59]. To further investigate this phenomenon, a H-1.0 film was cycled for 1000 cycles at 2 C. The results (Fig. S7) showed that the discharge capacity dropped from 370 to 350 mA h g$^{-1}$ during the first 30 cycles, which we ascribe to irreversible side reactions that result in low Coulombic efficiencies initially [12]. After that, the capacity increased with cycling and stabilized at ~540 mA h g$^{-1}$ after 800 cycles. The Coulombic efficiency approached 100% (right y-axis in Fig. S7a). The charge-discharge curves during the first 1000 cycles were shown in Fig. S7b, and obvious voltage plateaus were observed for the 1st and 2nd cycles. However, the plateaus disappeared after about 100 cycles, accompanied with significant capacity increase. This could be attributed to the improved electrolyte accessibility into the nanoscale electrode materials [60].

Fig. 3d compares the rate performance for the four Ti$_3$C$_2$T$_x$/Co$_3$O$_4$ hybrid films. At low current rates, the capacities increased with increasing Co$_3$O$_4$ content, indicating that the latter dominated the capacity contribution. At 0.1 C, the H-4.0 film achieved the reversible capacity of ~1200 mA h g$^{-1}$, which decreased dramatically to ~50 mA h g$^{-1}$ at 20 C. On the contrary, the capacity retention upon increasing current rates was much better for films with a larger amount

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**Fig. 4.** Spray-coated Ti$_3$C$_2$T$_x$/NiCo$_2$O$_4$ hybrid film. (a) TEM image, (b) high-resolution TEM image, (c) XRD pattern of the as-synthesized NiCo$_2$O$_4$ nanoflakes; (d) cross-sectional SEM image of a hybrid film.
of Ti\textsubscript{3}C\textsubscript{2}Tx. For instance, the H-0.5 film delivered a reversible capacity of ~450 mA h g\textsuperscript{−1} at 0.5 C, that is significantly lower than the ~800 mA h g\textsuperscript{−1} for the H-4.0 film at the same rate. However, the H-0.5 film retained a capacity of ~180 mA h g\textsuperscript{−1} at 20 C, which was about four times that of the H-4.0 film. A perusal of the results shown in Fig. 3c and d suggests that the H-2.0 films were optimal in that they exhibited the best Li-ion storage performance – delivering a capacity of ~810 mA h g\textsuperscript{−1} at 0.1 C – together with an impressive rate performance – ~370 mA h g\textsuperscript{−1} at 5 C and ~150 mA h g\textsuperscript{−1} at 20 C – along with excellent cycling stability.

3.2. Ti\textsubscript{3}C\textsubscript{2}Tx/NiCo\textsubscript{2}O\textsubscript{4} hybrid films from layer-by-layer spray coating

It is expected that the hybridization of Ti\textsubscript{3}C\textsubscript{2}Tx with NiCo\textsubscript{2}O\textsubscript{4} could offer further improvement of Li-ion storage capacity compared to Co\textsubscript{3}O\textsubscript{4} due to a better electrochemical performance of NiCo\textsubscript{2}O\textsubscript{4} [12,42]. The synthesis details of NiCo\textsubscript{2}O\textsubscript{4} flakes can be found in the Supporting Information. In short, the NiCo\textsubscript{2}O\textsubscript{4} nanoflakes were synthesized using a similar method as Co\textsubscript{3}O\textsubscript{4}, starting from NiCo\textsubscript{3}Al LDH flakes of ~1 µm in size (Fig. S8). After the selective removal of Al using KOH, the powders were heated in air at 650 °C for 1 h. This procedure resulted in 2D porous NiCo\textsubscript{2}O\textsubscript{4} nanoflakes with good crystallinity (Fig. 4a and b). In addition to strong peaks for NiCo\textsubscript{2}O\textsubscript{4} spinel, a weak peak for NiO was also observed (Fig. 4e), indicating the presence of a small amount of NiO due to the excess of Ni in the NiCo\textsubscript{3}Al LDH precursor.

The Ti\textsubscript{3}C\textsubscript{2}Tx/NiCo\textsubscript{2}O\textsubscript{4} hybrid films, with a 1:1 mass ratio, were prepared by a layer-by-layer spray coating method (Figs. 1a and S9). The latter is a well-developed technique for the large-scale production of films with no lateral dimension limitations [61]. In this work, a polypropylene membrane was used as the substrate to facilitate detaching the hybrid films after spray coating. The as-obtained hybrid films were ~3 µm thick and flexible (Fig. 4d). Comparing a cross-sectional SEM image of this film with its Ti\textsubscript{3}C\textsubscript{2}Tx/Co\textsubscript{3}O\textsubscript{4} counterpart – with the same 1:1 mass ratio – shows that the 2D flakes are more disordered in the NiCo\textsubscript{2}O\textsubscript{4} film (compare Fig. 4d with 2d). This disordering can be attributed to the absence of a flowing liquid as a driving force during spray coating, but it would facilitate the electrolyte diffusion throughout the films. Like the Co\textsubscript{3}O\textsubscript{4} films, the spray-coated films exhibited good flexibility and a high electrical conductivity of ~200 S cm\textsuperscript{−1}. They were thus used directly as anodes in the LIB tests, no binders or current collectors were needed.

![Fig. 5. Electrochemical response of spray-coated Ti\textsubscript{3}C\textsubscript{2}Tx/NiCo\textsubscript{2}O\textsubscript{4} films (m(NiCo\textsubscript{2}O\textsubscript{4})/m(Ti\textsubscript{3}C\textsubscript{2}Tx)=1) vs. Li/Li\textsuperscript{+}: (a) CVs at 0.1 mV s\textsuperscript{−1}; (b) cycling performance of the activated sample at 1 C; (c) rate performance and (d) corresponding charge-discharge profiles.](image-url)
increased with cycling presumably, again, due to improved electrolyte accessibility between the layers. The increase was from an initial ~450 to ~1200 mA h g$^{-1}$ after 250 cycles, after which the capacity stabilized (Fig. S10a). Therefore, the Ti$_3$C$_2$T$_x$/Co$_3$O$_4$ film electrodes were precycled for 250 times as an activation process and then retested. Stable capacity of ~1200 mA h g$^{-1}$ over 100 cycles was achieved by the activated electrodes at 1 C, with a Coulombic efficiency close to 100% (Fig. 5b). During the activation process, the 1st, 2nd, and 100th cycle charge-discharge curves are shown in Fig. S10b. Again, obvious voltage plateaus were observed for the 1st and 2nd cycles, and disappeared after about 100 cycles, similar to that of the Ti$_3$C$_2$T$_x$/Co$_3$O$_4$ films produced by alternating filtration.

The rate performance of the Ti$_3$C$_2$T$_x$/NiCo$_2$O$_4$ film electrode, without activation, is shown in Fig. 5c. The corresponding charge-discharge curves at different current rates are shown in Fig. 5d. A high reversible capacity of about 1330 mA h g$^{-1}$ was achieved at 0.1 C and kept increasing during the first several cycles. After pre-cycling at 0.1 and 0.5 C, the Ti$_3$C$_2$T$_x$/NiCo$_2$O$_4$ film electrode exhibited capacity of ~1010 mA h g$^{-1}$ at 1 C herein, much higher than the initial values shown in Fig. S10a. Cycling at low rates resulted in a better activation process. As a result, much fewer cycles were required to achieve the high and stable capacities compared to the films cycled at 1 C (Fig. S10 and 5c). At 5 C and 10 C, the films delivered capacities of ~650 and 330 mA h g$^{-1}$, respectively (Fig. 5c and d). Compared to Co$_3$O$_4$-based films with the 1:1 mass ratio, the spray-coated Ti$_3$C$_2$T$_x$/NiCo$_2$O$_4$ films showed much higher capacities at all rates. This can be ascribed to a combination of a more open film structure and a better electrochemical performance of NiCo$_2$O$_4$ compared to Co$_3$O$_4$.

3.3. Ti$_3$C$_2$T$_x$/NiCo$_2$O$_4$ hybrids from in-situ growth method

It is well established that MXene flakes’ surfaces are terminated by oxygen terminating functional groups and fluorine, and are consequently negatively charged [27,59], which in turn facilitates the adsorption of transition metal and other cations. As a result, MXenes are attractive substrates for in-situ growth of TMOs. Herein, in-situ precipitation of nickel/cobalt hydroxides (NiCo(OH)$_x$) on delaminated Ti$_3$C$_2$T$_x$ nanoflakes was carried out and the resulting Ti$_3$C$_2$T$_x$/NiCo(OH)$_x$ hybrid flakes were assembled into free-standing and flexible films through a vacuum-assisted filtration process [31]. The films were then heated at 400 °C for 1 h in Ar. The resulting films were flexible and possessed a electrical conductivity of ~2.0 S cm$^{-1}$.

Fig. 6. (a) TEM and (b) high resolution TEM images of the as-synthesized Ti$_3$C$_2$T$_x$/NiCo$_2$O$_4$ hybrid flakes; (c) cross-sectional SEM image and, (d) XRD pattern of the in-situ grown Ti$_3$C$_2$T$_x$/NiCo$_2$O$_4$ hybrid film.
Fig. 6a shows a TEM image of a Ti3C2Tx/NiCo2O4 hybrid flake, where the uniform distribution of NiCo2O4 nanorods is obvious. The crystallinity was also good (Fig. 6b). The mass ratio of Ti3C2Tx to NiCo2O4 was measured to be ca. 1:1 (details are provided in Supporting information). When the Ti3C2Tx/NiCo2O4 hybrid films were imaged in a SEM (Fig. 6c), the thickness was found to be ~10 µm. In this case, the in-situ grown NiCo2O4 nanorods served as excellent spacers and successfully prevented the re-stacking of individual Ti3C2Tx flakes. This is important because it ensured that the structure remained open and thus was more accessible to the electrolyte ions. The XRD pattern of this Ti3C2Tx/NiCo2O4 film (Fig. 6d) indicated the presence of Ti3C2Tx, NiCo2O4 and a small amount of TiO2. The reduced peak intensities of the Ti3C2Tx component is due to disordering shown in Fig. 6c. The TiO2 was most probably formed by the partial oxidation of Ti3C2Tx flakes, likely catalyzed by Ni and Co cations, resulting in the degraded conductivity of the hybrid film [57].

The in-situ grown films were also directly used as anodes in LIB tests. Their CV curves showed redox peaks at similar positions to those of their spray-coated counterparts (compare Figs. 5a and 7a). Fig. 7b and c show the cycling profile of the in-situ grown Ti3C2Tx/NiCo2O4 hybrids at 5 C and their charge-discharge curves, respectively. The first-cycle discharge capacity was ~675 mA h g⁻¹; the second cycle was ~460 mA h g⁻¹ after which the capacity stabilized at ~410 mA h g⁻¹ for the following 150 cycles. No obvious voltage plateaus were observed in the charge-discharge curves at 5 C (Fig. 7c), which can be ascribed to the nanoscale size of the NiCo2O4 nanorods.

Fig. 7d shows the rate performance of the in-situ grown electrodes; their corresponding charge-discharge curves are shown in Fig. S11. At ~1200 mA h g⁻¹, high reversible capacities were achieved at 0.1 C. At 5 C the capacity was ~390 mA h g⁻¹. This capacity retention with increasing current rates was not as good as that of the spray-coated films. This can be attributed to the degraded conductivity of the films due to partial oxidation of Ti3C2Tx during the in-situ growth process.

The Li storage capacities for the three different films obtained herein are comparable to those based on graphene and TMOs with similar compositions [1,7,12,38]. However, MXene/TMO hybrid films possess the following advantages: i) Superior rate performance. The metallic conductivity of MXenes results in high-conductivity electrodes which in turn leads to superior rate performances [30,32,59]; ii) Higher volumetric capacities. MXene/TMO hybrids are significantly denser than most graphene/TMO hybrids due to MXenes’ higher densities (~4.2 g cm⁻³ for Ti3C2Tx) [1,28], which in turn results in higher volumetric capacities. For example, the sandwich-like Ti3C2Tx/Co3O4 hybrids (H-1.0) exhibited volumetric capacities of ~2700 and ~750 mA h cm⁻³ at 0.1 and 5 C, respectively (Fig. S12), that exceed most of the graphene/TMO hybrids at similar current rates. This means that devices can become smaller when using MXene/TMO hybrids while storing the same amount of energy.

4. Conclusions

In summary, we have successfully achieved the hybridization of Ti3C2Tx with Co3O4 or NiCo2O4 using three different methods: alternating filtration, spray coating, and an in-situ growth process. All films were flexible and highly conductive due to the excellent mechanical flexibility and metallic conductivity of Ti3C2Tx, and were directly used as anodes in LIBs; no current collectors or binders were needed. At low currents, reversible capacities over 1200 mA h g⁻¹ were obtained for...
the hybrid films from all three production methods, along with impressive cycling performances and excellent rate capabilities. The spray-coated $\text{Ti}_3\text{C}_2\text{Tx}/\text{NiCo}_2\text{O}_4$ films showed the best electrochemical performance. High reversible capacities of $\approx 1330$, $650$, and $330 \text{ mA h g}^{-1}$ were achieved at $0.1$, $5$ and $10 \text{ C}$, respectively. This was ascribed to the use of a layer-by-layer assembly, the good electrochemical performance of $\text{NiCo}_2\text{O}_4$, the open film electrode architecture, and the preservation of the intrinsic electrochemical properties of $\text{Ti}_3\text{C}_2\text{Tx}$. These results could guide future work on designing high-performance MXene/TMO hybrids for energy storage, electrocatalysis, water desalination, and environmental applications.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.nanoen.2016.10.062.

References


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