Two-Dimensional Titanium Carbide/RGO Composite for High-Performance Supercapacitors

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Supporting Information

ABSTRACT: Ti₃C₂Tₓ, a 2D titanium carbide in the MXenes family, is obtained from Ti₃AlC₂ through selective etching of the Al layer. Due to its good conductivity and high volumetric capacitance, Ti₃C₂Tₓ is regarded as a promising candidate for supercapacitors. In this paper, the fabrication of Ti₃C₂Tₓ/RGO composites with different proportions of Ti₃C₂Tₓ and RGO is reported, in which RGO acts as a conductive "bridge" to connect different Ti₃C₂Tₓ blocks and a matrix to alleviate the volume change during charge/discharge process. In addition, RGO nanosheets can serve as a second nanoscale current collector and support as well for the electrode. The electrochemical performance of the as-fabricated Ti₃C₂Tₓ/RGO electrodes, characterized by CV, GCD, and EIS, are also reported. A highest specific capacitance (Cₛ) of 154.3 F/g at 2 A/g is obtained at the Ti₃C₂Tₓ: RGO weight ratio of 7:1 combined with an outstanding capacity retention (124.7 F/g) after 6000 cycles at 4 A/g.

KEYWORDS: Ti₃C₂Tₓ MXene, 2D material, reduced graphene oxide (RGO), supercapacitors

1. INTRODUCTION

The rapid growth of energy demands and gradual attention to globally environmental issues are calling for a pressing exploration for new clean energies as well as the energy storage systems (ESS).¹⁻⁴ Supercapacitors, known as electrochemical capacitors (EC), are among the ideal candidates for portable digital products and electric vehicles as energy storage systems (ESS).¹ Super capacitors, and supercapacitors.¹⁸ Some theoretical and experimental studies have already demonstrated that these kinds of materials are potentially promising as electrode materials for batteries, metal ion (Li⁺, Na⁺) capacitors, and supercapacitors.¹⁵⁻²² Lukatskaya et al. reported that binder-free Ti₃C₂Tₓ paper showed a capacitance in excess of 300 F/cm³ at 20 mV/s in potassium hydroxide (KOH) aqueous electrolyte.¹⁸ Ghidiu et al. also tested the electrochemical performance of rolled Ti₃C₂Tₓ clay as electrode in 1 M sulfuric acid (H₂SO₄). Capacity value of 900 F/cm³ at 2 mV/s and superior rate capability were observed.¹⁸ Meanwhile, Ling et al. showed that Ti₃C₂Tₓ/polymer films exhibit intriguing volumetric capacitance in KOH electrolyte, specifically, 528 F/cm³ at a scan rate of 2 mV/s, and 306 F/cm³ at
100 mV/s.\textsuperscript{24} Zhao et al. proposed a facial approach to fabricate flexible MXene/CNT composites with sandwich structure, which possess a high capacitance of 150 F/g at 2 mV/s and 117 F/g at 200 mV/s. The latter value is about 130\% higher than that offered by the Ti$_3$C$_2$T$_x$ paper at the same rate.\textsuperscript{23} However, there are still some challenges in the application of Ti$_3$C$_2$T$_x$. For instance, the contact between the Ti$_3$C$_2$T$_x$ blocks is loose due to the uneven size caused by the different numbers of titanium caride layers, which compromises its electrochemical performance because of the incomplete utilization of Ti$_3$C$_2$T$_x$ blocks. In addition, the volume changes of Ti$_3$C$_2$T$_x$ during the charge/discharge process in alkali hydroxide electrolyte also will limit the cycling stability of as-fabricated electrode.

Graphene, another important 2D material, due to its intrinsic features of high electronic conductivity (\sim 16 000 S/m), large specific surface area (\sim 2630 m\(^2\)/g), and superior mechanical properties, is often considered as an important coadjuvant to achieve higher performance of electrode materials.\textsuperscript{26-28} In previous works, we have found that reduced graphene oxide (RGO) acts as an important component in strengthening the electrode performance because of the incomplete utilization of Ti$_3$C$_2$T$_x$ due to the uneven size caused by the different numbers of titanium caride layers, which compromises its electrochemical performance because of the incomplete utilization of Ti$_3$C$_2$T$_x$ blocks. In addition, the volume changes of Ti$_3$C$_2$T$_x$ blocks during the charge/discharge process in alkali hydroxide electrolyte will also limit the cycling stability of as-fabricated electrode.

In this paper, Ti$_3$C$_2$T$_x$/RGO composite electrodes were fabricated by introducing RGO into MXenes with the hope that RGO nanosheets could act as conductive “bridges” to connect different blocks of Ti$_3$C$_2$T$_x$. The undersized Ti$_3$C$_2$T$_x$ in composite without adding RGO leads to low utilization. However, Ti$_3$C$_2$T$_x$ lying on the introduced soft and flexible RGO nanosheets can improve contact and thus smooth electronic transfer process to the current collector, which significantly improves the supercapacitor performance of the electrode. Also, flexible graphene may serve as a matrix for alleviating potential volume changes from intercalation of cations, particularly in the long term cycling test. Besides, RGO nanosheets could also act as a second nanoscale current collector supporting electronic conductivity in electrodes. As a consequence of this fact, we demonstrate that the Ti$_3$C$_2$T$_x$/RGO composite electrode (Ti$_3$C$_2$T$_x$: RGO = 7:1) shows a highest specific capacitance and best cycle stability.

2. EXPERIMENTAL SECTION

2.1. Synthesis of Graphene Oxides and MAX Phase Ti$_3$AlC$_2$

Graphene oxides (GO) were synthesized via a modified Hummers method using pristine graphite powders as raw materials.\textsuperscript{55,56} The detailed preparation process is given in the Supporting Information.

The MAX phase Ti$_3$AlC$_2$ (Kanthal Corporation, Sweden) powders with TiC (Sigma-Aldrich, Belgium) in a 1:1 molar ratio, followed by calcination at 1350 °C for 2 h under flowing argon. After ball-milling for 4 h in ethanol, the Ti$_3$AlC$_2$ powders were obtained (after drying).

2.2. Synthesis of RGO and Ti$_3$C$_2$T$_x$, RGO was reduced from GO using an Raman microscope (inVia, Renishaw Instruments, Wotton under Edge, England) with a 514 nm laser excitation line. The morphology was monitored by FESEM (Hitachi, S-4800, Japan), and the structure was confirmed by TEM (JEOL, JEM-2100, Japan). The elementary compositions of the composites were characterized by EDS (Bruker AXS, Quantax 400–30, Germany).

2.3. Preparation of Ti$_3$C$_2$T$_x$, RGO, and Ti$_3$C$_2$T$_x$/RGO Composite Electrodes.

The typical synthesis procedure of Ti$_3$C$_2$T$_x$/RGO composite electrode is as follows: RGO powder was first dispersed in ethanol (30 mL) by ultrasonication. A selected amount of Ti$_3$C$_2$T$_x$ powder was then mixed with RGO solution. After 1 h, the composite was separated from the solvent through filtration, and then washed thoroughly with water, filtered, and dried at 80 °C for 12 h. Different composites were obtained by adjusting the weight ratio of Ti$_3$C$_2$T$_x$/RGO to 5, 7, and 9, denoted as Ti$_3$C$_2$T$_x$/RGO-3, Ti$_3$C$_2$T$_x$/RGO-5, Ti$_3$C$_2$T$_x$/RGO-7, and Ti$_3$C$_2$T$_x$/RGO-9, respectively.

For the fabrication of electrode, the as-prepared samples as active materials were mixed with conductive carbon black (Super P, Imerys, France), and polyvinylidene fluoride (PVDF, Arkema Inc., Philadelphia, U.S.A.) at a weight ratio of 8:1:1. The resulting slurries were pasted on stainless steel mesh current collectors with an area of 1 × 1 cm\(^2\) and dried in a vacuum oven at 80 °C for 12 h. Different electrodes were obtained with the different Ti$_3$C$_2$T$_x$/RGO ratios. Pure Ti$_3$C$_2$T$_x$ and RGO electrodes were also accordingly prepared. Mass loading is 3.2, 3.7, 2.0, 2.2, 2.1, and 1.5 mg for Ti$_3$C$_2$T$_x$/RGO-9, Ti$_3$C$_2$T$_x$/RGO-7, Ti$_3$C$_2$T$_x$/RGO-5, Ti$_3$C$_2$T$_x$/RGO-3, and pure RGO electrode, respectively.

2.4. Materials Characterization.

XRD patterns of all samples were measured on an X-ray diffractometer (Cu K\(\alpha\), \(\lambda = 0.15406\) nm, RIGAKU, D/MAX 2550 V, Japan). Raman spectra were performed using an Raman microscope (inVia, Renishaw Instruments, Wotton under Edge, England) with a 514 nm laser excitation line. The morphology was monitored by FESEM (Hitachi, S-4800, Japan), and the structure was confirmed by TEM (JEOL, JEM-2100, Japan). The elementary compositions of the composites were characterized by EDS (Bruker AXS, Quantax 400–30, Germany).

2.5. Electrochemical Measurements.

All the electrochemical performances were measured in typical three-electrode cells in 2 M KOH electrolyte using the as-prepared electrodes as working electrode, a Pt foil (2 × 3 cm\(^2\)) as counter electrode, and a commercial SCE as reference electrode, respectively. Before the electrochemical measurements, a pretreatment process was carried out by immersing working electrodes in the KOH solution for 24 h. CV, GCD, and EIS were conducted on an electrochemical workstation (CH660e, Chenhua Instruments, Shanghai, China). EIS were carried out in 100 kHz ~ 0.01 Hz using a sinusoidal signal of 5 mV at open circuit potential. The discharge specific capacitances of tested electrodes were calculated via eq 1,\textsuperscript{37}

\[
C_s = \frac{1}{m} \frac{\Delta U}{\Delta t}
\]

where \(C_s\) is specific capacitance (F/g), \(m\) is mass of active materials in electrode (g), \(\Delta U\) is the actual potential window in the discharge process (V), \(\Delta t\) is applied current (A), and \(\Delta t\) is the discharge time (s).

3. RESULTS AND DISCUSSION

Figure 1 presents the XRD patterns of Ti$_3$AlC$_2$, Ti$_3$C$_2$T$_x$, and Ti$_3$C$_2$T$_x$/RGO-7 composite. Peaks at 2\(\theta\) values of 9.5\(^\circ\), 19.2\(^\circ\), 34.0\(^\circ\), 36.8\(^\circ\), 39.0\(^\circ\), 41.8\(^\circ\), 44.9\(^\circ\), 48.5\(^\circ\), 52.4\(^\circ\), 56.5\(^\circ\), and 60.3\(^\circ\) are assigned to the (106), (107), (108), and (110) planes of pure Ti$_3$AlC$_2$, respectively, according to JCPDS No. 52-0875.\textsuperscript{16,38} It can be seen in the XRD patterns that the crystallinity and structural order of Ti$_3$AlC$_2$ decrease after LiF/HCl treatment. As reported, the characteristic (002) peak at 9.5° 2\(\theta\) in the Ti$_3$AlC$_2$ is broadened and obviously shifted to a much lower value, which results from the larger d-spacing and can be
explained by the structural expansion from etching and substitution of Al with —F and —OH/≡O terminating groups. The most intense peak at 2θ = 39° nearly disappeared, confirming the removal of Al layers from Ti3AlC2 in a more convincing way.38,39 In the Ti3C2Tx/RGO-7 pattern, there is a weak peak at 24.8°, which belongs to RGO.

Raman spectra recorded for selected samples are presented in Figure 2. The peaks between 200 and 700 cm⁻¹ almost vanished after LiF/HCl treatment, which results from the structural deterioration and loss of crystallinity already evidenced from the XRD results.36,40 In the spectrum of Ti3C2Tx/RGO-7 composite, two legible Raman scattering peaks at 1358 cm⁻¹ (D band) and 1597 cm⁻¹ (G band) can be observed, which is always regarded as an evidence of graphene existence. Accordingly, ID:IG is usually calculated to semiquantitatively illustrate the reduction level of graphene oxides.41 Compared with pure GO (0.81), a high D/G ratio (1.1) is obtained for the Ti3C2Tx/RGO-7 composite, indicating that RGO was in a deeply reduced state from the hydrothermal method.

The EDS mapping of Ti3C2Tx (Figure 3) confirms that the Al atoms are mostly etched and substituted by the introduced O, F, and Cl groups. The presence of the latter can be explained by the termination of exposed Ti-surfaces groups after the removal of Al.42

Figure 4a exhibits FESEM image of Ti3AlC2, having smooth surfaces, but uneven sizes. The larger Ti3AlC2 is about 14 μm, while the smaller one is only about 1 μm. After LiF/HCl treatment, a layered structure due to the removal of Al from Ti3AlC2 is evident. Most delightful, the 2D structure of Ti3C2Tx (Figure 4b) looks pretty much like that of exfoliated transition metal oxides or, even, graphite.

Figure 4c is a high magnification FESEM image of Figure 4b. Such typically layered structure could improve the contact of electrode with electrolyte and be beneficial to the ion transport, resulting in better pseudocapacitance performance.43 The introduction of RGO further modifies the composite sample morphology. As shown in Figure 4d, in fact, the RGO nanosheets in the composite act as conductive “bridge” and nanoscale collector for electron transfer.30,34

TEM was used to further investigate the microstructure of the as-synthesized composite in detail (Figure 5a and b). The result in Figure 5a shows that some smaller Ti3C2Tx are loaded on the large graphene sheets, and a structure of restacked Ti3C2Tx MXene sheets can be recognized from Figure 5b, which is in good accordance with the FESEM images.
Figure 6a and b shows the CV and GCD curves of all electrodes, respectively. The almost rectangular shape of the CV profiles (Figure 6a) for all electrodes indicates a high reversibility of capacitive behavior. All the CV curves in Figure 6a show no peaks, which reveal that the electrodes performed as pseudocapacitors over the complete voltammetric cycle. The faradaic process of layered Ti$_x$C$_2$Tx in potassium hydroxide solution can be described as:

$$\text{Ti}_x\text{C}_2\text{Tx} + x\text{K}^+ + xe^- = \text{K}_x\text{Ti}_x\text{C}_2\text{Tx}$$

(2)

As show in Figure 6b, the charge and discharge profiles of all electrodes at 2 A/g are nearly linear with minor IR drop (Table S1), demonstrating the excellent capacitive performance of the composite material and concerting well with the CV curves. As the pure Ti$_x$C$_2$Tx electrode exhibits a higher specific capacitance than that of pure RGO, it is easy to understand that the specific capacitances of Ti$_x$C$_2$Tx/RGO composite increase with the addition of some Ti$_x$C$_2$Tx in the composite (from 3:1 to 7:1). However, with much more Ti$_x$C$_2$Tx (Ti$_x$C$_2$Tx/RGO/9:1), the specific capacitance of Ti$_x$C$_2$Tx/RGO composite drops. It is comprehensive that the RGO, acting as support and bridge for active materials, is inadequate to prevent all Ti$_x$C$_2$Tx from aggregation, which may induce more inefficient utilization of active materials and thus lower the electrochemical capacity. Therefore, the Ti$_x$C$_2$Tx/RGO-7 electrode exhibits the best performance, corresponding to the highest specific capacitance (154.3 F/g at 2 A/g). Table 1 lists the specific capacitances of all electrodes as obtained at various current densities. From the table, it can be seen that the Ti$_x$C$_2$Tx/RGO-7 composite always offers the best performance independent of the applied current density. Effect of Ti$_x$C$_2$Tx content on the capability in our work is consistent with Yan’s. Performance comparisons of Ti$_x$C$_2$Tx/RGO-7 electrode with other works is listed in Table S2. It is noteworthy that ultrasonic treatment (1 h) during the preparation process also plays a key role in fabricating high performance materials, and the Ti$_x$C$_2$Tx/RGO mixture prepared only by grinding at the same ratio with Ti$_x$C$_2$Tx/RGO-7 exhibits a smaller specific capacitance than the ultrasonic one which is similar to the pure Ti$_x$C$_2$Tx as shown in Figure S1.

Figure 7a presents the CV curves of Ti$_x$C$_2$Tx/RGO-7 electrode at different scan rates. When the scan rate is higher than 50 mV/s, the curves remain no longer the standard rectangular shape, possibly because the diffusion of K$^+$, especially inside the MXene structure according to eq 2, is limited. In addition, an immersion process in electrolyte is necessary before measurement, for those electrodes without immersion process possess a low electrochemical capacitance and an improvement during the initial cycles, e.g., 50 cycles, as shown in Figure S2. Figure 7b shows the GCD curves at different current densities. Even at a higher current density of 6 A/g, the Coulombic efficiency remains 96.5%.

The specific capacitance change with increasing scan rates is shown in Figure 8a, from which it can be observed as the capacitance retention is significantly improved with the introduction of RGO. The best performance is achieved using the Ti$_x$C$_2$Tx/RGO-7 electrode, offering the outstanding $C_s$ of 138 F/g at 6 A/g. Cyclic stability curves at constant current density of 4 A/g are illustrated for all the samples in Figure 8b. After 6000 cycles the Ti$_x$C$_2$Tx/RGO-7 electrode still maintains a $C_s$ of 124.7 F/g (corresponding to 85% of capacity retention).

Figure 4. FESEM images of (a) Ti$_x$AlC$_2$, (b) Ti$_x$C$_2$Tx, (c) enlarged view of (b), (d) Ti$_x$C$_2$Tx/RGO-7 composite.

Figure 5. TEM (a) and HRTEM (b) images of Ti$_x$C$_2$Tx/RGO-7 composite.

Figure 6. Electrochemical performance of RGO,Ti$_x$C$_2$Tx, and Ti$_x$C$_2$Tx/RGO electrodes. (a) CV curves at 20 mV/s and (b) GCD curves at 2 A/g.
To further elucidate the electrochemical performance of these composite materials, EIS was performed. Figure 9 presents the Nyquist plot of all electrodes. All the electrodes’ spectra are consisted of a semicircle and a straight line in the high-middle frequency and low frequency regions, respectively, which correspond to the charge-transfer process ($R_{ct}$) at the electrode/electrolyte interface and charge-accumulation in the electrode solid phase of Ti$_3$C$_2$Tx, respectively. The intercept of this last feature with the real axis ($Z^{′}$) is regarded as equivalent series resistance (ESR, Table S1), including intrinsic resistance of the active material and current collector ($R_e$), the diffusion resistance of the electrolyte ($R_{diff}$), and the contact resistance at the interface of electrode and electrolyte ($R_{cont}$).37,42

From the incorporation of large specific surface area of RGO and electric active sites of MXene in the composite, the obtained material exhibited highly enhanced electronic/ionic transport abilities and supercapacitance from the synergetic contribution of both double-layer and faradaic capacitances.45 It can be observed in the spectra that all the samples have a nearly vertical line in the low-frequency region, reflecting the fast ion diffusion in Ti$_3$C$_2$Tx/RGO bulk phase and ideally capacitive behavior of the electrodes.30,32 Ti$_3$C$_2$Tx/RGO-7 electrode has a relatively low ESR and $R_{ct}$ value (0.81 and 2.08 $\Omega$, respectively), implying that the charge transfer and ion diffusion are much easier than other electrodes during the electrochemical reactions.

Figure 10 presents the imaginary capacitance vs frequency plot. The imaginary capacitance was calculated based on eq 3,16

<table>
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<tr>
<th>samples</th>
<th>content of RGO (%)</th>
<th>1 A/g</th>
<th>2 A/g</th>
<th>3 A/g</th>
<th>4 A/g</th>
<th>5 A/g</th>
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<tr>
<td>Ti$_3$C$_2$T$_x$</td>
<td>0</td>
<td>135.5</td>
<td>123.0</td>
<td>115.5</td>
<td>108.0</td>
<td>101.7</td>
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<td>Ti$_3$C$_2$T$_x$/RGO-9</td>
<td>10.0</td>
<td>142.7</td>
<td>141.7</td>
<td>137.0</td>
<td>132.0</td>
<td>126.7</td>
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<td>12.5</td>
<td>154.3</td>
<td>154.3</td>
<td>151.0</td>
<td>146.7</td>
<td>141.7</td>
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<tr>
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<td>16.7</td>
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<td>142.7</td>
<td>138.0</td>
<td>133.3</td>
<td>128.3</td>
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<tr>
<td>Ti$_3$C$_2$T$_x$/RGO-3</td>
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<td>126.0</td>
<td>122.0</td>
<td>116.7</td>
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<tr>
<td>RGO</td>
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<td>129.5</td>
<td>99.7</td>
<td>87.0</td>
<td>76.0</td>
<td>45.8</td>
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where $C''$ means the imaginary part of the capacitance, $f$ is the frequency, $Z'$ is the real part of the impedance, and $Z$ is the electrochemical impedance. The imaginary part of the capacitance reaches a maximum value at a frequency $f_0$ defining a time constant as $\tau_0 = 1/f_0$. As seen in the inset of Figure 10, $\tau_0$ are 6.8s, 12.9s, 8.2s, 10s, 8.2s, and 82.5s for Ti$_3$C$_2$T$_x$/RGO-9, Ti$_3$C$_2$T$_x$/RGO-7, Ti$_3$C$_2$T$_x$/RGO-5, Ti$_3$C$_2$T$_x$/RGO-3, and pure RGO electrode, respectively. This means that the Ti$_3$C$_2$T$_x$/RGO-7 electrode can deliver its stored energy faster than other composite electrodes except the pure Ti$_3$C$_2$T$_x$. In other words, it makes the Ti$_3$C$_2$T$_x$/RGO-7 electrode more appropriate for power capacitor. Phase angle versus frequency plot is given in Figure S3. It can be clearly seen that in the low frequency, the phase angles of all electrodes are close to $90^\circ$, which indicates an ideal capacitor at low frequency range.

4. CONCLUSIONS

Composite Ti$_3$C$_2$T$_x$/RGO electrodes comprising 2D highly conductive Ti$_3$C$_2$T$_x$ nanosheets, prepared by an LiF/HCl treatment, and various amounts of RGO were synthesized and tested as supercapacitor electrode materials. Ti$_3$C$_2$T$_x$/RGO-7 electrodes deliver the highest capacitance of 154.3 F/g at 2 A/g and 138 F/g at a rate as high as 6 A/g. In addition, the fabricated electrodes exhibit superior cyclability, with capacity retention of 85% after 6000 cycles. We believe that these results represent a breakthrough in MXene-based materials, which can significantly prompt their rapid development and applications in supercapacitors.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b04767.

Nyquist plots and IR drop of all the electrodes; and performance comparisons with other work (PDF)

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Notes

The authors declare no competing financial interest.

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