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One-Step Synthesis of Nanocrystalline Transition Metal Oxide on Thin Sheets of Disordered Graphitic Carbon by Oxidation of MXenes

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Herein we show that heating 2D Ti3C2 in air resulted in TiO2 nanocrystals on thin sheets of disordered graphitic carbon structures that can handle extremely high cycling rates when tested as anodes in lithium ion batteries. Oxidation of 2D Ti3C2 in either CO2 or pressurized water also resulted in TiO2/C hybrid structure. Similarly, other hybrids can be produced, as we show here for Nb2O5/C from 2D Nb2C.

Among the myriad metal oxide/carbon materials, titania/carbon hybrids (TiO2/C) have attracted the most attention due to their superior performance in many applications. For example, nanocrystalline titania deposited on graphene is an excellent photocatalyst and an outstanding electrode material in lithium-ion batteries (LIBs).

To date, most of the synthesis techniques have been carried out using at least two main steps: graphene synthesis, followed by deposition of TiO2, with each step possibly consisting of multiple intermediate stages (e.g., solution deposition of amorphous TiO2 followed by calcination to crystallize the oxide structure). In addition, an advanced one-step synthesis of a TiO2/graphene hybrid was achieved by solvothermal treatment of graphene oxide mixed with titania precursor solutions.

Recently, we reported on the synthesis of a new family of two-dimensional (2D) transition metal carbides and carbonitrides, that we labeled MXenes.

The details of the delamination process are summarized in the electronic supplementary information (ESI†) and Ref. [17].

MXene powders and paper were placed in alumina boats, and flash oxidized at 1150 °C by rapidly (< 5 s) pushing the boat into the furnace’s hot zone where the boat was kept at 1150 °C for 30 s, before being rapidly removed from the furnace in < 5 s. One of the challenges of flash oxidation is the difficulty in controlling the process, especially if ignition of the powders takes place. To explore more controlled approaches MXene powders were: i) held for 1 h in pure CO2 at 150, 300, and 500 °C and, ii) heated hydrothermally in deionized (DI) water at 150, 200, and 250 °C for 48 h, 8-20 h and 2 h, respectively, in an autoclave. Further details can be found in the ESI†.

The as-synthesized Ti3C2Tx has a layered morphology resembling exfoliated graphite (Fig. 2A). After the flash oxidation, oxide nanocrystals were observed to grow between, and at the edges of the layers (Fig. 2B). Energy dispersive X-ray analysis (EDX) showed them to be comprised of Ti and O. Several relatively large (≤ 0.5 μm) bi-pyramidal TiO2 crystals (Fig. 2B) were observed as well which, morphologically, and their morphology suggests anatase formation. Similar nanometer-sized anatase bi-pyramids, with [101]-planes faceting were reported by Čaplovičová et al. for TiO2 derived from conventional mechano-chemical synthesis and found to be highly photoactive. Note that nanocuboids were also observed in some scanning electron microscope (SEM) images (inset, Fig. 2B).
The cuboids are likely to consist of [001] and [100] facets.\(^5\) The presence of the latter is not surprising, since the starting Ti\(_2\)C\(_x\) contained a significant fraction of -F surface terminations which are known to stabilize the [001] anatase surfaces.\(^21\) Sun \textit{et al.}\(^22\) showed a significant improvement in photocatalytic activity under visible light for composites of anatase nanocrystals with exposed [001]-facets on graphene sheets, as compared to pure TiO\(_2\) nanosheets. The existence of these various morphologies demonstrates that MXenes can be used as facile precursors to create tailored morphologies. Further experiments, however, are needed to tune the oxidation process to solely obtain a specific morphology.

Transmission electron microscope (TEM) images of oxidized Ti\(_2\)C\(_x\) (Fig. 2C) show that the nanocrystals are embedded in thin sheets. EDX of the sheets showed mainly C with some Ti and O. The \(d\)-spacing between the atomic planes in the nanocrystals was measured from lattice fringes in TEM images (inset, Fig. 2C), and matched the (101) \(d\)-spacing of anatase, viz. 3.5 Å. The conversion of Ti\(_2\)C\(_x\) into nanocrystalline anatase and amorphous C was confirmed by X-ray diffraction (XRD) and Raman spectroscopy and the results are shown in Figs. 2D and E, respectively. The average anatase domain size, estimated from the XRD patterns is ~ 60 nm using the Scherrer formula.

The Raman spectrum of oxidized Ti\(_2\)C\(_x\) powders (top spectrum in Fig. 2E) showed a strong peak at 144 cm\(^{-1}\) with a full width of half maximum (FWHM) of 14 cm\(^{-1}\), together with three other peaks at 394, 513, and 635 cm\(^{-1}\). These peaks can be assigned to the following anatase vibrational modes: \(E\)\(_{g(1)}\), \(B\)\(_{g(1)}\), \(A\)\(_{1g}\&B\)\(_{1g(2)}\), and \(E\)\(_{g(3)}\), respectively.\(^24\) The peak positions and FWHM of \(E\)\(_{g(1)}\) correspond to anatase particles with an average size of less than 15 nm.\(^24\) The discrepancy between the average sizes obtained from XRD patterns and Raman spectra relates to the nature of each technique. In XRD, the average domain size obtained is averaged over a larger sampling volume; the values obtained from Raman spectra are more strongly affected by crystal lattice defects within the grains that leads to smaller scattering domains.\(^25\) The two broad peaks between 1000 - 1800 cm\(^{-1}\) are characteristic for the D- and G-modes of graphitic carbon.\(^26\) The D-band position and its FWHM were 1391 cm\(^{-1}\) and 225 cm\(^{-1}\), respectively. The corresponding values for the G-band were 1596 cm\(^{-1}\) and 91 cm\(^{-1}\). The ratio of the D- and G-band intensities, \(I_D/I_G\), was ~ 0.78. The broadening of G- and D- bands and the \(I_D/I_G\) ratio evidence highly disordered (amorphous) carbon similar to what has been reported for carbide-derived carbons (CDCs) fabricated at 200 °C.\(^27\) The presence of carbon sheets covered by TiO\(_2\) particles on the surface implies that the innermost Ti atoms in the MXene structure migrated outward to react with oxygen. This outward migration of Ti is similar to what has been observed previously during the oxidation of TiN.\(^28\)

The N\(_2\) adsorption-desorption isotherms at -196 °C (Fig. 2F) show an increase in specific surface area (SSA) after oxidation. The SSA estimated using the BET equation\(^29\) for the oxidized sample was found to be ~ 50 m\(^2\) g\(^{-1}\), a factor of 5 greater that the as-synthesized MXene, which had a SSA of 10 m\(^2\) g\(^{-1}\). This increase in SSA could be explained by the: i) formation of nanometer-sized oxide particles and/or, ii) opening or swelling of the layers during oxidation that allows the adsorbate to penetrate between the layers.

Fig. 2: Characterization of Ti\(_3\)C\(_2\)T\(_x\) powders before and after flash oxidation in air at 1150 °C for 30 s. (A) SEM image of typical as-synthesized Ti\(_3\)C\(_2\)T\(_x\) multilayered flake; (B) SEM image after oxidation. Top left inset is another SEM image at a different location for the same sample; (C) TEM image after oxidation. Inset is a high-magnification image of one of the anatase particles embedded in the amorphous carbon; (D) XRD patterns before and after oxidation. Crosses denote anatase peak positions for (PDF#01-0562); squares denote Si peak positions which was used as an internal reference; (E) Raman spectra before and after oxidation; the * signs represent anatase while D and G represent the positions of D and G bands of disordered graphitic carbon; (F) Nitrogen adsorption-desorption isotherms at -196 °C for Ti\(_3\)C\(_2\)T\(_x\) before and after oxidation. The inset is a zoom in the Ti\(_3\)C\(_2\)T\(_x\) isotherms along Y-axis.
Flash oxidation of 2 - 4 µm thick d-Ti3C2Tx "paper" in air at 1150 °C for 30 s changed it from opaque black to translucent white. Interestingly, unlike the Ti3C2Tx powders, oxidation of the paper did not result in the formation of crystalline phases detectable by XRD (Figs. S1A-B, ESI†). This can be explained by an easier oxygen access to each single or few-layer- flakes of the MXene paper, resulting in more uniform oxidation and the formation of extremely thin and uniform TiO2 particles. For multilayered stacked Ti3C2Tx powders, a gradient of oxygen concentration (high outside the particle and lower inside) is expected. This in turn, results in formation of relatively large TiO2 crystals (Fig. 2B) on the surface, similar to oxidation of Si and hydrothermal oxidation in DI water are also show incomplete oxidation and the coexistence of Ti in oxidative powders, a gradient of oxygen concentration (high outside the particle and lower inside) is expected. The presence of unreacted MXene in the core and oxide particles after 30 cycles at a cycling rate of C/18, 210 mAh·g⁻¹, respectively, were obtained after more than 250 cycles. Those high cycling rates cannot be achieved with graphite electrodes and are better than what was reported for anatase. For example, Shin et al.²⁵ found that 5 to 10 nm anatase had no capacity at cycling rates of 30 C and 60 C, while nanoporous anatase had capacities of 77 mAh·g⁻¹ and 46 mAh·g⁻¹ at 30 C and 60 C, respectively. In that paper it was suggested that the good capacity at high cycling rates was due to interfacial storage.²⁵

The characterization results for the isothermal oxidation of Ti3C2Tx in CO2 and hydrothermal oxidation in DI water are presented and discussed in details in the ESI†. As shown in Fig. S2A (ESI†), anatase formation was observed by XRD when CO2 was used at 150 °C and higher temperatures. Note that the XRD patterns show the presence of some unreacted MXene along with the anatase after oxidation in CO2 at 500 °C. The presence of disabled carbon was confirmed using Raman spectroscopy (Fig. S2C, ESI†). The morphology of the material oxidized using CO2 (Fig. S2B, ESI†) is similar to what was observed after flash oxidation in air at 1150 °C. In the samples that were oxidized in CO2 no bi-pyramidal crystals were observed.

The XRD patterns (Fig. S3, ESI†) after hydrothermal treatment in DI water also show incomplete oxidation and the co-existence of Ti3C2Tx and anatase peaks. As shown in Fig. S4 (ESI†), the most uniform oxide morphology was obtained using this technique. No bare MXene sheets (similar to Fig. 2A) were observed by the SEM (Fig. S4, ESI†), which could be due to presence of unreacted MXene in the core and oxide particles on the surface (core-shell morphology).

To investigate the performance of the hybrid structures produced in here, we tested one of the samples that was produced by flash oxidation in air, as an electrode material in LIBs. Fig. 3A shows cyclic voltammograms (CVs) for flash-air oxidized Ti3C2Tx powders. The reversible lithiation and delithiation peaks, respectively, around 1.7 and 2.2 V vs. Li/Li⁺ are quite close to what was reported for nanocrystalline anatase anodes.³⁰,³¹ Similar peaks were observed for hydrothermally treated Ti3C2Tx (Fig. S5, ESI†). As shown in Fig. 3B, reversible capacities of 220 mAh·g⁻¹ after 30 cycles at a cycling rate of C/18, 210 mAh·g⁻¹ after more than 200 cycles at C/3, and 155 mAh·g⁻¹ after 250 cycles at 1 C were obtained. These capacities are higher than those reported for anatase-functionalized graphene sheets' hybrid structures.⁸ Cai et al. ³² reported a capacity of about 300 mAh·g⁻¹ at 1 C for TiO2-graphene composites within the same voltage window used here.

The higher capacity they reported can be explained by the amount of graphene used in their composites which was more than double the carbon content in this work. It is worth noting that the maximum amount of C in our work after oxidation - assuming that no carbon is oxidized - is about 10 wt.%. Said otherwise, if none of the carbon is oxidized and all the Ti is converted into TiO2, then the C:TiO2 ratio by mass should be 1:10.

When we tested our material at very high rates, viz. 40 C and 100 C, reversible capacities of 75 mAh·g⁻¹ and 45 mAh·g⁻¹, respectively, were obtained after more than 250 cycles. The cycling performance of the hybrid structures presented in Fig. 3B shows that these materials exhibit high stability up to 250 cycles.

We have to note that Ti3C2Tx is just one member of the much larger MXene family. It follows that this work opens the door for numerous hybrid structures, of different nanocrystalline early transition metal oxides, on disordered graphitic carbon thin sheets.

To prove the generality of the proposed approach, another MXene, viz. Nb2CTx powders ³³ were oxidized via hydrothermal treatment in DI water at 150 °C for 4 h and at 200 °C for 2 h. The experimental details are similar to those described in the ESI† for Ti3C2Tx. As shown in Fig. S6A (ESI†), this procedure produced Nb2O5 after 4 h at 200 °C. Interestingly, no peaks related to crystalline oxides were observed in XRD after treatment at 150 °C for 2 h. A broad Raman peak of Nb2O5 around 700 cm⁻¹ (Fig. S6B, ESI†), similar to what was reported by Ghosh et al. ³⁴ for Nb2O5 nanofores, was observed in both cases. The co-existence of amorphous carbon and metal oxide can be seen in the Raman spectra after oxidation at 200 °C. In some locations, both carbon and niobia peaks were observed (Fig. S6B, ESI†), in others carbon was not observed (dotted black spectrum in Fig. S6B, ESI†), which indicates that 200 °C may be too high if both oxide and carbon are desired. Further work is ongoing to fully convert Nb2CTx into nanosized oxides without sacrificing the carbon. For example, reducing the molar ratio of H2O to MXene during hydrothermal treatment would yield a higher carbon content, similar to what was reported for binary transition metal carbides.³⁵ Thus, composites of Nb2O5/C could be quite useful in electrochemical capacitors³⁶ and LIBs.³⁷

As shown in Fig. S6C (ESI†), featherlike nano-particles were formed on the surfaces of the Nb2CTx sheets after hydrothermal oxidation at 150 °C. A few barrel-shaped oxide particles, with diameters of ~200 nm, were observed as well. Those barrel-shaped oxide particles became the dominant morphology after the 200 °C treatment (Fig. S6D, ESI†). It follows that the 150 °C treatment resulted in a hybrid structure of Nb2CTx, featherlike niobia and amorphous carbon. The 200 °C treatment resulted in mainly barrel-shaped nanocrystalline oxide particles and amorphous carbon, with a small amount of unreacted Nb2CTx.
Conclusions

Flash oxidation of 2D Ti$_3$C$_2$T$_x$ in air resulted in the formation of a hybrid structure of thin sheets of disordered graphitic carbon decorated by nanocry stalline anatase. The flash oxidized MXene powder showed higher capacities than nano-anatase in LIBs and showed higher capacities than nano-anatase in LIBs. When Ti$_3$C$_2$T$_x$ powders were oxidized in CO$_2$ or hydrothermally, the resulting powders contained unreacted Ti$_3$C$_2$T$_x$, anatase, and C. Similarly, Nb$_2$O$_3$ with amorphous C and unreacted Nb$_2$CT$_x$ hybrid structures were obtained by hydrothermal treatment of the latter in DI water. Gaseous (CO$_2$) and hydrothermal oxidations of Ti$_3$C$_2$T$_x$ in DI water can also be used to produce hybrid structures of nanocry stalline anatase with amorphous C, but at significantly lower temperatures. Formation of the most uniform oxide particles was achieved by hydrothermal oxidation. When Ti$_3$C$_2$T$_x$ powders were oxidized in CO$_2$ or hydrothermally, the resulting powders contained unreacted Ti$_3$C$_2$T$_x$, anatase and C. Similarly, Nb$_2$O$_3$ with amorphous C and unreacted Nb$_2$CT$_x$ hybrid structures were obtained by hydrothermal treatment of the latter in DI water.

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Notes and references

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