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Authors	Ahmed, Bilal; Anjum, Dalaver H.; Hedhili, Mohamed N.; Gogotsi, Yury; Alshareef, Husam N.
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H₂O₂ Assisted Room Temperature Oxidation of Ti₂C MXene for Li-ion Battery Anodes

Bilal Ahmed¹, Dalaver H. Anjum¹, Mohamed N. Hedhili¹, Yury Gogotsi² and

Husam N. Alshareef^{1,*}

¹Materials Science and Engineering, King Abdullah University of Science and Technology (KAUST), Thuwal, 23955–6900, Saudi Arabia

²Department of Materials Science and Engineering, and A.J. Drexel Nanomaterials Institute, Drexel University, Philadelphia, PA, 19104, USA

Abstract

Herein we demonstrate that a prominent member of MXene family, Ti₂C, undergoes surface oxidation at room temperature when treated with hydrogen peroxide (H₂O₂). The H₂O₂ treatment results in opening up of MXene sheets and formation of TiO₂ nanocrystals on their surface, which is evidenced by high surface area of H₂O₂ treated MXene and X-ray diffraction (XRD) analysis. We show that the reaction time and amount of hydrogen peroxide used are the limiting factors, which determine the morphology and composition of the final product. Furthermore, it is shown that the performance of H₂O₂ treated MXene as anode material in Li ion batteries (LIBs) was significantly improved compared to as-prepared MXenes. For instance, after 50 charge/discharge cycles, specific discharge capacities of 389 mAh/g, 337 mAh/g and 297 mAh/g were obtained for H₂O₂ treated MXene at current densities of 100 mA/g, 500 mA/g and 1000 mA/g, respectively. In addition, when tested at a very high current density, such as 5000 mA/g, the H₂O₂ treated MXene showed a specific capacity of 150 mAh/g and excellent rate capability.

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These results clearly demonstrate that H₂O₂ treatment of Ti₂C MXene improves MXene properties in energy storage application, such as Li ion batteries or capacitors.

Highlights

Room temperature oxidation of Ti₂C MXene by H₂O₂ treatment

Preparation of TiO₂/Ti₂C nanocomposite for electrochemical applications

Very good Li-ion battery performance of H₂O₂ treated MXenes

*Corresponding author: husam.alshareef@kaust.edu.sa

Keywords: MXene, Ti₂C, TiO₂, anode, lithium ion battery

1. Introduction

Two-dimensional (2D) atomic crystals, such as graphene, are known to possess unique properties, which lead to their applications in various emerging research areas of scientific and technological importance.¹ Over the years, 2D materials other than graphene have been developed by exfoliating layered materials such as hexagonal boron nitride,² metal chalcogenides (MoS₂, etc.)³⁻⁶ and transition metal oxides (TMO).⁷⁻⁹ Owing to their high surface area and excellent electronic properties, 2D materials are considered as potential candidates for electrochemical energy storage, hydrogen storage and thermoelectrics.

About four years ago, a new family of 2D materials transition metal carbides named as MXenes was discovered and gained significant attention due to their excellent electrochemical and mechanical properties.¹⁰ MXenes produced by chemical etching of MAX phases, whereas MAX phases are represented by a general formula – M_{n+1}AX_n, where M is an early transition metal, A is an A-group element (mostly Al or Si) and X is carbon and/or nitrogen. The selective removal of A-layer by using hydrofluoric acid (HF) results in 2D layers of M_{n+1}X_n.¹¹ Due to their structural similarity with graphene, these newly formed 2D materials are termed MXenes.¹⁰ Various members of MXene family offer metallic conductivity and surface hydrophilicity.¹⁰ MXenes have already shown promise in supercapacitors,¹²⁻¹⁴ Li-ion batteries (LIBs),¹⁵⁻¹⁸ Li-sulfur batteries,¹⁹ sensors,^{20, 21} as filler in multifunctional polymer composites²² and water purification.²³ In addition, theoretical studies suggest that several members of this family can become potential candidate for hydrogen storage²⁴ and thermoelectric²⁵ applications.

Typically, the exfoliated MXene sheets are terminated by –OH, –O and/or –F functional groups (marked as T_x) due to aqueous HF treatment and their formula is written as Ti₂CT_x or Ti₃C₂T_x.¹⁰

Furthermore, it has been reported that band gap of these materials can be finely tuned by changing the nature of functional groups.¹⁰ Also, based on density functional theory (DFT) studies, it has been predicted that bare MXene sheets have a higher theoretical capacity in Li ion batteries than terminated ones.^{26, 27} In recent reports, heat treatment has been reported as an efficient way to alter the surface chemistry of MXene sheets.^{28, 29} Rakhi *et. al* reported that heating Ti_2CT_x in different atmospheres significantly improves its capacitive performance.²⁹ Naguib *et. al* reported that flash oxidation of $Ti_3C_2T_x$ MXene in air results in growth of nanocrystalline TiO_2 on disordered graphitic carbon sheets.²⁸ The resulting TiO_2/C composite showed promising performance when tested as anode material in LIBs. *In situ* transmission electron microscopy (TEM) revealed that either anatase or rutile nanocrystals of TiO_2 can be formed by controlling time, temperature and heating rate.³⁰ In addition, hydrothermal treatment of $Ti_3C_2T_x$ resulted in a hybrid TiO_2/Ti_3C_2 structure with an enhanced photocatalytic activity. The amount of produced TiO_2 depended on temperature and time of hydrothermal treatment.³¹

In this study, we aimed to alter the surface chemistry of Ti_2CT_x MXene by simple and scalable room-temperature oxidation in hydrogen peroxide (H_2O_2) solution. It resulted in the formation of TiO_2 nanocrystals on the surface of MXene sheets, which significantly improved the performance of the material in Li-ion battery anodes.

2. Experimental Section

2.1 Synthesis of Ti_2CT_x MXene, H_2O_2 Treatment and Material Characterization

Chemical exfoliation of commercially available Ti_2AlC (–325 mesh, Maxthal 211, Kanthal, Sweden) resulted in 2D titanium carbide (Ti_2CT_x) nanosheets. The exfoliation procedure was the

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same as reported elsewhere³²; Ti_2AlC powder was immersed in 10% HF for 10 h at room temperature. The resulting suspension was washed with DI water and filtered to obtain 2D Ti_2CT_x powder and dried at 60 °C for 24 hrs under vacuum. The as-prepared MXene powder was allowed to react with H_2O_2 solutions of different concentrations for different times. In a typical reaction, 0.5 grams of Ti_2CT_x powder was immersed in 50 mL of water under constant magnetic stirring and 5 mL of 30 wt. % H_2O_2 was added afterwards. The H_2O_2 treated MXene powder was washed several times with DI water and dried under vacuum for 24 hours before further experiments.

The as-prepared and H_2O_2 treated MXene powders were characterized by using a powder X-ray diffractometer (XRD, Bruker, D8 ADVANCE) with $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406$ nm). Raman spectroscopy was carried out using a LabRam Aramis Raman spectrometer with a diode pumped solid-state blue laser having an excitation wavelength of 473 nm. XPS studies were carried out in a Kratos Axis Ultra DLD spectrometer equipped with a monochromatic $\text{Al K}\alpha$ x-ray source ($h\nu=1486.6$ eV) operating at 150 W, a multichannel plate and a delay line detector under a vacuum of $1\approx 10^{-9}$ mbar. The survey and high-resolution spectra were collected at fixed analyzer pass energies of 160 eV and 20 eV, respectively and quantified using empirically derived relative sensitivity factors provided by Kratos analytical. Samples were mounted in floating mode in order to avoid differential charging. Charge neutralization was required for all samples. Binding energies were referenced to the C 1s peak of (C-C, C-H) bond, which was set at 284.8 eV. The data were analyzed with commercially available software, CasaXPS. The surface morphology and microstructure of as-prepared and H_2O_2 treated MXene powders were characterized with a field emission scanning electron microscope (FESEM, Nova NanoSEM from FEI), and a TEM (Titan G² 80-300 ST, FEI). Surface area and pore size distribution measurement was carried out

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by using nitrogen as adsorbent at liquid nitrogen temperature (ASAP 2420, Micromeritics) and samples were degassed at 150 °C for 12 hours before analysis.

2.2 Electrochemical characterization

The working electrodes were prepared by mixing the active material (H_2O_2 treated MXene powder) with acetylene black (MTI, Inc.) and poly(vinylidene fluoride) (PVDF, MTI Inc) in a weight ratio of 80:10:10. The prepared slurry was uniformly pasted on a copper foil (MTI, Inc.) and dried at 80 °C for 24 hrs under vacuum. The average mass of active material after drying is $\approx 0.75 \text{ mg/cm}^2$. To assess the electrochemical performance, 2032 coin-type (MTI, Inc.) half-cell devices were fabricated. The H_2O_2 treated MXene powder, pasted on copper foil, served as working electrode, Lithium foil was used as counter electrode and Celgard 3501 micro porous membrane was used separator. 1 M LiPF_6 in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 by weight) was used as electrolyte. The cells were assembled in an argon-filled glove box (MBRAUN) with the concentrations of O_2 and $\text{H}_2\text{O} < 0.5 \text{ ppm}$. The electrochemical performance of the assembled cells was measured at different current densities (100–5000 mA/g) in the 0.005–3.00 V range. Cyclic voltammetry was performed to examine the reduction and oxidation peaks in the voltage range of 0.005 – 2.8 V (V vs. Li/Li^+) at a scan rate of 0.2 mV/s.

3. Results and Discussions

3.1 Material Characterization

Three different samples will be discussed in this paper: 1) As-prepared Ti_2CT_x , 2) Ti_2CT_x treated in H_2O_2 for 5 minutes and 3) Ti_2CT_x treated in H_2O_2 for 5 hours. Figure 1a shows the XRD patterns of as-prepared and H_2O_2 treated (5 minutes) powders. It can be readily observed that (0002) peak of Ti_2AlC MAX phase shifts towards lower angles in the as-prepared Ti_2CT_x , which

indicates the removal of Al and increase of the c lattice parameter.³² In addition, the (0002) peak, mentioned as MXene peak, broadens as compared to the sharper parent phase peak which corresponds to the decreasing structural order.³² However small amount of residual Ti_2AlC remained in the Ti_2CT_x powder. The XRD spectrum of H_2O_2 treated MXene powder shows the presence of anatase (TiO_2). A sharp peak at $2\theta \approx 25^\circ$ corresponds to (101) plane of anatase TiO_2 (JCPDS card no. 00–021–1272).²⁹ Despite the formation of anatase, the (0002) peak of MXene phase is also present, which indicates that the resulting product is mainly MXene phase. Figure 1b shows the Raman spectra of as-prepared MXene and H_2O_2 treated MXene (immersion time \approx 5 minutes) powders. The H_2O_2 treated MXene powder showed a major peak around 150 cm^{-1} , which corresponds to the anatase.^{28, 33} The other three Raman bands ($\approx 250, 400$ and 600 cm^{-1}) represent the vibration modes which can be assigned to nonstoichiometric titanium carbide.³⁴ Furthermore, it can be observed that after H_2O_2 treatment the Raman band centered at 400 cm^{-1} shifted towards higher wavenumbers, which can be attributed to the layers exfoliation.²⁹ As previously reported, the decrease in layer thickness shifts the band position to a higher energy due to slight hardening of the bonds.²⁹ Another interesting observation in Raman spectra is the absence of D and G bands after H_2O_2 treatment. In previous reports, when flash oxidation of MXene powder²⁸ was carried out, the final product was nanocrystalline TiO_2 supported on disordered carbon sheets due to insufficient amount of oxygen or oxidation time to oxidize carbon. However, in this case, the absence of D and G bands indicates that our final product is nanocrystalline TiO_2 supported on MXene (Ti_2CT_x) sheets. The chemical reaction of MXene oxidation in H_2O_2 can be written as follow:



When Ti_2CT_x powder is immersed in H_2O_2 solution, it oxidizes to form TiO_2 and emits CO/CO_2 . The nitrogen adsorption/desorption isotherms of the as-prepared and H_2O_2 treated MXene powders are shown in. The specific surface area (SSA) values were calculated by using Brunauer–Emmett–Teller (BET) model, where the as-prepared MXene powder showed the SSA of $\approx 12.6 \text{ m}^2/\text{g}$, while H_2O_2 treated MXene powder exhibited an increase in SSA to $58 \text{ m}^2/\text{g}$ (Figure S1). This fivefold increase in SSA values can be explained by the formation of TiO_2 nanoparticles and opening/swelling of the layers after H_2O_2 treatment. Figure 1c shows the SEM image of H_2O_2 treated MXene where layers are being opened up and TiO_2 formation on their surface is initiated. The XRD and Raman results presented earlier also support this conclusion.

XPS investigations were performed to characterize the chemical composition of prepared powder and to determine the oxidation state of titanium (Ti). The detailed survey spectrum for the as-prepared MXene powder shows the presence of Ti, fluorine (F), oxygen (O), and carbon (C) (Figure S2). High-resolution XPS spectra of Ti 2p and C 1s core levels from the same sample are shown in Figures 2a and 2b, respectively. The Ti 2p core level was fitted with four doublets (Ti 2p $2p_{3/2}$ – Ti $2p_{1/2}$) with a fixed area ratio equal to 2:1 and doublet separation of 5.7 eV. The Ti $2p_{3/2}$ components were located at 454.4 eV, 455.9 eV, 457.4 eV and 458.6 eV, respectively. The Ti $2p_{3/2}$ component centered at 458.6 eV is associated with Ti ions with a formal valence $4+$,³⁵ while the peak at lower binding energy 457.4 eV is associated with Ti ions with reduced charge state (TiO_{2-x}).³⁶ The Ti $2p_{3/2}$ component centered at 454.4 eV corresponds to Ti-C bond.³⁶⁻³⁸ The Ti $2p_{3/2}$ component centered at 455.9 eV can be assigned to the Ti-X peak in Ti_2CT_x (a combination of a sub-stoichiometric TiC_x ($x < 1$) and to titanium oxycarbides TiC_xO_y).³⁹ The C 1s core level was fitted using six components located at 281.0 eV, 282.1 eV, 284.1, 284.8 eV, 286.3, 288.0 and 288.9 corresponding to C-Ti,^{38, 40} C-Ti-O, C=C (sp²), C-C/C-H (sp³), C-O,

C=O^{41, 42} and (O-C=O and C-F) bonds,⁴²⁻⁴⁴ respectively. The survey spectrum for H₂O₂ treated MXene powder (immersion time \approx 5 minutes) shows presence of Ti, F, O and C (Figure S3). High-resolution XPS spectra of Ti 2p and C 1s core levels have been obtained and presented in Figure 2c and 2d, respectively. The same fitting parameters were used to deconvolute the Ti 2p and C 1s core levels as in Figure 2a and 2b. It can be readily observed that there was a substantial decrease in the intensity of Ti 2p_{3/2} components at 454.4 eV, 455.9 eV and 457.4 eV for the Ti 2p spectrum accompanied with a decrease in the intensity of the C 1s component at 281.1 eV for the C 1s spectrum. This indicates that TiO₂ was formed at the expense of Ti₂C and the ratio of titanium carbides and titanium oxycarbides to TiO₂ was 0.25.

Similarly, the detailed XPS spectrum for H₂O₂ treated MXene powder (immersion time \approx 5 hours) also shows the presence of Ti, F, O and C (Figure S4). High-resolution XPS spectra of Ti 2p and C 1s core levels are presented in Figure 2e and 2f, respectively. The Ti 2p core level was fitted with two doublets (Ti 2p 2p_{3/2} – Ti 2p_{1/2}) with a fixed area ratio equal to 2:1 and doublet separation of 5.7 eV. The Ti 2p_{3/2} components were located at 456.6 eV and 458.8 eV respectively. The dominant Ti 2p_{3/2} component centered at 458.8 eV is associated with Ti⁴⁺ ions, while the peak at lower binding energy 456.6 eV is associated with Ti³⁺ ions.³⁵ Interestingly, this sample didn't indicate the presence of any titanium carbides and/or oxycarbides. This result was confirmed by the high resolution XPS spectrum of C 1s core level and presented in Figure 2f. The C 1s core level was fitted using four components located at 284.8 eV, 286.4, 288.0 and 288.9 corresponding to C-C/C-H, C-O, C=O and (O-C=O and C-F) bonds, respectively. The absence of Ti-C bonds (which were expected to be observed at around 281 eV) is evident. These results demonstrate that with the extended reaction time, Ti₂C is completely converted into TiO₂.

The morphology and microstructure of as-prepared and H₂O₂ treated MXene powders were investigated using TEM. Figure 3a shows a relatively low magnification TEM micrograph of as-prepared MXene powder. The stacked, layered and flake-like nature of MXene sheets can be readily observed. Figure 3b presents the high-resolution (HR) TEM image, which shows the lattice planes of MXene and some surface defects. Similar type of defects has been reported for functionalized graphene⁴⁵ and it has been proposed that these defects might act as nucleation sites for metal oxide formation.^{46, 47} This idea supports our previously mentioned hypothesis that when MXene powder is placed in H₂O₂ environment, TiO₂ growth is observed on the surface of MXene sheets with its nucleation starting at defects. The selected area electron diffraction (SAED) of as-prepared MXene sample, presented in Figure 3c, shows the hexagonal symmetry of the structure. It can be concluded that the MXene powder retained the crystallinity and symmetry of parent phase – Ti₂AlC.^{10, 32}

Figure 3d and 3e show the TEM images of H₂O₂ treated MXene powder (immersion time \approx 5 minutes). The flake-like MXene morphology can be seen in Figure 3d, however, when observed at a high magnification, the TiO₂ nanocrystals are found to be nucleated on the surface of MXene sheets. This is a clear evidence of TiO₂ growth on MXene sheets which is also supported by SAED pattern, presented in Figure 3f. The SAED pattern consists of two distinct phases; MXene phase, which is evidenced by the hexagonal symmetry, and anatase TiO₂ which is confirmed by the appearance of diffraction rings. It should be noted that the sample prepared under the same conditions was used for electrochemical characterization. However, as mentioned earlier, there are two parameters which determine the growth rate of TiO₂ in H₂O₂; the amount of H₂O₂ and the reaction time. Figures 3g and 3h presents the TEM and HRTEM images of an H₂O₂ treated sample with prolonged immersion time (\approx 5 hours). It can be readily observed that almost 100%

MXene is converted into TiO_2 phase in agreement with our XPS data presented in Figure 2e and 2f. The size (20–100 nm) and shape of TiO_2 nanoparticles can be seen from Figure 3g. The HRTEM image and SAED pattern confirmed the presence of pure anatase TiO_2 phase. Based on HRTEM and SAED results, it can be concluded that room temperature oxidation of Ti_2CT_x with H_2O_2 produces a hybrid structure of TiO_2 and Ti_2C .

3.2 Electrochemical Characterization

To assess the potential of using H_2O_2 treated MXene in Li-ion batteries (LIBs), we studied its electrochemical behavior with respect to Li^+ ion insertion and extraction. The cyclic voltammetry (CV) study of as-prepared MXene and H_2O_2 treated MXene (immersion time ≈ 5 minutes) electrodes was performed in the potential window of 5.0 mV to 2.8 V, at the scan rate of 0.2 mV/s and measured current–voltage (I–V) curves are presented in Figure 4a. The CV scan for as-prepared MXene matches with the previously published data,^{15, 16} where two distinct oxidation and reduction peaks were observed on charging/discharging. Interestingly, the CV scan for H_2O_2 treated MXene is not entirely different from the as-prepared MXene, except the higher values of obtained current which, in turn, indicates a higher capacity. In addition, typical oxidation and reduction peaks for TiO_2 were not observed, which implies that the major capacity contribution is still coming from Ti_2CT_x . Thus, the observed increase in specific capacity after H_2O_2 treatment is mainly due to opening of layer spacing and improved accessibility of MXene surface to Li ions. When the CV scan was initiated from open circuit voltage (OCV), four distinct peaks were observed at ≈ 1.75 V, ≈ 1.30 V, ≈ 0.95 V and ≈ 0.60 V (vs. Li/Li^+). Two peaks among these are irreversible and do not appear in the succeeding cycles. The presence of irreversible peaks can be assigned to the formation of solid electrolyte interface (SEI) and/or reaction with the electrode material.¹⁶ The broad oxidation and reduction peaks imply that

lithium is stored over a larger voltage range which makes it a better candidate for Li ion capacitors.¹⁵ The CV curves for the H₂O₂ treated MXene (immersion time \approx 5 hours) are presented in Figure S5. With more immersion time, the MXene sheets are fully oxidized and converted into TiO₂ (Figure 2e and 2f), leading to distinct TiO₂ lithiation/delithiation peaks in CV scans..

The galvanostatic charge/discharge curves at current densities 100 mA/g (C/3.5), 200 mA/g (C/1.75), 300 mA/g, 400 mA/g, 500 mA/g and 1000 mA/g (Figure 4b) show similar voltage plateaus (the C-rates were calculated based on theoretical capacity of Ti₂CO₂ \approx 350 mAh/g). These data are consistent with the observations made using CV scans. The cyclic performance of H₂O₂ treated MXene at three different current densities has been measured and presented in Figure 4c. The first discharge capacity was measured as 1015 mAh/g, 826 mAh/g and 681 mAh/g at 100 mA/g, 500 mA/g and 1000 mA/g, respectively. The second discharge capacity values were 507 mAh/g, 429 mAh/g and 384 mAh/g at 100 mA/g, 500 mA/g and 1000 mA/g, respectively. Again, the irreversible capacity loss could be attributed to the formation of SEI layer or reaction of Li ions with -F and -OH groups on the surface of MXenes.⁴⁸ After 50 cycles, the observed specific capacity was 389 mAh/g, 337 mAh/g and 297 mAh/g at 100 mA/g, 500 mA/g and 1000 mA/g, respectively. These values are almost two times higher when compared with the specific capacity of as-prepared MXene at similar current densities, presented in the same figure (hollow symbols). The most probable reason is the formation of TiO₂ nanoparticles and improved accessibility of MXene surface after H₂O₂ treatment. At this stage, we won't assign this high specific capacity to the presence of TiO₂ because we have not observed its contribution towards capacity in CV scans or charge/discharge curves. One should note that the previously published literature also suggests that whenever surface area of MXene was increased

either by delamination^{13, 49} or flash oxidation,²⁸ the specific capacity increased tremendously. Furthermore, the observed specific capacity of oxidized Ti_2CT_x allows it to compete with the graphite anodes and suggests that partial oxidation of MXenes, which holds promise for increasing their capacity, is a valuable route for practical applications in energy storage devices.

Besides this promising gravimetric capacity and cyclic performance, H_2O_2 treated Ti_2CT_x demonstrated excellent performance at current densities as high as 1000–5000 mA/g. After being cycled at 5000 mA/g, the cell was retested at 1000 mA/g, showed the specific capacity of 280 mAh/g at the 1000th cycle (compared to 297 mAh/g after the 50th cycle), indicating excellent rate performance of oxidized Ti_2CT_x . This ability of handle high current densities makes Ti_2CT_x a suitable candidate for Li ion capacitors.

4. Conclusions

We have demonstrated that H_2O_2 treatment is a scalable and cost effective room temperature method to produce $\text{TiO}_2/\text{Ti}_2\text{C}$ hybrid materials. The presence of TiO_2 was observed by XRD, Raman, XPS and HRTEM. The MXene powder treated in H_2O_2 for 5 min showed the fivefold increase in specific surface area, as compared to as-prepared MXene powder. In addition, when H_2O_2 treated MXene powder was tested as anode in Li ion batteries, it showed a significantly improved performance. The excellent battery performance is mainly attributed to the higher surface area accessible to Li ions, which comes from the opening/swelling of MXene layers due to the H_2O_2 treatment and titania formation. Furthermore, the high rate performance and excellent cycle life make partially oxidized MXene a viable candidate for Li ion capacitors.

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List of Figures

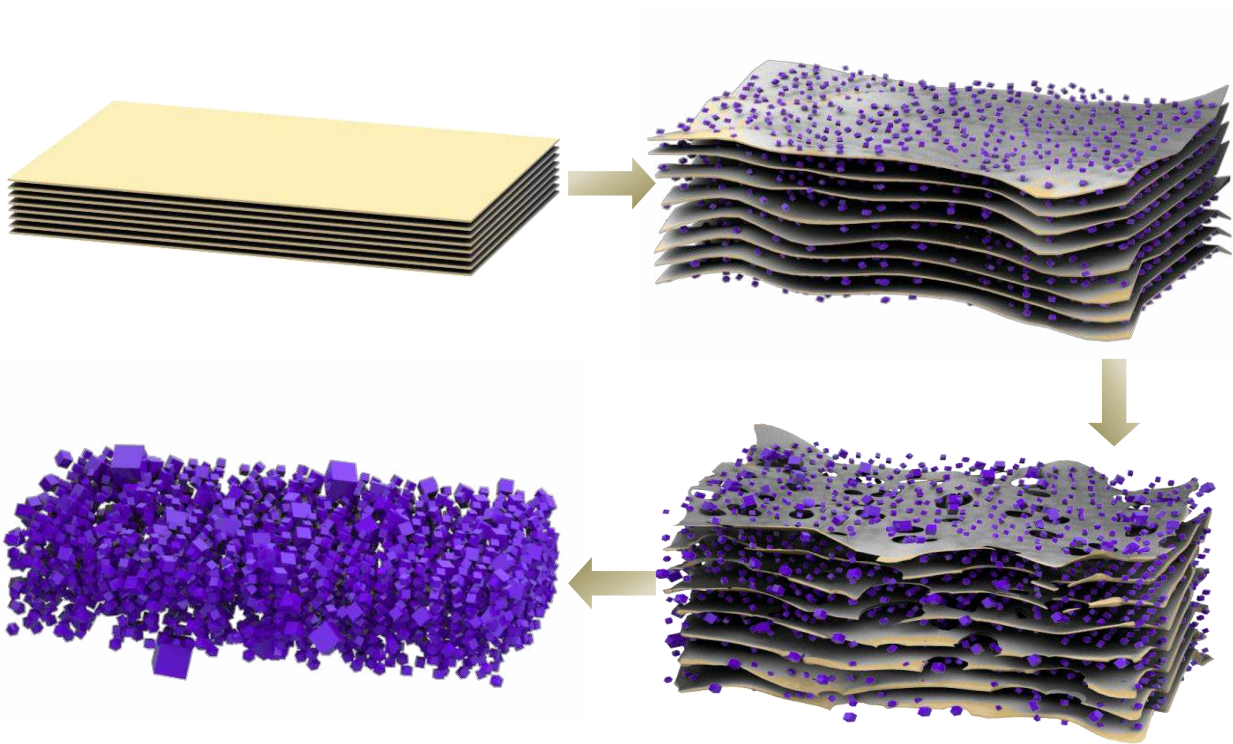
Figure 1: Characterization of as-prepared and H₂O₂ treated MXene powder (immersion time \approx 5 minutes): (a) XRD patterns (b) Raman spectra and (c) SEM image of a typical H₂O₂ treated MXene flake

Figure 2: High-resolution Ti 2p and C 1s XPS spectra: (a, b) as-prepared MXene, (c–d) H₂O₂ treated MXene (\approx 5 minutes) and (e–f) H₂O₂ treated MXene (\approx 5 hours)

Figure 3: Low- and high-magnification TEM images, and SAED patterns: (a–c) as-prepared MXene, (d–f) H₂O₂ treated MXene (\approx 5 minutes) and (g–i) H₂O₂ treated MXene (\approx 5 hours)

Figure 4: Electrochemical characterization of as-prepared and H₂O₂ treated MXenes (immersion time \approx 5 minutes): (a) CV curves, (b) galvanostatic charge/discharge curves for H₂O₂ treated MXene, (c) cyclic performance at 100 mA/g, 500 mA/g and 1000 mA/g (solid points - H₂O₂ treated MXene; hollow points - as-prepared MXene) and (d) rate-ability assessment of H₂O₂ treated MXene (\approx 5 min) at different current densities

TOC:



Schematic illustration of room temperature oxidation of MXene (Ti_2CT_x) by H_2O_2

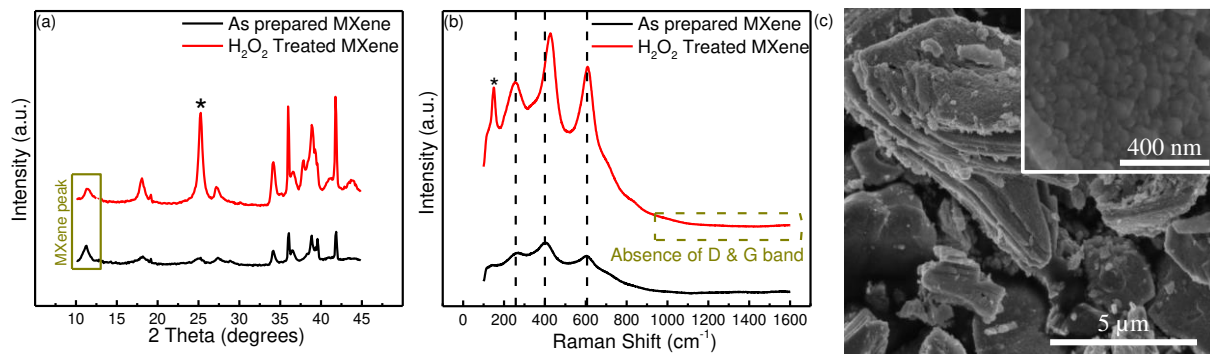


Figure 1: Characterization of as-prepared and H_2O_2 treated MXene powder (immersion time ≈ 5 minutes): (a) XRD patterns (b) Raman spectra and (c) SEM image of a typical H_2O_2 treated MXene flake

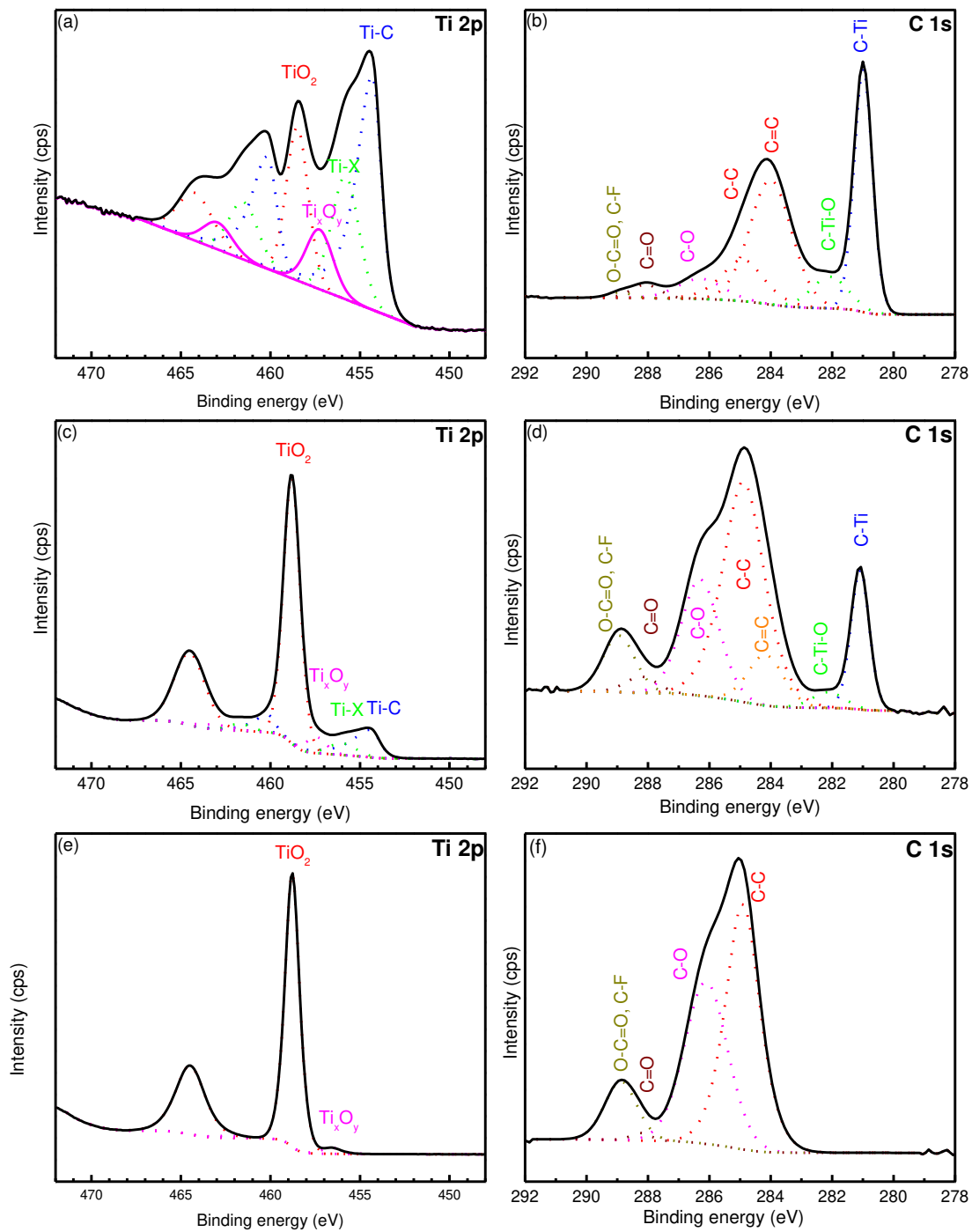


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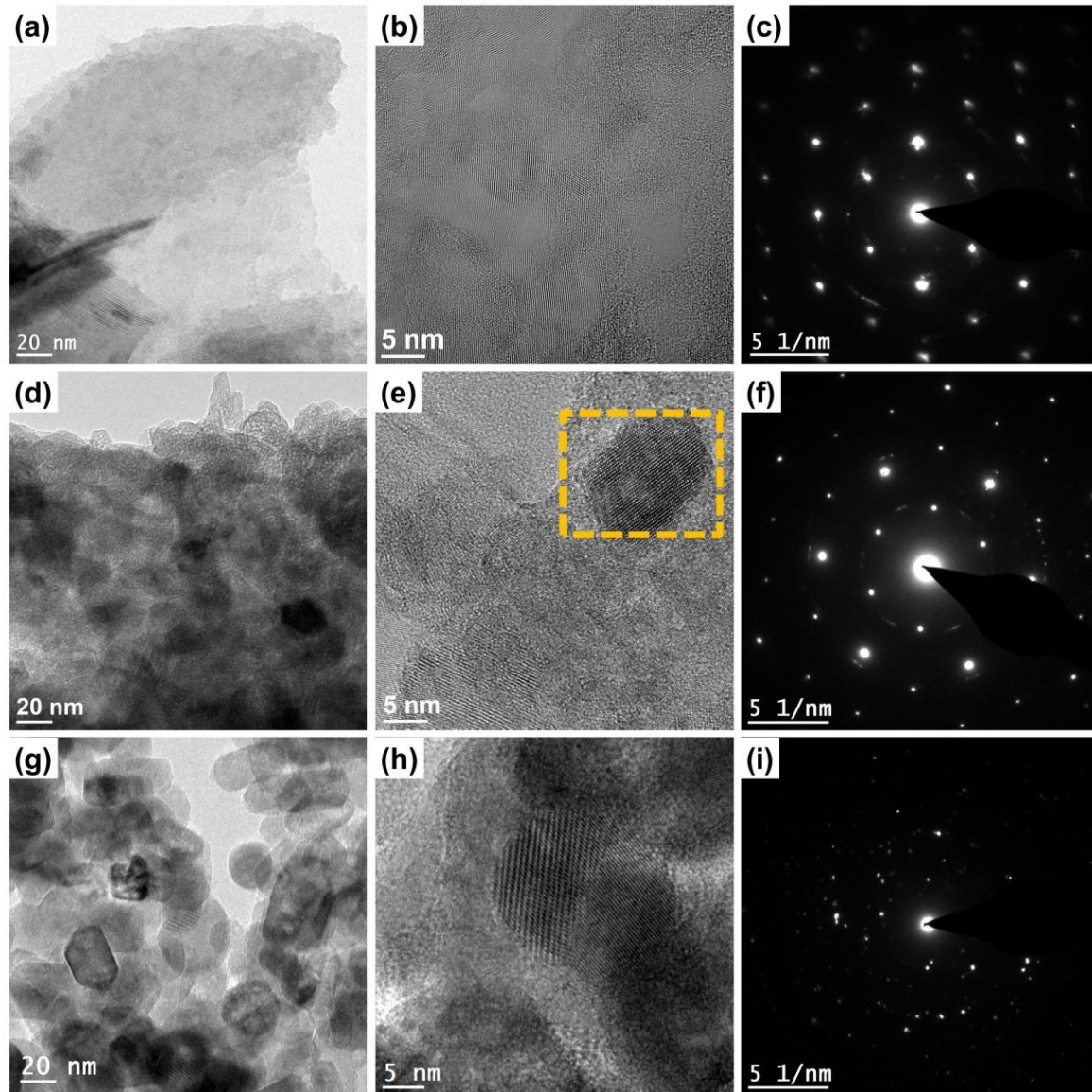


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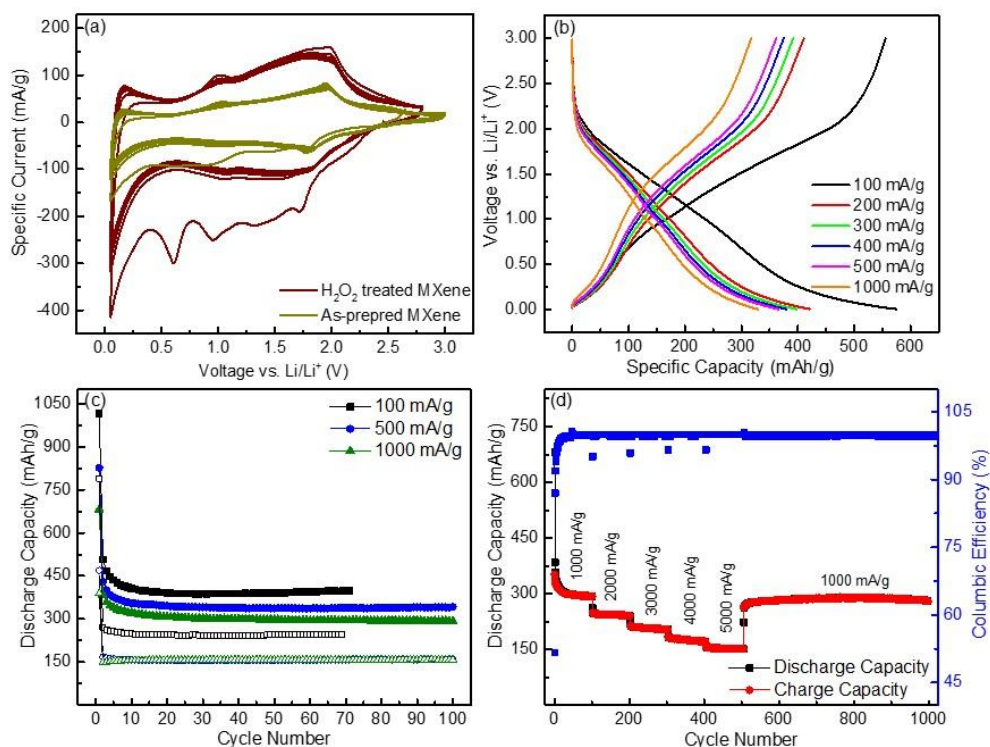


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