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Delamination of MXenes using bovine serum albumin



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ABSTRACT

Delamination of two-dimensional materials is a requisite step for exploiting their unique properties. Herein, we report on the formation of stable colloidal solutions of Ti_3C_2 and $Mo_2Ti_2C_3$ MXene nanosheets by the dispersion and electrostatic exfoliation of stacked multilayer MXenes in the presence of albumin. Delamination of multilayered MXenes into atomically thin nanosheets resulted in stable colloidal solutions with good stability due to the adsorption of albumin, which prevents re-aggregation of the few-layer nanosheets. Cascading centrifugation was used to produce monodisperse colloids. This study demonstrates a processing method that can be utilized to prepare MXenes for biomedical applications. Since protein adsorption onto nanomaterial surfaces plays a significant role in many fields, including medicine, biology, pharmaceuticals, and environmental engineering, albumin coated MXenes may find many applications.

1. Introduction

Two-dimensional (2D) materials, such as graphene and its modifications, transition metal dichalcogenides (TMDs), hexagonal boron nitride, and black phosphorous, have received considerable attention in recent years due to their diverse range of electrochemical, optical, electronic, and chemical properties [1–4]. 2D materials are generally produced *via* exfoliation, or separation, of the individual 2D sheets from their bulk, layered structures by breaking the weak van der Waals interactions between adjacent layers. Solution processable 2D nanomaterials are suitable for a wide range of applications due to their ease of processing and unique surface chemistries. For instance, liquid-phase exfoliation (LPE) techniques, such as shear exfoliation, sonication, and intercalation induced delamination, have been widely used to produce solution processable, high yield batches of 2D materials suitable for large-scale manufacturing [3,5]. Solution stabilization methods that employ polymers and protein-based stabilizing agents are also applicable to solutions containing 2D materials [6,7].

The family of 2D transition metal carbides, carbonitrides and nitrides known as MXenes are a rapidly growing class of 2D materials. MXenes are usually produced by the selective etching of the 'A' atomic layers from ternary, layered MAX phases, where M is a transition metal (Ti, V,

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Cr, Nb, etc.), A is an element from group IIIA or IVA (Al, Si, Sn, In, etc.), and X is C and/or N [8]. In contrast to the parent MAX phase, the 2D sheets of MXenes have surface terminations (-O, -OH, and -F) due to the wet chemical etching process. The hydrophilic 2D MXene sheets are easily dispersed in aqueous media to form highly stable colloidal solutions. The chemical formula of the most widely studied MXene, titanium carbide, following the etching process can be represented as $Ti_3C_2(OH)_rO_vF_z$, where the exact surface terminations composition depends on the synthesis method used [9-11]. However, for brevity Ti₃C₂(OH)_xO_yF_z will be referred to as Ti₃C₂ throughout the remainder of the manuscript. Previous studies have demonstrated that Ti₃C₂ can be dispersed in aqueous solutions as well as polar organic solvents resulting in stable colloidal solutions of MXene nanosheets [12,13] and showed that adsorption of amino acids on a Ti₃C₂ MXene was dominated by van der Waals forces [14]. To use Ti₃C₂ or any other MXene, in biomedical or therapeutic treatments [15], the 2D MXene flakes must be dispersed in biological fluids. In these situations, the biocompatibility of the dispersed MXene is of paramount importance [16]. To test the feasibility of dispersing MXenes in biologically fluids, it was demonstrated that exfoliated Ti3C2 suspended in water could be solvent exchanged with solutions containing the synthetic protein TR42 to create jettable MXene-protein inks [17]. While these MXene-protein inks are advantageous for printing, there are several processing steps required to disperse Ti₃C₂ in the protein containing solutions. To reduce the number of processing steps required to suspend MXenes in biological solutions, we investigated the use of one of the most common proteins, bovine serum albumin (BSA), to delaminate Ti₃C₂. BSA-assisted delamination resulted in stable, colloidal MXene-BSA solutions in a single step, directly from freshly etched multilayer MXene.

Due to the amphiphilic nature of BSA, solutions of albumin have been used to produce stable aqueous dispersions of graphene from graphite, atomically thin tungsten trioxide (WO₃) nanosheets from WO₃ powder, and transition metal dichalcogenides, specifically MoS₂, from their bulk precursors [18–21]. These studies demonstrated that the high dispersibility and stability of the nanomaterial colloidal solutions was due to BSA functioning as a surface ligand. In addition to serving as an effective exfoliating agent, BSA is a strong stabilizing agent that prevents re-aggregation of few-layer nanosheets due to the large dimensions of the BSA molecule (14 nm \times 4 nm \times 4 nm) [22]. The negatively charged groups of the first and second domains of the amino acid sequences of BSA are positioned inside the globular structure of the protein, resulting in the positively charged regions being located at the surface of the protein [23].

In this study, we report on the formation of stable colloidal solutions of Ti₃C₂ nanosheets by the electrostatic exfoliation and dispersion of Ti₃C₂ in a BSA phosphate-buffered saline (PBS) solution in a single step by using sonication without any further chemical treatment. BSA was chosen for producing dispersions of exfoliated Ti₃C₂ since albumin is the most plasma abundant protein, which makes BSA solutions a proper biological model system. Furthermore, we show that stable colloidal solutions of Ti₃C₂ at concentrations of 4 mg/mL in BSA are possible with good stability. It should be noted that the as-produced Ti₃C₂ suspensions were polydisperse in terms of the lateral dimensions of the Ti₃C₂ flakes and the number of MXene layers contained in each colloidal particle. Therefore, to produce monodisperse colloidal solutions, we differentiated the Ti₃C₂-BSA suspensions using cascading centrifugation. To show that this method is applicable to various MXenes, we expanded the study to include another MXene composition, namely Mo₂Ti₂C₃, which has a larger number of atomic layers (M₄C₃ structure) and a different surface chemistry (Mo-transition metal surface). Ti $_3C_2$ and Mo $_2Ti_2C_3$ could both be exfoliated into few-layer nanosheets using BSA solutions, which may result in attractive properties arising from the 2D anisotropy and highly accessible surface area of 2D flakes. This method of exfoliating MXenes may prove useful in applications where aqueous, protein-stabilized suspensions of nanomaterials are needed in photothermal therapy, medical imaging or drug delivery.

2. Materials and methods

2.1. Synthesis of Ti_3C_2 and $Mo_2Ti_2C_3$

 $\rm Ti_3C_2$ was synthesized by selective etching of the A element from $\rm Ti_3AlC_2$ using 30 wt% hydrofluoric acid (HF) for 5 h at 35 °C. $\rm Mo_2Ti_2C_3$ was synthesized from $\rm Mo_2Ti_2AlC_3$ by etching in 50 wt% HF at 55 °C for 96 h. Both reaction mixtures were washed by centrifugation (3500 rpm for 3 min), followed by decantation of the acidic supernatant, and redispersion of the sediment with deionized water. This process was repeated until the pH reached ~6. Multilayered powder (ML-Ti_3C_2 or ML-Mo_2Ti_2C_3) was obtained by re-dispersing the sediment after the final wash and vacuum filtering the dispersed sediment through a porous PVDF membrane (0.45 μm pore size, Millipore-Sigma, USA) before drying the powder in a desiccator overnight.

2.2. Delamination using a BSA solution

ML-Ti₃C₂ powder was used for the fabrication of colloidal solutions of MXene nanosheets by delamination in BSA phosphate-buffered saline solutions. In the first step ML-Ti₃C₂ (600 mg) was dispersed in 120 mL of an aqueous phosphate-buffered saline (PBS, 1X) solution using an ultrasonic bath for 2 h (Branson Ultrasonic Cleaner, USA, 40 kHz). The ML-Ti₃C₂-PBS suspension was then equilibrated by allowing the suspension to rest in the PBS aqueous solution for 24 h. ML-Ti₃C₂ particles settled at the bottom of the vial and were separated from the PBS aqueous solution by decantation. Afterwards, the ML-Ti₃C₂ was redispersed in another 120 mL of PBS aqueous solution. For delamination, 30 mL of the ML-Ti₃C₂-PBS aqueous suspension (concentration of 5 mg/mL) was added to 20 mL solutions of BSA with different known concentrations of BSA (0.025, 1.0, 5.0 and 10 mg/mL). The final concentrations of BSA in the Ti₃C₂ suspensions were 0.01, 0.4, 2.0 and 4.0 mg/mL. The Ti₃C₂-BSA solutions were sonicated for 2 h and then shaken at 150 rpm for 24 h. The Ti₃C₂-BSA suspension kept stationary for 24 h to allow larger ML-Ti₃C₂ particles to sediment out prior to decanting the black supernatant. Size selection was performed via cascading centrifugation from 1000 to 12,000 rpm in 1.5 mL Eppendorf centrifuge tubes.

2.3. Materials characterization

Particle size and zeta potential measurements (Nano ZS Zetasizer, Malvern Panalytical, UK) were conducted in a polystyrene cuvette and a capillary cell, respectively. Five measurements were recorded for each test and the averages reported. Ultraviolet-visible (UV-Vis) spectroscopy (Evolution 201, Thermo Scientific, US) was performed from 250 to 1100 nm in a 10 mm path length quartz cuvette. UV-Vis spectroscopy measurements were performed on the as-produced solutions with no dilution. Raman spectra were recorded using a Renishaw Raman microscope (Renishaw, UK) with a LEICA CTR6000 (Leica, DE) setup with a 785 nm laser, a 1200 lines mm⁻¹ grating at a laser power of 1% with a 63x objective. Two accumulations were collected for each spectrum with a dwell time of 20 s for each accumulation. Scanning electron microscopy (SEM) images were taken using a Zeiss Supra 50VP (Zeiss, DE) with an accelerating voltage of 5 kV.

3. Results and discussion

The variable interlayer spacing of MXenes (10–20 Å) allows for spontaneous intercalation of a variety of inorganic and organic cations which are beneficial for intercalation assisted delamination. However, BSA (14 nm \times 4 nm \times 4 nm) [22] is too large to enter the interlayer spacing of MXene, therefore the mechanism of delamination must differ from intercalation. The amphiphilic nature (hydrophobic/hydrophilic domains) of BSA enables delamination of MXene *via* a similar mechanism as the separation of graphene from graphite using the "scotch-tape" method [24]. BSA molecules cover the ML-MXene particles and peel

 Ti_3C_2 flakes off of the large particles to form a colloidal solution of few-layer nanosheets (Fig. 1a).

A transparent supernatant was obtained by sonicating Ti_3C_2 multilayered powder in a PBS solution at pH 7.2 with a BSA concentration of 0.01 mg/mL (Fig. 1b). By increasing the concentration of BSA to 0.4 mg/mL a dark colloidal solution was produced, indicating the exfoliation of Ti_3C_2 using a biological fluid. Increasing the concentration of BSA further results in Ti_3C_2 being delaminated to form stable colloidal solutions of MXene nanosheets. SEM images of the multilayer particles show the accordion-like morphology that is typically observed after HF etching (Fig. 1c). Following BSA solution processing, exfoliated fewlayer particles can be seen (Fig. 1d). These thin multi-layer particles are not transparent under the electron beam, unlike single layer flakes [25].

The colloidal state of the Ti₃C₂ flakes in the BSA solutions, after the supernatant was separated from the MXene sediment, was also confirmed by SEM images of Ti₃C₂ flakes from the supernatant that were filtered through a porous alumina membrane (Fig. 1d). From the SEM images, Ti₃C₂ flakes larger than 1 µm in their lateral dimensions can be observed, however, from dynamic light scattering (DLS) measurements, the average particle size distribution of the supernatant solutions was estimated to be approximately 300 nm. The BSA-Ti₃C₂ solution was vacuum filtered through a porous polypropylene membrane (0.064 µm pore size, Celgard 3501, Celgard USA) to create a freestanding film, where the cross-section SEM image shows a several micron thick, densely packed assembly of Ti₃C₂ flakes (Fig. 2a).

Raman spectroscopy is a fast, reliable and non-destructive technique for characterizing MXenes [26]. As shown in Fig. 2b, the Raman spectra of Ti_3C_2 -BSA and Ti_3C_2 have similar peaks, indicating that delamination by BSA does not affect the chemical nature of the MXene. The Raman spectrum showed the typical signatures of Ti₃C₂ that have been reported in the literature [26]. The mode at \sim 126 cm⁻¹ is due to in-plane vibrations of middle plane Ti and carbon atoms (Eg symmetry) due to the transverse surface plasmonic of Ti_3C_2 at ~780 nm, which meets the resonance condition since a red diode laser was used for acquiring the Raman spectra. The peaks from 200 to 500 cm^{-1} correspond to in-plane (E_g) vibrations of surface functional groups bonded to Ti atoms. Bare Ti_3C_2 should have an E_g mode at 158 cm⁻¹ [27], which was shifted to lower wavenumbers due to surface functional groups. Similarly, the mode at 514 \mbox{cm}^{-1} was assigned to A_{1g} out-of-plane breathing of the surface terminations. The mode at 712 cm^{-1} corresponds to the A_{1g} out-of-plane vibrational mode of the C atoms, which is strongly dependent on the surface chemistry [26]. As shown in Fig. 2b, the Eg mode at 126 cm⁻¹ for Ti₃C₂-BSA is sharper relative to Ti₃C₂ while the A_{1g} breathing mode at 728 \mbox{cm}^{-1} for the Ti_3C_2 -BSA is softened relative to the 712 cm⁻¹ peak for Ti₃C₂. Thus, the prominence of the 514 cm⁻¹ band and the relative shifts of the positions of the E_g and A_{1g} modes for Ti₃C₂-BSA relative to Ti₃C₂, indicate interactions of the MXene functional groups with the BSA molecules through hydrogen bonding and electrostatic forces, which facilitates the delamination of multilavered MXenes. X-ray diffraction (XRD) patterns of Ti₃C₂ and the Ti₃C₂-BSA freestanding film are shown in Fig. S1.

To probe the stability of the delaminated solution, as well as to isolate different flake sizes, cascading centrifugation was performed at various centrifugation speeds. The Ti_3C_2 -BSA suspension with a BSA concentration of 4.0 mg/mL was centrifuged at speeds ranging from 1000 to 12,000 rpm for 3 min at each cascading step. After centrifugation, UV-Vis spectra were recorded for the resulting supernatants. The dependence of the extinction intensity at 790 nm on the rotation speed is shown in Fig. 3b. The inset image is a digital photograph of the colloidal



Fig. 1. a) Schematic of the layer-by-layer delamination method for the exfoliation of Ti_3C_2 multilayer particles to produce colloids of few-layer nanosheets (not to scale); b) A photograph of PBS aqueous solutions containing Ti_3C_2 colloids with different concentrations of BSA after separation of the supernatant from the sediment; Scanning electron microscopy (SEM) images of as-produced multilayer (ML) Ti_3C_2 MXene particles, scale bar is 10 μ m (c) and exfoliated Ti_3C_2 MXene flakes on a porous alumina membrane (d) produced by delamination using BSA, scale bar is 1 μ m.



Fig. 2. Cross-sectional SEM image of a freestanding Ti_3C_2 film produced from few-layer Ti_3C_2 flakes from a Ti_3C_2 -BSA aqueous solution, scale bar is 1 μ m. b) Raman spectra of Ti_3C_2 and Ti_3C_2 -BSA.



Fig. 3. a) UV-Vis spectroscopy analysis of BSA (orange curve) and colloidal solutions of Ti_3C_2 -BSA after centrifugation at different speeds; b) Dependence of the extinction intensity at 790 nm with increasing rotation speed. The inset is a photograph of aqueous colloidal solutions of Ti_3C_2 -BSA after centrifugation at different speeds.

 Ti_3C_2 -BSA solutions after centrifugation at different speeds. As the centrifugation speed increases, the concentration of the nanosheets dispersed in the BSA solutions clearly decreases, which is consistent with various literature on other classes of 2D materials [19–21]. However, more significantly, the extinction peak of Ti_3C_2 remains even at high centrifuge speeds, confirming that the Ti_3C_2 remains dispersed.

The as-produced (before centrifugation) Ti_3C_2 solution was composed of flakes with a Z-average (intensity distribution mean) size of 245 nm (Fig. 4a). The dynamic light scattering main intensity peak (a_{DLS}) was at 297 nm for Ti_3C_2 and ~10 nm for the BSA protein alone (Fig. S2). By increasing the centrifuge speed to 1000 rpm, the Z-average and a_{DLS} decreased to 212 and 272 nm, respectively. The size further decreased with increased centrifugation speed, and the sample centrifuged at 12,000 rpm was composed of the smallest flakes (119 and 203 nm, Z-average and a_{DLS} , respectively). The as-produced BSA- Ti_3C_2 solution had a zeta potential value of -10.9 mV at a pH of 7.2 (Fig. 4b). By increasing the centrifuge speed, the zeta potential increased to -10.8 mV (1000 rpm), -8.4 mV (6000 rpm), and -6.0 mV (12,000 rpm). The zeta potential of BSA in a PBS solution at a concentration of 4.0 mg/mL is -10.9 mV at neutral pH and is classified as having low (or incipient) stability in solution. Decreasing the concentration of BSA in the PBS solution (0.01-2.0 mg/mL) results in a decrease in the zeta potential, suggesting that lower concentrations of BSA in PBS solution have a higher degree of colloidal stability (Fig. 4c). However, the concentration of the MXene in solution is higher at higher BSA concentrations, showing there is a correlation between the degree of exfoliation and the protein concentration. The zeta potential is measured *via* an electrophoretic measurement technique, where the conductivity (mobility) of the solution can also be measured (Fig. 4d). Increasing the BSA concentration results in an increase in the conductivity of the solution, as the large protein molecules can transfer charge from one particle to another more rapidly at higher concentrations. When compared to graphene nanoplatelets, which have been studied for the adsorption of BSA [28], Ti₃C₂ performs similarly over a BSA concentration range from 0.025 to 10 mg/mL (Fig. S3).

As a proof of concept, this approach was extended to another MXene composition, $Mo_2Ti_2C_3$, a member of the double-M transition metal carbides family, that has a M_4X_3 structure with Mo atoms on the surface. After exposure to BSA, the exfoliation potential for $Mo_2Ti_2C_3$ is BSA-concentration dependent as the higher concentrations of BSA in PBS



Fig. 4. Characterization of Ti_3C_2 delaminated in aqueous BSA solutions. a) Particle size *versus* centrifugation speed (rpm) determined by dynamic light scattering (DLS): average particle size (blue) and the DLS main intensity peak, often termed a_{DLS} , (green); b) Zeta potential and particle size *vs.* rotation speed; c) Zeta potential and particle size *vs.* BSA concentration in mg/mL; d) Conductivity and mobility measured in BSA aqueous solution.



Fig. 5. $Mo_2Ti_2C_3$ delamination by BSA: a) A photograph of PBS aqueous solutions of the $Mo_2Ti_2C_3$ colloids at different concentrations of BSA after static separation (24 h) of the supernatant from the sediment; b) The freestanding films of Ti_3C_2 –BSA (left) and $Mo_2Ti_2C_3$ -BSA (right), obtained after filtration using a polypropylene membrane (Celgard 3501, pore size 0.064 μ m); c) UV-Vis spectroscopy analysis of BSA (orange curve) and colloidal solutions of $Mo_2Ti_2C_3$ -BSA (concentration of BSA is fixed at 4 mg/mL) for different centrifugation speeds and d) Dependence of the extinction intensity at 375 nm on the centrifugation speed. Inset photograph shows BSA aqueous solutions of $Mo_2Ti_2C_3$ obtained at different centrifugation speeds.

also yielded solutions with higher concentrations of $Mo_2Ti_2C_3$, especially when compared to the 0.01 mg/mL solution of BSA (Fig. 5a). By vacuum filtering the as-produced $Mo_2Ti_2C_3$ solutions, a freestanding film was fabricated (Fig. 5b). Size selection of the $Mo_2Ti_2C_3$ -BSA solutions displays a different UV-Vis extinction spectrum (Fig. 5c), however, the size selection process follows the same trend as the Ti_3C_2 -BSA solutions, where the MXene concentration decreases with increasing centrifugation speed (Fig. 5d).

4. Conclusion

In this work, we have demonstrated exfoliation of Ti_3C_2 and $Mo_2Ti_2C_3$ MXenes in bovine serum albumin media. By performing cascading centrifugation, the concentration and particle size of the MXene in solution could be controlled. The ability to exfoliate (or delaminate) MXenes directly into BSA solutions demonstrates the feasibility of using protein solutions for the exfoliation and stabilization of 2D MXenes for biomedical and composite applications. These stable MXene-protein dispersions may facilitate the use of MXenes in therapeutic and biomedical applications and demonstrate that protein solutions can be used as an exfoliation agent and stabilization media for MXenes.

CRediT authorship contribution statement

Mykola Seredych: Conceptualization, Methodology, Data analysis and Interpretation, Writing – original draft, Visualization, Writing – review & editing, Supervision. Kathleen Maleski: Conceptualization, Data analysis and Interpretation, Writing – original draft, Writing – review & editing. Tyler S. Mathis: Data analysis and Interpretation, Writing – review & editing. Yury Gogotsi: Conceptualization, Methodology, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.colsurfa.2022.128580.

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