Colorless-to-colorful switching of electrochromic MXene by reversible ion insertion

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ABSTRACT
Electrochromic (EC) materials that change color with voltage have been widely studied for use in dynamic windows. However, colorless-to-colorful switching with high contrast ratio is generically unattainable, especially for colorless-to-black electrochromic materials with an ultrahigh contrast ratio over the entire visible region. In this work, we developed Nb2/3C MXene-based dynamic windows with colorless-to-black switching of up to 75% reversible change in transmittance from 300 to 1,500 nm. By exploring the electrochromic effects of different electrolytes through in situ optical changes and electrochemical quartz crystal microbalance (EQCM), it is found that electrochromic behavior is greatly influenced by the extent of reversible Li+ insertion/deinsertion between the two-dimensional Nb2/3C MXene nanosheets. In addition, a colorless-to-black EC device based on Nb2/3C with an overall integrated contrast ratio over 80% was successfully constructed by a solution-processable spin coating method. This work enables a simple route to fabricate MXene-based high-performance electrochromic smart windows, which is important for further expanding the application of MXenes to optoelectronic and photonic applications.

KEYWORDS
MXenes, electrochromic materials, colorless-to-black switching, high contrast ratio, reversible Li+ insertion

1 Introduction

As smart windows can allow dynamic controlling, tuning and optimizing the ingress and egress of light to flow through buildings and motor vehicles, they have attracted more attention over the world [1–3]. Altering the optical or thermal properties of windows will not only significantly reduce the energy consumption in lighting, heating and air conditioner cooling systems by up to 40%, but also improve the esthetics of interior spaces. Therefore, it is important to develop light-adjusting devices to control and modulate light transmittance of windows with the reduction in energy consumption, versatile colors and fast switching properties [4–6].

Many research efforts have focused on the production of electrochromic materials (ECMs), such as transition metal oxides [7], polymers [8, 9], and small organic molecules [10]. Tungsten oxide (WO3) is a widely studied inorganic ECM because its superior optical memory and cyclic as well as environmental stability can meet commercial requirements [11, 12]. Polyythiophenenes and their derivatives with low-power consumption, facile color tunability through molecular design, and high processability of highly flexible are among the most promising conjugated polymers for the manufacture of electrochromic (EC) devices [13–16]. However, because the design of completely reversible absorptions in transmissive and colored states is extremely difficult, the colorless-to-colorful ECMs, especially the colorless-to-black ECMs with ultrahigh contrast ratio in the entire visible spectrum, are still challenging to achieve [17]. Therefore, until now it is still hard for electrochromic smart windows to replace traditional curtains for providing a private environment, and most of them are used in dimmable architectural windows.

In 2011, a new family of two-dimensional (2D) metal carbides and/or nitrides with metallic conductivity and hydrophobic surfaces was reported. These novel 2D materials are labeled MXenes, which means that they are prepared by etching the A layers in the layered Mn + 1AXn phase [18, 19]. MXenes have already shown great potential for applications in, e.g., energy storage [20–22], electromagnetic interference shielding [23, 24], and transparent conductors [25]. In 2017, a new type of MAX phase was reported (Mo2S3C2AIC), with in-plane chemical ordering for the two M-elements, hence it is referred to as i-MAX [26]. After selective etching of Sc and Al, a Mo2S3C MXene with ordered vacancies was achieved, displaying superior volumetric capacitance and high conductivity. Inspired by the above results, a series of i-MAX phases and their 2D counterpart, either with in-plane chemical ordering or ordered vacancies, were reported [27–30]. Also formation of disordered vacancies in an Nb2/3C MXene was obtained through selective etching of a solid solution MAX phase, (Nb3/5C5/3)2AIC [31].

It is generally accepted that the EC phenomenon based on transition metals can be attributed to the injection/extraction of electrons and ions. EC performance usually depends on the electron transport efficiency of the ECMs and the reversible solid phase diffusion of ions in the EC films. Therefore, MXenes, with
high conductivity for electron transport and with a highly-specific surface area could be excellent potential candidates for ECMs. Thus far, however, there are few reports on the use of MXenes for ECMs, focusing on Ti$_3$C$_2$ MXenes only, likely due to poor performance shown and a lack of explanation for these results. This provides a rationale to go beyond previously explored MXenes, and also explore the effect of introduction of vacancies.

In this research, we developed EC smart windows based on the Nb$_{1.33}$C MXene using a spin coating method. The electrochromic property of Nb$_{1.33}$C was investigated by in situ spectroelectrochemical characterization with uniform switching between colorless and colorful black states over the entire visible region. The results from electrochemical quartz crystal microbalance (EQCM) and Raman spectroscopy indicate reversible lithium-ion intercalation is related to the electrochromic behavior of Nb$_{1.33}$C MXene. Finally, the excellent performance for the colorless-to-black EC device based on Nb$_{1.33}$C MXene with the contrast ratio up to 80% was achieved.

2 Experimental

2.1 Preparation of the Nb$_{1.33}$C MXene

Powders of (Nb$_{2/3}$Sc$_{1/3}$)$_2$AlC were synthesized by a solid state reaction of elemental powders as previously demonstrated [15]. Powders of Nb, Sc, Al, C were placed in an agate mortar with a 4/3/2/3:1:1 molar ratio and manually mixed. The mixture was heated at a rate of 5 °C·min$^{-1}$ to 1,400 °C and held for 2 h. After furnace cooling, the lightly sintered sample was crushed with the agate mortar and pestle and sieved through a 450-mesh sieve. Nb$_{1.33}$C MXene was synthesized by selectively etching Sc and Al. Briefly, 1 g of (Nb$_{2/3}$Sc$_{1/3}$)$_2$AlC was added to a Teflon bottle containing 20 mL 48% HF and stirred for 24 h at room temperature (RT). The acid was removed by washing with deionized (DI) water for several cycles, multilayer MXene was delaminated to a single layer or few layers of Nb$_{1.33}$C MXene by intercalating with TBAOH. The concentration of Nb$_{1.33}$C solution was measured by filtering a known volume of colloidal dispersion through a polypropylene filter (3501 Coated PP, 0.064 μm pore size, Celgard LLC, USA), followed by overnight drying under vacuum and weighing.

2.2 Preparation of Nb$_{1.33}$C transparent film

The transparent thin films were fabricated by a spin-coating approach. The substrates of indium tin oxide (ITO) were cleaned by detergent and followed by TL-1 treatment. Then 30 μL delaminated Nb$_{1.33}$C colloidal solution (15 mg mL$^{-1}$) was pipetted onto the substrate, which was fastened to the rotating plate of a spin-coater. By varying the spinning speed (ranging from 1,000 to 4,000 rpm), we controlled the film thickness, and in turn the transmittance. The obtained thin films were kept in a vacuum desiccator overnight before characterization.

2.3 EC device fabrication

For the preparation of gel electrolyte of EC device, we mixed poly(methyl methacrylate) (10 kDa) and LiClO$_4$ (with a molar ratio of 10:1) and dissolved them in 25% w/v acetonitrile. The acetonitrile solvent was stirred and evaporated at 80 °C before gelation. The polydimethylsiloxane (PDMS) as a frame was placed on the ITO and the gel electrolyte was dropped within the PDMS frame. Then the MXene coated ITO glass was placed face-down on the gel-coated slide and the two electrodes were pressed together. Finally, ultraviolet (UV) curing glue was dripped on the edge of the device and cured for 60 s under a 256 nm UV lamp.

2.4 Characterization

The zeta potential and dynamic light scattering of Nb$_{1.33}$C MXene was tested using a Zetasizer ZEN3600 (Malvern Instruments Ltd., UK). Scanning electron microscopy (SEM) imaging was performed using a SEM LEO 1550 Gemini operated with an acceleration voltage at 5 keV. Scanning transmission electron microscope (STEM) was combined with high angle annular dark field imaging (STEM-HAADF) in a double-corrected Linköping FEI Titan360–300, operated at both 300 and 60 kV. X-ray diffraction (XRD) was carried out on a PANalytical X’Pert powder diffraction with Cu source ($\lambda$$_{Cu}$$ = 1.54 Å). Graded Bragg-Brentano with a 1/4° divergent and 1/2° anti-scatter slits, and a 5 mm anti-scatter slit together with a Soller slit (with an opening of 0.04 radian) in the incident and the diffracted beam sides were used, respectively. The optical spectra of the MXene thin films were measured in the range of 300–1,500 nm by ultraviolet–visible–near infrared ray (UV–vis–NIR) spectroscopy (LAMBDA 950, Perkin Elmer). Atomic force microscopy (AFM) was performed at ambient conditions (room temperature in a lab) using a Veeco DI Dimension 3100 scanning probe microscope, equipped with the nanoscope IV electronics. The measurements were performed in tapping mode using Si tips (PPPNCCHR-50 from Nanosensors) with a tip radius of curvature < 7 nm. The thicknesses of spin-coated films were determined with a Bruker Stylus Profiler (Model: Dektak XT). Raman spectroscopy was done using an inverted reflection mode with a Renishaw microscope (2008, Gloucestershire, UK), equipped with 50× objective and a LEICA CTR6000 setup with 532 nm laser, 1,800 lines·mm$^{-1}$, grated at 10% of maximum intensity. Electrochemical experiments were performed using autolab PGSTAT30 MBA.

3 Results and discussion

3.1 Synthesis and characterization of Nb$_{1.33}$C MXene film

The 2D Nb$_{1.33}$C MXene was synthesized by etching a laminated solid solution (Nb$_{2/3}$Sc$_{1/3}$)$_2$AlC MAX phase for removal of both the Sc and Al atoms. The target MXene with hydrophilic surface can be easily processed in aqueous solvents to form a colloidal solution at room temperature through intercalation and delamination using TBAOH. The synthesized Nb$_{1.33}$C colloidal dispersion has the Tyndall effect and exhibits inherent colloidal stability caused by negative surface charges (Fig. S1 in the Electronic Supplementary Material (ESM)). The lateral size distribution of the Nb$_{1.33}$C single sheets in the colloidal solution is concentrated at the range 0.5–2 μm (Fig. 1(a) and Fig. S2 in the ESM) and the thickness of the flakes is around 2 nm, according to the AFM measurements in Fig. 1(b). The hydrophilic surface of MXene makes it solution processable, allowing formation of MXene films through a variety of techniques, such as vacuum assisted filtration, spray, spin, or dip coating [32–35]. In order to meet the requirements of transparent electrodes for smart windows, MXene films obtained by spin-coating are chosen for this work, which could yield smooth and transparent films on any substrates, such as conductive or nonconductive and even flexible substrates (Fig. S3 in the ESM). The XRD patterns of the etched materials show the typical increase in the interlayer spacing compared to the parent phase. This is a typical phenomenon of the conversion from MAX phase to MXene which reflects the replacements of Sc and Al by the surface terminations of –O, –OH, and/or –F and presence of water layers [19, 36, 37]. Compared with the Nb$_{1.33}$C paper obtained by vacuum filtration, the layer spacing of the film obtained by spin coating increased from 14.3 to 19.6 Å (Fig. 1(c)),
which is consistent with the less compact structure from cross-sectional SEM images (Figs. 1(d) and 1(e)). The relatively loose arrangement of Nb$_{1.33}$C nanosheets will facilitate the insertion and extraction of ions in the spin-coated MXene film. In addition, as seen from the STEM images, it can be found that the Nb$_{1.33}$C flakes contain vacancies and local clusters thereof, in size ranging between 0.1 and 2 nm (Fig. 1(f)). These additional vacancies may provide channels for ion transport.

3.2 In situ electrochemical and optical characterization of Nb$_{1.33}$C thin films

As shown in Fig. 2(a), the cyclic voltmetric (CV) curve of the Nb$_{1.33}$C film is recorded within the potential range from 1.3 to 5.3 V vs. Li/Li$^+$. The CV curve shows an obvious oxidation and reduction couple from 3.3 to 1.3 V. Spectroelectrochemical studies of spin-coated Nb$_{1.33}$C films on ITO were performed in an electrochemical cell with commercial UV-visible cuvette to evaluate the electrochromic properties. The electro-optical properties of Nb$_{1.33}$C films were studied by in situ UV-vis-NIR spectroscopy with propylene carbonate (PC) containing 1 M LiClO$_4$ as an electrolyte. The spectroelectrochemistry of Nb$_{1.33}$C film upon reduction was reflected by a series of UV-vis-NIR absorbance curves, which were changed under various applied potentials, as shown in Fig. 2(b). The corresponding colors of the spin-coated film are related to the different electrode potentials. The Nb$_{1.33}$C film possesses initial low absorbance across the visible to infrared spectrum. Stepwise reduction of the Nb$_{1.33}$C film from 5.3 to 1.3 V vs. Li/Li$^+$ causes an increase in absorbance over the entire wavelength range, especially when the potential drops to 1.7 V. This is consistent with the onset reduction potential in the CV curve. Moreover, the absorbance profile during switching is relatively flat over the entire visible spectrum, which gives rise to an esthetically pleasing clear-to-grey-to-black transition. Therefore, the corresponding color of Nb$_{1.33}$C film is visible transparency in the oxidized state (Fig. 2(b), top left inset) and black in the reduced state (Fig. 2(b), top right inset). Furthermore, the absorbance spectra demonstrate that the window also effectively modulates infrared light, which makes it useful for controlling the flow of heat in and out of spaces such as buildings and motor vehicles.

The optical switching is qualitatively evidenced by applying a square wave potential-step coupled with optical spectroscopy in PC containing 1 M LiClO$_4$. The electrochromic parameters, such as optical contrast ratio ($\Delta T\%$), response time and coloration efficiency of the Nb$_{1.33}$C films were investigated by switching the transmission with respect to potentials at the specific absorption wavelength of 700 or 1,200 nm, as shown in Fig. 3 (summarized in Table S1 in the ESM). Based on the CV data, the electrochemical potentials used for the coloration/bleach conversion were selected to ensure the reduction and oxidation reactions (Fig. 2(a)). Therefore, the color switching was qualitatively evidenced by applying a square wave potential between 5.3 and 1.3 V vs. Li/Li$^+$ at high frequency of 0.01 Hz. For Nb$_{1.33}$C, a reversible oscillation between black and colorless states was observed. The optical contrast ratios of Nb$_{1.33}$C between colored state at 1.3 V and bleached state at 5.3 V are 75.0% at 700 nm and 68.1% at 1,200 nm (Figs. 3(a) and 3(b)), respectively. It is worth noting that the Nb$_{1.33}$C films have very high integrated contrast ratios in both the visible and infrared regions, making them suitable not only for truly smart curtains, but also to control the temperature by adjusting infrared light in and out.

3.3 Understanding the mechanism involved in electrochromic changes

Currently, the most well-developed electrochromic technology is based on intercalation/deintercalation of small ions in electrode materials. Among the best known representatives is WO$_3$, which has already been commercialized and appears in our daily.
To understand the EC mechanism of Nb$_{13}$C MXene, transmittance changes under different states (Fig. S5 in the ESM), observed from in situ EQCM (Fig. 4), and transmittance changes with time (Fig. 5) were analyzed using different electrolytes. The transmittance of Nb$_{13}$C film shows a relatively flat curve in both the colored state and the bleached state at LiClO$_4$ electrolyte, and the integrated contrast ratio almost reaches 75% (Fig. S5(a) in the ESM). LiBF$_4$ and NaClO$_4$ electrolytes show a similar higher contrast ratio compared with LiClO$_4$ (Figs. S5(b) and S5(c) in the ESM). However, the transmittance of Nb$_{13}$C showed no significant difference between the colored state and the bleached state for tetrabutylammonium tetrafluoroborate (TBABF$_4$) electrolyte with the very low contrast ratio of $\Delta$T% < 10% (Fig. S5(d) in the ESM). From the above results, it seems that cations have a greater impact on the electrochromic properties of Nb$_{13}$C than anions.

To corroborate our hypothesis, in situ EQCM was performed within a three-electrode configuration. The triangle wave potential step method was employed for studying anion and cation contributions to the electrochromic properties of Nb$_{13}$C. According to Sauerbrey’s equation (Eq. (S3) in the ESM), frequency response ($\Delta f$) and the electrode mass ($\Delta m$) are inversely proportional. The potential scan and simultaneous EQCM response are collected for Nb$_{13}$C films processed by four different electrolytes, as shown in Fig. 4 and Fig S6 in the ESM. The potential first started from 3.8 to 1.3 V and then switched back to 5.3 V. For LiClO$_4$, the frequency shows the same change versus the potential variation. The increase of the electrode mass observed during the negative potential is associated with cation adsorption (Li$^+$), while the electrode mass decreases during desorption at positive potentials. In addition, with multiple cycles, the electrode material exhibits a reversible mass change with the potential switch. In addition, from the mass change calculated by the frequency change, we can get that the number of lithium ions inserting into each Nb$_{13}$C is 2.83 (Fig. S7 in the ESM). In Fig. 4(b), the mass of the electrode material with LiBF$_4$ electrolyte also shows a reversible change with the switch of the potential, which is similar to LiClO$_4$. However, when the electrolyte is changed to TBABF$_4$ with the same anion as LiBF$_4$, the mass of the electrode gradually increases with multiple cycles, indicating that the anion TBA$^-$ is partly trapped in the Nb$_{13}$C film and does not migrate out at the positive potential. It must be mentioned that TBA$^-$ is used as an intercalant when preparing single layer Nb$_{13}$C, and negatively charged Nb$_{13}$C and positively charged TBA$^-$ have a strong interaction, which makes TBA$^-$ difficult to migrate out under positive potential, resulting in a continual increase in electrode mass (as shown in Fig. 4(c)). This irreversible ion migration in and out is very detrimental to electrochromism.
Finally, we chose NaClO₄ with the same anion as LiClO₄ but with a different metal cation as the electrolyte. Similar to LiClO₄, the increase and decrease of the electrode mass were observed during the negative and positive potentials, respectively (Fig. 4(d)). However, the mass of the electrode is not completely reversible, but slightly increases with the cycle. This shows that a small number of cations (Na⁺) are trapped in the electrode material. Based on the results of in situ EQCM, we conducted optical switching in different electrolytes at the absorption wavelength of 700 nm (Fig. 5). Nb₁₃C films show the same stable optical switching in the electrolytes containing Li cation (Figs. 5(a) and 5(b)), but exhibit very low optical contrast ratio in the organic electrolytes (TBABF₄, Fig. 5(c)). In NaClO₄, the Nb₁₃C exhibits higher optical contrast ratio at the beginning, but gradually decreases with the cycle (Fig. 5(d)), as the metal cations are captured by the Nb₁₃C film corresponding to the colored state. Combined with the variations of spectra and mass of Nb₁₃C films in different electrolytes with potentials, it indicates that the excellent electrochromic performance of Nb₁₃C is due to the reversible intercalation of Li cations. To further prove further our preliminary conclusion, in situ electrochemical Raman spectroscopy was performed in a three-electrode configuration in the LiClO₄ electrolyte. Figure 6(a) shows the Raman spectra obtained from the Nb₁₃C film during the coloring process. By applying a cathodic potential from 3.8 to 1.3 V vs. Li/Li⁺, the electrostatic repulsion between adjacent layers in the layered Nb₁₃C will decrease with increase of lithium content, resulting in the Raman peak (400 cm⁻¹) shifting up to higher wavenumbers. Finally, an obvious broad peak is formed by merging with the peak at 570 cm⁻¹ due to the formation of Li₃Nb₁₃C. Similar Raman results have been reported by lithium intercalated metal oxide [40, 41]. Furthermore, the ex situ XRD was analyzed in the 2θ region between 3° and 7° to probe the lattice expansion or contraction at different applied potentials (Fig. S8 in the ESM). When potentials are applied from 3.8 to 1.3 V, a shift of the peak (2θ = 4.5°) is observed, corresponding to an increase of the c-lattice parameter due to the intercalation of the electrolyte cation.

3.4 Electrochromic device performance

To evaluate further the EC performance of Nb₁₃C film in a practical application, particularly the potential of this as an absolute opaque “smart” curtain with high integrated contrast ratio of transmittance changes, the EC device of Nb₁₃C was fabricated with device architecture of ITO/Nb₁₃C/electrolyte/ITO (Fig. 6(b) inset). The transmission spectra of the device in bleached and colored states are shown in Fig. 6(b), presenting an ultrahigh integrated contrast ratio up to 80%. In the colored state, the transmittance of the device is almost zero. Besides, the EC device at 700 and 1,200 nm after power-off shows excellent performance stability (Figs. 6(c) and 6(d)). In addition, the cycling performance was conducted to examine the durability of the Nb₁₃C-based EC device by repeated switching test between bleach and colored states at 700 nm (Fig. 6(e)). After 1,000 coloration-bleaching cycles, the device showed 95.7% retention of contrast ratio, which demonstrates the excellent stability performance of the EC device during switching operation. It is worth noting that the outstanding performance not only comes from the loosely arranged Nb₁₃C nanosheets obtained by spin coating, but also related to the negligible traps in the lithium ion intercalation process. The superior performance of the Nb₁₃C MXene can significantly expand the industrial market for electrochromic smart-window applications from public places to private places, and brings greater flexibility to build facade design, paving the way for further industrial applications.

4 Conclusions

In summary, the colorless to colorful EC Nb₁₃C MXene was investigated using the dynamic photoelectrochemical test. Electrochromic performance is dependent on the electrolytes, where the optimal performance was observed in the LiClO₄ electrolyte (∆T₇₀₀nm ≈ 75%) under a three-electrode electrochemical testing setup. The mechanism of the electrochromic behavior was studied by in situ transmittance and EQCM spectroscopy. The reversible lithium ion intercalation plays an

Figure 5  In situ measured transmission at 700 nm during cycles between 1.3 and 5.3 V vs. Li/Li⁺ in different electrolytes of (a) LiClO₄, (b) LiBF₄, (c) TBABF₄, and (d) NaClO₄.
important role in EC performance. Furthermore, we demonstrate that the Nb$_{1.33}$C-based hybrid dynamic windows uniformly switch between clear and black states with ~80% optical contrast, and the transmittance of the colored state is almost zero. In addition, the dynamic windows show good transmittance stability in both visible and near infrared regions. This work suggests that MXene-based dynamic window is a promising candidate for the development of new generation electrochromic devices.

Acknowledgements

This work was financed by the SSF Research Infrastructure Fellow Program (No. RIF 14–0074), the SSF Synergy Program EM16–0004, and by the Knut and Alice Wallenberg (KAW) Foundation through a Fellowship Grant, a Project Grant (No. KAW2020.0033), and for support of the electron microscopy laboratory in Linköping University. Support from the National Natural Science Foundation of China (No. 61774077), the Guangdong Joint Research Fund (No. 2020A1515120073) and the Guangzhou Key laboratory of Vacuum Coating Technologies and New Energy Materials Open Projects Fund (No. KFVE20200006) are also acknowledged.

Funding note: Open access funding provided by Linköping University.

Electronic Supplementary Material: Supplementary material (the zeta potential, DLS of Nb$_{1.33}$C and CV of Nb$_{1.33}$C in different electrolytes) is available in the online version of this article at https://doi.org/10.1007/s12274-021-3913-y.

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