

### LETTER • OPEN ACCESS

# Fabrication of MXene transparent conductive films via transfer process

To cite this article: Yuki Shibata et al 2023 Appl. Phys. Express 16 037001

View the article online for updates and enhancements.

## You may also like

- <u>Ti<sub>3</sub>C<sub>2</sub>T\_MXene as surface-enhanced</u> <u>Raman scattering substrate</u> Hayk Minassian, Armen Melikyan, Manuel Rodrigues Goncalves et al.
- Dielectric anisotropy in self-assembling MXene-based lyotropic nematic compounds Marius Andrei Olariu, Tchi Vlad-Bubulac, Tudor Alexandru Filip et al.
- Dielectrophoretic direct assembling of Mxene flakes at the level of screen-printed interdigitated microelectrodes and their evaluation in gas sensing applications Ina Turcan, Tudor Alexandru Filip, Tchi Vlad-Bubulac et al.





This content was downloaded from IP address 130.54.130.253 on 30/06/2025 at 01:21

#### **OPEN ACCESS**

Applied Physics Express 16, 037001 (2023)

https://doi.org/10.35848/1882-0786/acbbb8

## Fabrication of MXene transparent conductive films via transfer process

Yuki Shibata<sup>1</sup>, Rie Suizu<sup>1,2</sup>, Kunio Awaga<sup>1</sup>, Jun Hirotani<sup>2,3\*</sup>, and Haruka Omachi<sup>1,4\*</sup>

<sup>1</sup>Department of Chemistry, Graduate School of Science, Nagoya University, Nagoya, Aichi 464-8602, Japan <sup>2</sup>JST PRESTO, Saitama, 332-0012, Japan

<sup>3</sup>Department of Micro Engineering, Graduate School of Engineering, Kyoto University, Kyoto 615-8540, Japan

<sup>4</sup>Integrated Research Consortium on Chemical Sciences, Nagoya University, Nagoya, Aichi 464-8602, Japan

\*E-mail: hirotani.jun.7v@kyoto-u.ac.jp; omachi@chem.nagoya-u.ac.jp

Received January 25, 2023; accepted February 12, 2023; published online March 9, 2023

In this study, we fabricate MXene transparent conductive films via a transfer process. The results show that the transferred transparent conductive films using titanium carbide MXene have ca. 100 times higher electrical conductivity than conventional spray-coated samples. Transparency and electrical conductivity are easily controlled by changing the amount of MXene materials. The scanning electron microscopy observations reveal that the transferred films have a smooth and uniform MXene flake network. The closer interlayer distance of the MXene flakes when compared to the spray-coated sample, which enables superior electrical conductivity, is confirmed by the X-ray diffraction measurement. © 2023 The Author(s). Published on behalf of The Japan Society of Applied Physics by IOP Publishing Ltd

Xenes, which are emerging two-dimensional (2D) nanomaterials represented by the general formula  $M_n$  $_{+1}X_nT_x$  (M: early transition metals; X: C and/or N, T: a terminal functional group, such as -F, -OH, and =O), have attracted attention in many fields [Fig. 1(a)].<sup>1–5)</sup> Adding to the optical transparency and mechanical flexibility derived from the layered structure, their electronic band structures are drastically varied from semiconducting to metallic characters depending on the M, X, and T atom combinations.<sup>6,7)</sup> MXenes also possess facile solution processability because they are dispersible in aqueous and polar organic solvents without surfactants [Fig. 1(b)] due to the presence of the surface hydroxy groups (-OH), which are different from other 2D nanomaterials, such as graphene, hexagonal boron nitride, and transition metal dichalcogenides. Therefore, various applications, including batteries,  $^{8-10)}$  hydrogen evolution catalysts,  $^{11,12)}_{16-19}$  supercapacitors,  $^{13-15)}$  and flexible sensors,<sup>16–18)</sup> have been demonstrated in recent years.

The titanium carbide MXenes (e.g.  $Ti_2CT_x$  and  $Ti_3C_2T_x$ ) used in transparent conductive film applications have particularly been well studied due to their excellent electrical conductivity.<sup>19–28)</sup> These transparent conductive films are generally fabricated via spin casting<sup>19–23)</sup> or spray coating methods,<sup>24–27)</sup> but both have limitations. Spin casting is only applicable to hydrophilic substrates because of its solvent polarity. It also requires time-consuming optimization and significant material waste to avoid uneven coating. Although the spray coating method is applicable to any kind of substrate, the electrical conductivity of spray-coated films is several hundreds of times lower than that of spin-casted ones. Thus, a concise and versatile method must be developed to realize MXene transparent conductive films exhibiting a sufficiently practical electrical conductivity.

This study describes the transfer method for fabricating  $Ti_3C_2T_x$  MXene transparent conductive films. We recently established the exfoliation of Al-residual multilayer MXene using tetramethylammonium bases to obtain an aqueous  $Ti_3C_2T_x$  dispersion.<sup>27)</sup> A  $Ti_3C_2T_x$  sheet prepared on a membrane filter showed a sheet resistance of ca. 0.2 k $\Omega$ ·sq<sup>-1</sup>, which is a superior conductivity compared to that of the spray-coated transparent conductive films

(i.e.  $\sim 10 \text{ k}\Omega \cdot \text{sq}^{-1}$ ). Therefore, we decided to investigate the transfer of  $\text{Ti}_3\text{C}_2\text{T}_x$  MXene sheets from the filter to the desired substrates. Accordingly, we conducted microscopic observations and spectroscopic characterizations of the fabricated films to clarify the differences in the fabrication process.

To begin our investigation on the  $Ti_3C_2T_x$  MXene film transfer, we first examined a membrane dissolution process used to fabricate carbon nanotube (CNT) transparent conductive films<sup>29,30)</sup> and CNT thin film transistors.<sup>31,32)</sup> During the dissolution process of a nitrocellulose-based membrane filter, most of the  $Ti_3C_2T_r$  flakes were leached out from the substrate to the solvent. Ishizaki and Kurihara recently reported an alternative transfer method for the CNT films instead of dissolving the membrane filter.<sup>33)</sup> Referring to this, we tested the wetted transfer method here [Fig. 2(a)]. A  $Ti_3C_2T_x$  MXene sheet was prepared through the suction filtration of diluted dispersions in 50 ml DI water on a hydrophilic polytetrafluoroethylene (PTFE) membrane filter (H010A047A, ADVANTEC). The filtrated sheet on a membrane filter was immersed into DI water. The upper  $Ti_3C_2T_x$ side of the filter was then affixed to a polyethylene naphthalate (PEN) substrate (Teonex® Q65FA, DuPont Teijin Films). The  $Ti_3C_2T_x$  sheet was transferred onto the substrate after drying over the wetted film composite by heating at 110 °C and peeling off the PTFE membrane filter. Some of the  $Ti_3C_2T_r$  flakes remained on the PTFE filter, and the resultant film showed a mottled pattern, unsuitable for transparent conductive film applications [Fig. 2(b)]. As regards extensive screening, the use of a mixed cellulose ester (MCE) membrane filter (VMWP04700, MF-Millipore) provided uniform  $Ti_3C_2T_x$  MXene films. After the heating treatment until the solvent drying, a composited MCE filter was spontaneously peeled off, and the filtrated  $Ti_3C_2T_x$ MXene sheet was completely transferred onto the PEN substrate. The developed transfer method enabled the fabrication of MXene transparent conductive films on various substrates, including silicon, glass, and stretchable polymers [Fig. 2(c)].

Next, the electrical conductivity of the transparent conductive  $Ti_3C_2T_x$  MXene films was evaluated. The fabricated

Content from this work may be used under the terms of the Creative Commons Attribution 4.0 license. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI. © 2023 The Author(s). Published on behalf of





**Fig. 1.** (Color online) (a) Chemical structures of  $Ti_3C_2T_x$  MXene. (b) Photographic image of the  $Ti_3C_2T_x$  MXene dispersion.

transparent conductive film was dried at 30 °C for 16 h under vacuum conditions (<5 Pa) prior to the measurement. The transparency was determined by the absorption spectra recorded on an ultraviolet-visible spectrophotometer (V-770, JASCO). The sheet resistance ( $R_s$ ,  $\Omega \operatorname{sq}^{-1}$ ) was measured using the four-probe method with a Loresta-AX resistivity meter (MCP-TP06P, Mitsubishi Chemical Analytech). We easily changed the film transparency by tuning the amounts of the MXene dispersion during the filtration process. Figure 3 (red solid circles) depicts the transmittance at the 600 nm wavelength versus the average



**Fig. 3.** (Color online) Plots of the transmittance at 600 nm versus average sheet resistance of the  $Ti_3C_2T_x$  MXene transparent conductive films via the transfer and spray coating methods.



Fig. 2. (Color online) (a) Scheme image of the MXene transparent conductive film fabrication via the transfer method. (b) Photographic images of the transparent conductive films using PTFE or MCE membrane filters. (c) Photographic images of the stretchable transparent conductive film.

sheet resistance of the fabricated transparent conductive films. For comparison, we also prepared spray-coated transparent conductive  $Ti_3C_2T_x$  MXene films (Fig. 3, blue sold squares).  $R_{\rm s}$  at 87% transmittance was 4.7  $\times$  10<sup>3</sup>  $\Omega$  sq<sup>-1</sup>, which was  $\sim 100$  times lower than the sheet resistance of the spray-coated films (3.5  $\times$  10<sup>5</sup>  $\Omega$  sq<sup>-1</sup> at 82% transmittance), including those in the previous reports  $(0.3-1.6 \times 10^6 \Omega \text{ sq}^{-1} \text{ at ca. } 90\%$  transmittance.<sup>24–26)</sup> A smaller deviation was confirmed as an advantage of this transfer method. The transferred  $Ti_3C_2T_x$  MXene films exhibited a higher electrical conductivity compared to the transparent films using graphene dispersion in the aqueous sodium cholate solution  $(2.7 \times 10^5 \ \Omega \ \text{sq}^{-1}$  at 92% transmittance)<sup>34)</sup> or chemically reduced graphene oxide  $(1.1 \times 10^4 \ \Omega \text{ sq}^{-1} \text{ at } 87\%$ transmittance).<sup>35)</sup> They were also comparable to those of the CNT transparent electrodes  $(3.8 \times 10^3 \ \Omega \ \text{sq}^{-1}$  at 87% transmittance).<sup>30)</sup>

Scanning electron microscopy (SEM) measurements of the transparent conductive films were conducted using ETHOS NX5000 (Hitachi, Ltd.) to reveal the origin of the conductivity difference between the transfer process and spray coating. Despite the smooth and uniform surface of the transferred films in Fig. 4(a), the spray-coated films obtained a fish scale-like shape [Fig. 4(b)]. Figures 4(c) and 4(d) illustrate magnified SEM images of the transferred and spray-coated films, respectively. Many  $Ti_3C_2T_x$  flake aggregates were confirmed in Fig. 4(d), implying the increase of the contact resistance in the electric conductive pathway. Some aggregates laying on the top surface did not contribute to the network formation.

For further structural information, the X-ray diffraction (XRD) measurement was conducted using SmartLab (Rigaku) through Cu K $\alpha$  radiation [Fig. 5(a)]. We also fabricated the Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> film on a Si(100) substrate through the transfer process to omit the peaks from the PEN substrate

at a lower angle region. The (002) peaks of  $Ti_3C_2T_x$  on the transferred ( $2\theta = 7.00^{\circ}$ ) and spray-coated ( $2\theta = 5.54^{\circ}$ ) films indicated that the corresponding average interlayer distances between the flakes were 2.70 and 3.19 nm, respectively. The difference in the interlayer distances represented that the filtrate conditions provided a closer contact of the  $Ti_3C_2T_r$ flakes with each other, consequently enabling the interconnect resistance reduction between the flakes. Compared to the peak from the spray-coated film, a broad band was observed in the transferred film spectrum. The green solid line in Fig. 5(a) depicts the diffraction pattern of the  $Ti_3C_2T_x$ powder. The sharp peak at  $6.12^{\circ}$  meant that the  $Ti_3C_2T_x$ flakes were highly stacked, and the interlayer distance was 2.89 nm at a powder state. Judging from the spectra shapes, the spray-coated sample morphology was similar to that of the powder sample and consistent with the SEM microscopic observations. Figure 5(b) illustrates a schematic image of the morphology of the transferred and spray-coated  $Ti_3C_2T_x$ MXene films. The suction filtration flow forced the  $Ti_3C_2T_x$ flakes to randomly stack with a slight tilt. The transferred  $Ti_3C_2T_x$  sheet maintained the close interlayer distance and smooth surface network, enabling superior macroscale electric conductivity. In contrast, multilayer  $Ti_3C_2T_x$  aggregates were generated when the condensed droplet on the surface was dried. It was difficult for them to provide a sufficient conductive pathway.

In conclusion, we successfully fabricated  $Ti_3C_2T_x$  MXene transparent conductive films via the transfer process. The  $Ti_3C_2T_x$  sheet prepared on the MCE membrane filter was directly transferred to the desired substrate through a simple drying method without the membrane dissolve technique. The transferred transparent conductive films showed ~100 times lower sheet resistance than the conventional spray-coated samples. The film transparency and electrical conductivity were easily controlled by changing the amount of



**Fig. 4.** Typical low-magnification SEM images of the  $Ti_3C_2T_x$  MXene transparent conductive films via the (a) transfer and (b) spray coating methods. Highmagnification SEM images of the  $Ti_3C_2T_x$  MXene transparent conductive films via the (c) transfer and (d) spray coating methods.



**Fig. 5.** (Color online) (a) XRD spectra of the transferred, spray-coated  $Ti_3C_2T_x$  MXene films and powder state  $Ti_3C_2T_x$  MXene sample. (b) Schematic representation of the MXene sheets via the filtration/transfer or spray coating process.

the MXene material. The SEM microscopic observations and XRD characterizations revealed that the transferred film has a smooth and uniform MXene flake network and a closer layer distance than the spray-coated sample, enabling superior electrical conductivity.

**Acknowledgments** This work received financial support from a Japan Society for the Promotion of Science (JSPS) Grant-in-Aid for Scientific Research (JP19H02168, 20KK0087 22K04855), Japan Science and Technology Agency (JST) CREST (JPMJCR19H4) and PRESTO (JPMJPR20B6).

ORCID iDs Haruka Omachi D https://orcid.org/0000-0001-8513-2982

- M. Naguib, M. Kurtoglu, V. Presser, J. Lu, J. Niu, M. Heon, L. Hultman, Y. Gogotsi, and M. W. Barsoum, Adv. Mater. 23, 4248 (2011).
- M. Naguib, V. N. Mochalin, M. W. Barsoum, and Y. Gogotsi, Adv. Mater. 26, 992 (2013).
- M. Ghidiu, M. R. Lukatskaya, M.-Q. Zhao, Y. Gogotsi, and M. W. Barsoum, Nature 516, 78 (2014).
- Y. Wang, Y. Xu, M. Hu, H. Ling, and X. Zhu, Nanophotonics 9, 1601 (2020).
- J. S. Meena, S. B. Choi, and J.-W. Kim, Electron. Mater. Lett. 18, 256 (2022).
- 6) M. Khazaei, M. Arai, T. Sasaki, C.-Y. Chung, N. S. Venkataramanan,
- M. Estili, Y. Sakka, and Y. Kawazoe, Adv. Funct. Mater. 23, 2185 (2012).
  Y. Xie and P. R. C. Kent, Phys. Rev. B 87, 235441 (2013).
- M. Naguib, J. Come, B. Dyatkin, V. Presser, P.-L. Taberna, P. Simon, M. W. Barsoum, and Y. Gogotsi, Electrochem. Commun. 16, 61 (2012).
- 9) X. Liang, A. Garsuch, and L. F. Nazar, Angew. Chem. Int. Ed. 54, 3907 (2015).
- V. Natu, M. Clites, E. Pomerantseva, and M. W. Barsoum, Mater. Res. Lett. 6, 230 (2018).
- 11) Z. W. Seh, K. D. Fredrickson, B. Anasori, J. Kibsgaard, A. L. Strickler, M. R. Lukatskaya, Y. Gogotsi, T. F. Jaramillo, and A. Vojvodic, ACS Energy Lett. 1, 589 (2016).
- 12) S. Intikhab, V. Natu, J. Li, Y. Li, Q. Tao, J. Rosen, M. W. Barsoum, and J. Snyder, J. Catal. 371, 325 (2019).
- 13) M. R. Lukatskaya, O. Mashtalir, C. E. Ren, Y. Dall'Agnese, P. Rozier, P. L. Taberna, M. Naguib, P. Simon, M. W. Barsoum, and Y. Gogotsi, Science 341, 1502 (2013).

- 14) Y. Dall'Agnese, P.-L. Taberna, Y. Gogotsi, and P. Simon, J. Phys. Chem. Lett. 6, 2305 (2015).
- 15) X. Wang, S. Kajiyama, H. Iinuma, E. Hosono, S. Oro, I. Moriguchi, M. Okubo, and A. Yamada, Nat. Commun. 6, 6544 (2015).
- 16) L. Zhao, L. Wang, Y. Zheng, S. Zhao, W. Wei, D. Zhang, X. Fu, K. Jiang, G. Shen, and W. Han, Nano Energy 84, 105921 (2021).
- 17) L. Wu, C. Xu, M. Fan, P. Tang, R. Zhang, S. Yang, L. Pan, and Y. Bin, Composites A 152, 106702 (2022).
- 18) H. Wang, J. Xiang, X. Wen, X. Du, Y. Wang, Z. Du, X. Cheng, and S. Wang, Composites A 155, 106835 (2022).
- A. D. Dillon, M. J. Ghidiu, A. L. Krick, J. Griggs, S. J. May, Y. Gogotsi, M. W. Barsoum, and A. T. Fafarman, Adv. Funct. Mater. 26, 4162 (2016).
- 20) M. Mariano, O. Mashtalir, F. Q. Antonio, W.-H. Ryu, B. Deng, F. Xia, Y. Gogotsi, and A. D. Taylor, Nanoscale 8, 16371 (2016).
- 21) C. J. Zhang, B. Anasori, A. Seral-Ascaso, S.-H. Park, N. McEvoy, A. Shmeliov, G. S. Duesberg, J. N. Coleman, Y. Gogotsi, and V. Nicolosi, Adv. Mater. 29, 1702678 (2017).
- 22) G. Ying, A. D. Dillon, A. T. Fafarman, and M. W. Barsoum, Mater. Res. Lett. 5, 391 (2017).
- 23) L. Qin, J. Jiang, Q. Tao, C. Wang, I. Persson, M. Fahlman, P. O. Å. Persson, L. Hou, J. Rosen, and F. Zhang, J. Mater. Chem. A 8, 5467 (2020).
- 24) K. Hantanasirisakul, M. Zhao, P. Urbankowski, J. Halim, B. Anasori, S. Kota, C. E. Ren, M. W. Barsoum, and Y. Gogotsi, Adv. Electron. Mater. 2, 1600050 (2016).
- 25) B. Zhou, Z. Li, Y. Li, X. Liu, J. Ma, Y. Feng, D. Zhang, C. He, C. Liu, and C. Shen, Compos. Sci. Tech. 201, 108531 (2021).
- 26) D. Wen, X. Wang, L. Liu, C. Hu, C. Sun, Y. Wu, Y. Zhao, J. Zhang, X. Liu, and G. Ying, ACS Appl. Mater. Interfaces 13, 17766 (2021).
- 27) E. Saita, M. Iwata, Y. Shibata, Y. Matsunaga, R. Suizu, K. Awaga, J. Hirotani, and H. Omachi, Front. Chem. 10 (2022).
- 28) Y. Yang, S. Umrao, S. Lai, and S. Lee, J. Phys. Chem. Lett. 8, 859 (2017).
- 29) Z. Wu et al., Science 305, 1273 (2004).
- 30) P. J. King, T. M. Higgins, S. De, N. Nicoloso, and J. N. Coleman, ACS Nano 6, 1732 (2012).
- 31) J. Hirotani, S. Kishimoto, and Y. Ohno, Nanoscale Adv. 1, 636 (2019).
- 32) Y. Matsunaga, J. Hirotani, Y. Ohno, and H. Omachi, Appl. Phys. Express 14, 017001 (2020).
- 33) M. Ishizaki, D. Satoh, R. Ando, M. Funabe, J. Matsui, and M. Kurihara, Adv. Mater. Interfaces 8, 2100953 (2021).
- 34) S. De, P. J. King, M. Lotya, A. O'Neill, E. M. Doherty, Y. Hernandez, G. S. Duesberg, and J. N. Coleman, Small 6, 458 (2010).
- 35) Y. Zhu, W. Cai, R. D. Piner, A. Velamakanni, and R. S. Ruoff, Appl. Phys. Lett. 95, 103104 (2009).