Preparation of MXene/N, S doped graphene electrode for supercapacitor application

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Abstract. In this study, novel MXene/N, S doped graphene electrode composites were successfully prepared via the simplistic drop casting process. The successful etching of Ti₃AlC₂ was evidently confirmed by SEM and XRD technique. The effect of N, S doped graphene adding at various ratio on electrochemical performance was examined by cyclic voltammetry and galvanic static charge-discharge, revealing that the intercalating structure of MXene-N, S doped graphene exhibits the synergistic effect to enhance the electrochemical properties. Especially, at MXene/N, S doped graphene ratio of 95 to 5, the highest specific capacitance of 599.7 F g⁻¹ at 1 A g⁻¹ is obtained, which is greater than that of the pristene MXene (185.8 F g⁻¹ at 1 A g⁻¹) in 6M KOH.

1. Introduction
The recent discovery of two-dimension redox surface, namely MXene, has attracted attention from the scientific community for various applications including battery and supercapacitors because of its high redox properties and high surface area. The two-dimensional inorganic compounds combining metallic conductivity of transition metal carbides and hydrophilic nature can yield the beneficial features of electrochemical performance. Technically, the two dimension structure features of MXene originated from Ti₃AlC₂ can be synthesised by etching process with hydrofluoric acid (HF) to remove Al layers [1]. However, several reports demonstrated that the restack of titanium layer can easily occur with irreversible process, leading to the loss of active surface area for redox reaction. Thus, the delamination of titanium layer is required to maintain 2D layer structure. According to the literature regarding the delamination process of MXene, the methodology including of the swelling process reveals the efficient method to expand the interlayer spacing, but the self-restacking still can occur under high pressure and temperature. Thus, it is still a challenge to find the suitable method to exfoliation the 2D features of MXene. Using intercalating materials has been proven for weakening the interactions between 2D layers. The insertion of small molecules such as activated carbon and
carbon nanotube into titanium carbide layer is purposed to exfoliate and maintain the 2D structure of MXene. Among of carbon materials, graphene is an interested candidate for inserting into MXene layers. Furthermore, graphene is well known considering as electric double layer materials for supercapacitors application due to its high electrical conductivity and high surface area. Especially, graphene doped with nitrogen/sulfur atom possesses the outstanding electrochemical performance due to more electron donor structure. Thus, in this work, through the intercalation structure of MXene-N, S doped graphene is purposed to exfoliate/eliminate the self-restacking of titanium carbide layer and to improve the electrochemical activity.

2. Experimental

2.1. Synthesis of MXene via etching process
MXene powders were synthesized by etching of Al atom layers from the Ti3AlC2 precursors. Briefly, MXene powders were produced by immersing 0.5 g Ti3AlC2 in 10 mL 49% HF solution at 60 °C for 24 h. The obtained powders were washed, centrifugally separated and followed by drying in a vacuum oven at 70 °C for 24 h. Then, 0.5 g of the detached powders was combined with 10 ml of dimethyl sulfoxide (DMSO) for 24 h. Finally, the powders were rinsed with distilled water and drying in a vacuum oven at 60 °C overnight.

2.2. Synthesis of N, S doped graphene
Graphene oxide (GO) was prepared by a modified Hummers method from graphite powder. N, S doped graphene (N, S-G) was synthesized by refluxing of 2 mg/mL GO solution with thiourea solution at equivalent weight for 12 h. N, S-G was obtained after filtration and freeze-drying process.

2.3. Preparation of the MXene/N, S doped graphene electrode
MXene/ N, S-G samples were prepared at different ratio of 100:0, 99:1, 95:0 and 90:10, denoted as MXene, MXene99_ N, S-G1, MXene95_ N, S-G5 and MXene90_ N, S-G10, respectively. Briefly, the MXene95_ N, S-G5 was prepared by mixing of 0.01 g of MXene powder with 0.005 g of N, S-G in 20 mL dispersed water. Then the mixture was sonicated under ultra-sonication for 30 minutes at room temperature. The mixture was dropped onto the nickel foam sheet (2 cm x 1 cm) and dry at 60 °C.

2.4. Electrochemical measurements
The electrochemical properties of the as-prepared MXene/N, S-G electrodes were examined in 6M KOH using three-electrode system configuring with platinum as counter electrode and Ag/AgCl as reference electrodes. PGSTAT 12 equipment was used for cyclic voltammetry (CV) measurements and galvanostatic charge/discharge (GCD). CV experiments were executed in the range of 0 and 0.55 V at different scan rates. The range of 0-0.5 V potential at different current densities was adjusted for measuring the GCD curves.

2.5. Characterization

2.5.1. Fourier-transform infrared spectroscopy (FT-IR). FT-IR is used to identify the functional groups in the range of 500-4000 cm⁻¹ fabricating with KBr.

2.5.2. X-ray diffractometer (XRD). XRD is used to determine the interlayer spacing between Ti3AlC2 and MXene layer. XRD patterns were obtained on a Bruker XRD using Cu Kα radiation (λ = 0.15406 nm) with a scan speed of 2° min⁻¹ at wide-angle range (20 value 8 to 60°), the accelerating voltage of 40 kV and the emission current of 40 mA. The positive integer (n) is 1.

3. Results and discussion
XRD is used to analyze of exfoliation process to synthesis MXene. Fig. 1 presents the XRD pattern of Ti3AlC2 before (1a) and after etching with HF (2b). The starting Ti3AlC2 reveals the typical XRD quite
pure Ti$_3$AlC$_2$ [2]. Meanwhile, after exfoliation process by HF, the most intense peak at 2θ = 39.5° corresponding to the plane (104) is disappeared. The (002) peak is broadened and shifted to lower angles from 2θ = 9.7° (d$_{002}$=0.91 nm) to 8.7° (d$_{002}$=1.02 nm), indicating that the successful extraction of Al layer and the loss of its original layered structure after etching process [3]. In addition, XRD pattern of anatase TiO$_2$ at 2θ = 25.3º, 37.9º, 48.0º and 53.6º is found corresponding to (101), (004), (002), and (105) planes, respectively [4], implying that MXene has been partially oxidized during the annealing and etching process. [5]. The impurity of TiC are also indexed at 2θ = 36.4º (111) and 42.3º (200) [6].

![Figure 1. XRD patterns of (a) Ti$_3$AlC$_2$ and (b) MXene](image1.png)

The morphology of the Ti$_3$AlC$_2$ and MXene are investigated by SEM technique. Typical SEM images of the Ti$_3$AlC$_2$ and the exfoliated MXene nanosheets are shown in fig. 2(a) and 2(b), respectively. As seen in fig. 2(b), after HF-etching, the brick morphology of Ti$_3$AlC$_2$ is obviously transform to accordion-like morphology of Ti$_3$C$_2$, confirming that Al atom in Ti$_3$AlC$_2$ phase are selectively etched [7]. Fig. 2(d) shows the homogenous surface of MXene95_N, S-G5 in micro/nano structure on nickel foam.

![Figure 2. Typical SEM images of the (a) Ti$_3$AlC$_2$, (b) MXene, (c) Nickel foam (d) Nickel foam coated MXene95_N, S-G5](image2.png)

FT-IR spectrum of graphite, graphite oxide and N, S-G materials are shown in fig. 3. It is clear that no distinct peak can be found from the graphite spectra. Graphite oxide exhibits representative peaks at 3270, 1714, 1606, 1389 and 1070 cm$^{-1}$ corresponding to O-H stretch, C=O stretch, aromatic C=C, C-O stretch, respectively [8]. The FT-IR spectra of N, S-G reveals the peak at 3145 cm$^{-1}$ and 3433 cm$^{-1}$ attributing to N-H and O-H stretching vibrations, respectively. These considerable amino and hydroxyl groups can enable hydrophilicity. The peak at around 1728 cm$^{-1}$ corresponds to the stretch vibration of C=O carboxylic groups and the peak at 1375 cm$^{-1}$ can be assigned to the vibration of C-N. Furthermore, the existence of C-O and S=O bonds on N, S-G is confirmed by the peak of 1211 and 1110 cm$^{-1}$, respectively [9].
Figure 3. FT-IR spectra of graphite, graphite oxide and N, S doped graphene.

Figure 4. (a) CV curves of the as-prepared samples at 10 mV s$^{-1}$, (b) CV curves of MXene$_{95}$ N,S-G5 electrode at different scan rates, (c) GCD profiles of the as-prepared samples at 1 A g$^{-1}$, (d) GCD profiles of MXene$_{95}$ N, S-G5 electrode at different current densities and (e) the calculated specific capacitance by GCD of the as-prepared samples.

Fig. 4(a) shows the CV curves of the MXene and Mxene/N, S-G electrodes at different ratio (MXene$_{99}$ N, S-G1, MXene$_{95}$ N, S-G5 and MXene$_{90}$ N, S-G10) at 10 mV s$^{-1}$ in 6M KOH. MXene, Mxene$_{90}$/N, S-G10 and MXene$_{99}$/N, S-G electrodes show similar CV areas. Remarkably, The largest CV area is MXene$_{95}$/N, S-G5 implying the highest electrochemical performance. In addition, fig. 4 (b) demonstrates CV curves of MXene$_{95}$/ N, S-G5 electrode with different scan rates from 10 to 100 mV s$^{-1}$. A pair of redox peaks of samples was clearly observed for each curve within 0-0.55 V and can be maintained, even at high scan rate, indicating that the capacitance mainly comes from the pseudocapacitance associated with reversible intercalation/deintercalation of protons along with the change of Ti oxidation state [10]. GCD profiles of MXene and Mxene/N, S-G electrodes at 1 A g$^{-1}$ is revealed as seen in fig. 4(c), demonstrating the longest discharge time of MXene$_{95}$/ N, S-G5. These results are also corresponded with CV results, implying that the MXene$_{95}$/ N, S-G5 can yield the highest specific capacitance. GCD curves of MXene$_{95}$/ N, S-G5 at various current densities are shown.
in Fig. 4(d) revealing that the electrochemical performance can maintain 52.6% with the increase current from 1 to 10 A g\(^{-1}\). The calculated specific capacitance values by GCD for all electrode samples at the different proportion of N, S-G are presented in fig. 4(e). Among of these electrodes, MXene95\(_N\), S-G5 electrode exhibits the highest specific capacitance of 599.7 F g\(^{-1}\) at a current density of 1 A g\(^{-1}\), slightly higher than those of pristine MXene (185.8 F g\(^{-1}\)), MXene99\(_N\), S-G1 (169.0 F g\(^{-1}\)) and MXene90\(_N\), S-G10 (319.9 F g\(^{-1}\)). Clearly, MXene95/N, S-G5 yield the optimum condition.

4. Summary
In summary, MXene/N, S-G electrodes were successfully synthesized through drop casting method. The experiments indicate the highest specific capacitance of MXene/N, S-G electrode is MXene95\(_N\), S-G5 (599.7 F g\(^{-1}\)) at 1 A g\(^{-1}\) which is arisen from the intercalation structure of MXene-N, S doped graphene exhibiting the synergistic effect to enhance the electrochemical properties. Evidence results confirmed that MXene/N, S-G electrodes are promised material for the supercapacitor application in the future.

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References
[1] B. Anasori, M. R. Lukatskaya and Y. Gogotsi: Nat. Rev. Mater. Vol. 2 (2017)
[2] P .Yan, R. Zhang, J. Jia, C. Wu, A. Zhou, J. Xu and X. Zhang: J. Power Sources. Vol. 284 (2015), p. 38-43
[3] G. Lv, J. Wang, Z. Shi and L. Fan: Mater. Lett. Vol. 219 (2018), p. 45-50
[4] H. Wang, R. Peng, Z. D. Hood, M. Naguib, S. P. Adhikari and Z. Wu: Wiley-VCH
[5] Q. X. Xia, J. Fu, M. Yun, S. Mane and K. Ho: RSC Adv. Vol. 7 (2017), p. 11000–11011
[6] W. Sen, H. Sun, B. Yang, B. Xu, W.Ma, D. Liu and Y. Dai: Int. J. Refract. Met. Hard Mater. Vol.28 (2010), p. 628-632
[7] S. Xu, G. Wei, J. Li, Y. Ji, N. Klyui,V. Izotov and W. Han: Chem. Eng. J. Vol. 317 (2017), p. 1026–1036
[8] J. C. Yan, X. Q. Zeng, T. H. Ren and E. van der Heide: Biosurf. Biotribol. Vol. 1 (2015), p. 113-123
[9] P. Guo, F. Xiao, Q. Liu, H. Liu, Y. Guo, J. R. Gong, S.Wang and Y. Liu: Sci. Rep. Vol. 3 (2013) p. 1-6
[10] J. Yan, C. E. Ren, K. Maleski, C. B. Hatter, B. Anasori, P. Urbankowski, A. Sarycheva and Y. Gogotsi: Adv. Funct. Mater. Vol. 1701264 (2017), p. 1–10