Iontronics Using $V_2CT_x$ MXene-Derived Metal—Organic Framework Solid Electrolytes

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ABSTRACT: Electronic applications of porous metal—organic frameworks (MOFs) have recently emerged as an important research area. However, there is still no report on using MOF solid electrolytes in iontronics, which could take advantage of the porous feature of MOFs in the ionic transport. In this article, MXene-derived two-dimensional porphyric MOF (MX-MOF) films are demonstrated as an electronic-grade proton-conducting electrolyte. Meanwhile, the MX-MOF film shows high quality, chemical stability, and capability of standard device patterning processes (e.g., dry etching and optical and electron beam lithography). Using the commercialized nanofabrication processes, an electric double-layer (EDL) transistor is demonstrated using the MX-MOF film (derived from $V_2CT_x$, MXene) as an ionic gate and MoS$_2$ film as a semiconducting channel layer. The EDL transistor, operated by applying an electric field to control the interaction between ions and electrons, is the core device platform in the emerging iontronics field. Therefore, MX-MOF, confirmed as a solid electrolyte for EDL transistor devices, could have a significant impact on iontronics research and development.

KEYWORDS: metal—organic framework, film patterning, solid electrolyte, MoS$_2$, electric double-layer transistor

Metal—organic frameworks (MOFs) are an important class of materials that have found a large number of potential applications in their bulk form. Such applications include gas separation and storage, catalysis, and chemical and biological sensing. Recently, there has been increasing attention on using MOFs in various microelectronic applications. So far it has been reported that MOFs can be used as a semiconductor channel or a dielectric layer in thin-film transistors, an active layer in memristors, and a photoresist for lithographic patterning. These preliminary studies demonstrated that MOFs have some potential applications in electronics. However, to date, there is still no report on using MOFs as solid electrolytes in iontronics, which is a recently emerging branch of electronics.

Iontronics is a recently emerging interdisciplinary concept, which is based on the electrochemical transistor platform using a gate electric field to control the interaction between ionic and electronic transport behaviors. One of the core device architectures is the electric double-layer (EDL) transistor. The EDL is formed at the interface between an electrolyte (ionic conductor) and a semiconductor (electron conductor) when an electric field is applied to the gate electrode. During the EDL formation, the electronic current flowing through the semiconductor could be hugely modulated. Based on this device operating mode, abundant physical, chemical, and biological signals could be collected using different material platforms and device working environments.

Some MOFs have been demonstrated as excellent ionic (especially proton) conductors when their pores are filled with water molecules or nonvolatile proton carriers. They were normally reported as an electrolyte for fuel cells. However, no literature reports exist, to the best of our knowledge, showing that MOF solid-state films can be used as ionically conductive electrolytes in EDL transistors.

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using standard microelectronic fabrication methods has been very challenging, but a highly desired objective of the MOF community.\textsuperscript{1,7} In this article, we demonstrate a feasible and low-cost process to make high-quality proton-conducting MOF films, which can be deposited, patterned, and integrated into electronic devices.

**RESULTS AND DISCUSSION**

Figure 1a schematically shows the fabrication process of the MX-MOF/MoS\textsubscript{2} EDL transistor. The V\textsubscript{2}CT\textsubscript{X} MXene, an atomically thin 2D vanadium carbide with surface functional groups (−F, −OH, and −O), was utilized as the metal source and soft template for the synthesis of the MX-MOF 2D nanosheets (see Methods). V\textsubscript{2}CT\textsubscript{X} MXene nanosheets with 2D morphology were confirmed by the scanning electron microscope (SEM) and atomic force microscopy (AFM) images in Figures S1 and S2. Using these MXene nanosheets and commercial H\textsubscript{2}TCPP (H\textsubscript{2}TCPP = meso-tetra(4-carboxyphenyl)porphyrin) ligand, we successfully synthesized the 2D MX-MOF nanosheets by a simple hydrothermal method. After purification, these nanosheets were dispersed in methanol as a stable suspension. The liquid sample in Figure 1b shows a red-violet color, with a concentration of 1 mg/mL (MX-MOF weight/methanol volume). This suspension was used to form high-quality uniform MX-MOF films by spin-coating, as shown in Figure 1c.

Figure 1a also displays how MoS\textsubscript{2} films were prepared. The MoO\textsubscript{2} precursor film (Epi-MoO\textsubscript{2}) was epitaxially grown on a sapphire substrate by pulsed laser deposition. Through a high-temperature sulfurization process, continuous high-quality epitaxial MoS\textsubscript{2} (Epi-MoS\textsubscript{2}) films could be obtained (sample in Figure 1d, optical and AFM images, Raman spectrum in Figures S3 and 4 confirmed the MoS\textsubscript{2} uniformity and continuity). This MoS\textsubscript{2} formation process has been described elsewhere by our group.\textsuperscript{24,25} The MoS\textsubscript{2} film was patterned through a dry etching process, and source/drain (S/D) contact and side-gate Au/Ti electrodes were patterned through a lift-off process. Then, the MX-MOF film was spin-coated on the entire seminished device from a methanol-based MX-MOF suspension. The MX-MOF film thickness was controlled by spin-coating time. The device after MX-MOF film coating is shown in Figure 1e. A nice feature of this device fabrication process is that the MX-MOF film can be processed through conventional photolithography and dry etching without degradation. The EDL transistor device obtained after MX-MOF patterning is displayed in Figure 1f. It must be mentioned that the capping photoresist layer should be reserved after the MX-MOF patterning to keep the stable ionic transport environment in the MX-MOF layer. After H\textsubscript{3}PO\textsubscript{4} acid treatment for a certain time, the functioning MX-MOF/MoS\textsubscript{2} EDL transistor is finally obtained.

Preparation and characterization of the patterned MX-MOF films are shown in Figure 2. For preparing the MX-MOF film, spray- and spin-coating methods were explored. The spray coating of the MX-MOF suspension on a substrate showed randomly distributed MX-MOF rings, as shown in Figure 2a. In contrast, the spin coating can realize a continuous and uniform MX-MOF film on a substrate, as shown in Figure 2b. In order to confirm the film quality, it was further characterized by AFM. Figure 2c displays a large-scale AFM image that shows a dense MX-MOF film morphology (inset shows a single 2D MX-MOF flake with thickness about 12.5 nm and lateral size about 300 nm). Figure 2d shows the higher resolution AFM image of the MX-MOF film formed from
stacked 2D flakes. The root mean square (RMS) roughness is about 5.5 nm, which is an excellent surface flatness that is even comparable to some inorganic films prepared by high-vacuum deposition. The RMS roughness data comparison is shown in Table S1. Previously reported methods for preparing MOF films required specific substrates (as a seeding or template layer as discussed in Table S2). However, our MX-MOF nanosheet suspension can be used to spin coat high-quality MX-MOF films on any substrate. Taking the sapphire, gold, and MoS₂ film as representative substrates with different hydrophilic surfaces (insets in Figure 2e−g), all the films were formed by densely stacked MX-MOF nanosheets, as displayed in Figure 2e−g. We can see that all the MX-MOF films are dense (Figure 2e−g). This feature shows that our MX-MOF films have great potential in microelectronic applications.

The compatibility of the MX-MOF films to the standard lithography process was evaluated by exposing to the chemicals involved in cleanroom fabrication processes. We immersed the freshly prepared MX-MOF film in acetone, isopropanol, DI water, and AZ726 developer solution for 2 min (as shown in Figure S5), followed by blow-drying under a nitrogen gun. The MX-MOF films did not exhibit any clear degradation (demonstrated by XRD characterization). Actually, we put our MX-MOF film in...
acetone and separately in chloroform solutions for 5 h at a holding temperature of 80 °C, and the MX-MOF films still retained its pristine morphology. The above experiments convincingly demonstrate that the MX-MOF films have sufficient chemical stability for the standard electronic device fabrication processes. Using the UV-light photolithography and plasma-dry-etching process, we successfully patterned the MX-MOF film, as shown in Figure 2h,i (also Figure S7). Figure 2h shows arrays of patterned MX-MOF concentric square ring shapes. The enlarged figure of a single square ring shows sharp pattern edges indicating the ability to pattern MX-MOF by UV photolithography with several-micrometer resolution. Figure 2i shows a patterned MX-MOF in the form of circle arrays. The specific enlarged single circle pattern indicates that the morphology of the MX-MOF-nanosheet film is well retained. Electron-beam lithography (EBL) was also used to demonstrate the capability to pattern our MX-MOF films. The optical and SEM images of MX-MOF EBL patterns are shown in Figure 2j (and Figure S8) and Figure 2k,l, respectively. The demonstration of using the EBL technique to pattern MX-MOF films indicates their potential in nanoelectronics. These results clearly demonstrate that the MX-MOF films can tolerate the standard and state-of-the-art cleanroom patterning process.

The capability of our H₃PO₄ acid-treated MX-MOF film as a solid electrolyte is discussed in Figure 3. To understand its polarization mechanism, we fabricated two-terminal MX-MOF devices with finger electrodes and then performed electrochemical impedance spectroscopy (EIS) measurement. To be consistent with the working environment of iontronic devices reported in the following text, the devices were sealed with capping PDMS film at room temperature (Figure S9), while the PDMS capping process was done just after the 20% H₃PO₄ treatment, as discussed in the Methods. Figure 3a displays the Nyquist plot and the relevant equivalent circuit model used for the analysis. The raw data are represented by the black dots, and the fitting is represented by the red line. From the fitting analysis together with the calculation (Note S1), we obtained the proton conductivity value of $2.39 \times 10^{-3}$ S·cm⁻¹. This value is higher than our previous report because the PDMS-protected MOF device has a sealed environment with internal humidity close to 100%.²⁶ The proton transport of the acid-doped MX-MOF film was shown to follow the Grotthus mechanism in our previous report.²⁶ Figure 3b schematically displays the hydrogen-bonding network formed between the MX-MOF nanosheets and H₃PO₄, which enables proton transport. The increased proton conductivity in a higher humidity environment results from the higher concentration of water molecules inside the hydrogen-bonding network, which could further reduce the barrier for proton movement, as illustrated in Figure 3c.

The polarization mechanism of acid-doped MX-MOF films can be inferred from Figure 3d, which exhibits frequency-dependent capacitance and phase angle. The difference of
capacitance between lower and higher frequency ranges results from different polarization mechanisms, as illustrated in Figure S10. Ionic pair relaxation dominates the polarization when the frequency regime is above 3.5 kHz, where the phase angle is higher than $-45^\circ$. When the frequency is below 3.5 kHz (phase angle is lower than $-45^\circ$), the rapidly increasing capacitance corresponds to the typical EDL polarization at the interface between the electrode and the MX-MOF film. When the frequency is around 0.1 Hz, the EDL capacitance reaches the maximum value of 6.64 μF·cm$^{-2}$, which is a similar value to other solid electrolytes (see Table S3). Therefore, our results demonstrate that our MX-MOF films are excellent proton-conducting solid electrolytes.

In order to confirm that the acid-doped MX-MOF electrolyte could perform as an ionic gating dielectric layer in microiontronic devices, we fabricated a coplanar-gate EDL transistor device using MoS$_2$ as the semiconductor channel and Au/Ti as the source and drain (S/D) and gate electrodes. The real device is shown in Figure 4a, where the channel length and width are 30 and 400 μm, respectively. The schematics of the device cutaway and three-dimensional views are shown in Figure 4b, where the photoresist is preserved as a capping layer to keep the acid-doped MX-MOF film as a stable proton-conductive medium. The detail of the device fabrication is discussed in the Methods. The output curve is shown in Figure 4c. The $I_{DS}$–$V_{DS}$ curves were obtained at different fixed $V_{GS}$ values in the range 0–5 V, with 0.5 V per step. Figure 4d shows the single-sweep transfer curve obtained at different $V_{DS}$ voltages on a logarithmic scale, through which we could obtain an excellent subthreshold swing (SS) value of about 238 mV·dec$^{-1}$ and an acceptable S/D current on/off ratio about $10^5$, showing much better performance than the device without a photoresist capping layer on the MX-MOF electrolyte layer (Figure S11). Figure 4e shows the corresponding linear scale transfer curve, where the field-effect mobility was calculated to be $1.9 \times 10^{-3}$ cm$^2$·V$^{-1}$·s$^{-1}$. The reason for this low mobility value might be that the long-time aqueous-acid treatment of the MX-MOF/MoS$_2$ devices chemically degraded the MoS$_2$ electronic properties. Some nonaqueous ionic liquids are proposed as better candidates for MX-MOF proton-doping to enhance electric performances. Figure 4f displayed the dual-sweep transfer curve (dark cyan) and gate leakage current (red) curve on a logarithmic scale. The hysteresis in the transfer curve might result from the degraded quality of the MoS$_2$ film or the lower EDL relaxation speed. The leakage current is in the nanoampere scale and 100 times less than the S/D on current, indicating reliable device performance. These results demonstrate our MX-MOF as a viable solid-electrolyte gate in EDL transistors. This finding can open various applications for this emerging family of 2D MOFs. Possible applications include superconductivity, ferromagnetism, phase transition, thermoelectric, and integrated electronics based on EDL transistor device platform.
CONCLUSION

In summary, we have successfully demonstrated high-quality V2CTi MXene-derived MOF films on various substrates. These films are chemically and mechanically stable enough to go through a cleanroom fabrication process, including lithography (UV-light and electron-beam lithography) and dry etching. The MX-MOF thin films were demonstrated as a proton-conducting solid electrolyte in iontronic devices. A MoS2 EDL transistor using the MX-MOF solid electrolyte was confirmed with reasonable device performance. Therefore, our MXene-derived MOF films can serve as solid ionic gates, leading to applications of various promising devices.

METHODS

Synthesis of V2CTi MXene. V2CTi MXene was prepared according to the literature.20 In detail, 1 g of V2AlC MAX (300 mesh) was added slowly into 20 mL of high-concentrated hydrogen fluoride and stirred at 35 °C for 24 h. Then, the mixed solution was centrifuged (3000 rpm) to collect the sediment, which was washed repeatedly with deionized (DI) water until the pH of the supernatant reaches ~6. Next, 10 mL of tetramethylammonium hydroxide (TMAOH, 1 M) was added in the sediment and stirred for 4 h at room temperature. Subsequently, the supernatant was discarded by centrifugation (10 000 rpm) to collect the sediment. Finally, a delaminated V2CTi MXene supernatant was obtained by centrifugation (4000 rpm).

Preparation of MX-MOF Nanosheets. To fabricate MX-MOF nanosheets, 20 mg of as-prepared V2CTi MXene was added in 20 mL of dimethylformamide (DMF). Then, 300 mg of tetraakis(4-carboxyphenyl)porphyrin (TPCP) linkers was added and transferred to a Teflon autoclave (50 mL). The autoclave was maintained at 150 °C for 4 h in an oven. Subsequently, the precipitation was obtained by centrifugation (11 000 rpm) followed by solvent exchange with methanol three times (24 h per time). The purified V-PMOF powder was dispersed in methanol with a concentration of ~1 mg/mL for film preparation.

Preparation of MX-MOF Film. The MX-MOF film was prepared by a spin-coating process. The precleaned substrate (sapphire, gold film, MoS2 wafer, or the patterned chips) was vacuum sucked on the spin coater holder, and the spinning speed is 2000 rpm. A 1 μL amount of MX-MOF solution was dropped on the substrate drop by drop within 30 s, and this was repeated 20 times to prepare the MX-MOF electrolyte layer of the MoS2 EDL transistor. Then, the MX-MOF film sample was put in a vacuum oven at 70 °C for 2 h to remove the methanol residue.

Fabrication of the Two-Terminal MOF Device. The two-terminal finger electrodes (50/10 nm thick Au/Ti) were deposited on a glass substrate by an e-beam evaporation method and patterned by a cleanroom lift-off process. Then, the MX-MOF film was prepared on the glass with electrodes by the above-mentioned spin-coating process. For the H+ doping, the as-prepared two-terminal MOF device was quickly merged in the 20% H3PO4 solution and taken out to a Te photoresist AZ3027 layer should still be retained after the MX-MOF patterning. Then the whole device sample was immersed in the 20% (v/v) aqueous H2PO4 solution about 15 h for acid doping the patterned MX-MOF electrolyte. Here, it is mentioned that the MX-MOF film will loosen and peel off from the device during the acid treatment without the protection of the photoresist capping layer.

Materials and Device Characterization. The morphology of MX-MOF and MoS2 film was observed through an scanning electron microscope (FEI Quantum 6000FEG, FESEM), AFM (Bruker, Dimension Icon SPM), and an optical microscope (Zeiss AXIO Scope). The Raman spectrum of the MoS2 film was characterized using a Horiba Aramis Raman spectrometer (Horiba Scientific). The hydrophilicity of the sapphire substrate, Au film, and MoS2 film was indicated by testing static contact angles using a contact angle system (OCA 3S, DataPhysics, Filderstadt, Germany). The frequency-dependent capacitances and phase angles of H+-doped MX-MOF films were characterized using a VMP3 multichannel electrochemical workstation (Bio-Logic). The EDL MX-MOF-MoS2 transistor performance was measured by a semiconductor device analyzer (Agilent B1500A) at room temperature in the air.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsnano.0c02497.

Figures S1–S2 and Tables S1–S3 (PDF)

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Notes

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