Scalable, and low-cost treating-cutting-coating manufacture platform for MXene-based on-chip micro-supercapacitors

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**Abstract**

The rapid development of silicon-based microelectronic devices urgently demand for compatibly silicon-based micro-supercapacitors (MSCs) with smaller size, higher power density, and higher integration density. However, there are still some challenges in fabricating silicon-based MSCs, such as weakly-connected interface and expensively-manufactured process. Here we demonstrate a scalable and low-cost treating-cutting-coating (TCC) manufacture platform for Ti$_3$C$_2$T$_x$ MXene-based on-chip MSCs. The hydrophilical treating of silicon/silicon dioxide (Si/SiO$_2$) surface can effectively enforce MXene-silicon interface adhesion, resulting in the improved integrity and uniformity of MXene films. Subsequently, cold laser-cutting followed by spin-coating can rapidly prepare the MXene-based electrodes on the kapton-masked Si/SiO$_2$ substrates. This as-obtained MSC displays a high areal and volumetric capacitance of 472 μF cm$^{-2}$ and 21.4 F cm$^{-3}$, incorporating with outstanding cycling stability of over 87.6% capacitance retention after 10 000 cycles. Evidently, this treating-cutting-coating manufacture process will support a general platform toward scalable on-chip energy storage devices based on 2D materials.

1. Introduction

The rapid progress of portable electronic devices urgently requires the development of on-chip energy devices, especially silicon-compatible on-chip energy devices, toward miniaturization, high performance and high integration density [1–4]. Considering that, thin film batteries and micro-supercapacitors (MSCs) have become the most potential candidate, which can save space for other electronic components and further decrease the overall device size [5–7]. Compared with thin film batteries, MSCs possess superior charge-discharge rate, power density and much longer cycling life, and thus are the optimal choice for microelectronic devices [8,9]. In practice, for further compatibility of all-in-one silicon semiconductor devices, planar silicon-based MSCs have obtained much attention [3,10]. However, although some efforts have been made on silicon-based MSCs, there are still many challenges, such as the weak interface connection, low energy density and complex manufacture process, thereby hindering their integration with silicon chips [11,12]. Besides, the intrinsic properties of electrode materials usually play the most important role in the performance of on-chip MSCs. The reported electrode materials are mainly divided into electric double layer and pseudocapacitor materials, such as carbonaceous materials [13,14], transition metal oxides/hydroxides [15–19], sulphides [20–23], and conductive polymers [24]. In most cases, carbon-based materials, including carbon nanotubes [11], carbide-derived carbons [10,12] and graphene [25], have been used in on-chip MSCs. However, among the previous reports, their volumetric capacitances and energy density were always limited, intrinsically caused by the low packing density and the poor electrical conductivity of the electrode materials [26]. So it is the key to find one material which can achieve outstanding electrochemical performance while possessing superior electronic conductivity. Fortunately, MXenes (two-dimensional transition metal carbides and...
nitrides), which have high metallic conductivity (up to 6500 S cm\(^{-1}\)) [27], rich chemical properties [28], and high volumetric capacitance (1500 F cm\(^{-3}\) in H\(_2\)SO\(_4\)) [29], have shown great potential in many applications, including electrostatic shielding, sensors, conductive reinforcement additives to polymers, and electrochemical energy storage materials. Although some related works on MXene-based MSCs have been reported [30,31], few attempts have been made to fabricate MSCs on silicon substrates with Ti\(_3\)C\(_2\)T\(_x\) MXene [32], ascribing to low interfacial adhesion and high manufacturing cost. In addition, traditional micro-manufacturing technologies like magnetron sputtering, electrochemical deposition and chemical vapor deposition are usually complex and expensive, which are difficult to satisfy the current demand of large-scale production.

Herein, we developed a scalable and low-cost treating-cutting-coating (TCC) manufacture platform for silicon-based on-chip MSCs based on Ti\(_3\)C\(_2\)T\(_x\) MXene. Combined with hydrophilical treating, cold laser cutting and spin coating, the interdigitated electrodes are successfully manufactured on the polyimide (Kapton) tape masked Si/SiO\(_2\) wafer. And the as-produced MXene films on Si/SiO\(_2\) chip are extremely thin, with the thickness ranging from 100 to 600 nm, along with outstanding uniformity and stability. Also, this manufacture platform is easy to extend to other MXene materials. Moreover, due to the high electrical conductivity of Ti\(_3\)C\(_2\)T\(_x\) MXene and the in-plane geometry of the interdigitated architecture, the as-fabricated MSCs deliver a maximum areal capacitance of 472 \(\mu\)F cm\(^{-2}\) and a volumetric capacitance of 21.4 F cm\(^{-3}\). Further, the MXene-based on-chip MSCs show an energy density of 1.1 mWh cm\(^{-3}\) and a power density of 12 W cm\(^{-3}\). Also, the on-chip MSCs exhibit good cycling stability of over 87.6% capacitance retention after 10 000 cycles at a current density of 10 \(\mu\)A cm\(^{-2}\), in association with good rate-capability. Thus, this treating-cutting-coating manufacture platform may make great contribution to on-chip energy storage devices based on 2D materials.

2. Results and discussion

Fig. 1a shows the MXene electrodes fabricated in batches on a hydrophilically treated Si/SiO\(_2\) wafer with the size of 10*10 cm, including the single, in series, and in parallel devices. The on-chip MSCs can be easily integrated into all-in-one micro-electronic devices with other components, which can effectively increase integration density while greatly reducing the overall device size (Fig. 1b). The detailed manufacture steps are illustrated in Fig. 1c. Since there are many tunable surface terminations (such as O\(^{2-}\), OH\(^{-}\), F\(^{-}\)), Ti\(_3\)C\(_2\)T\(_x\) MXene possess rich chemistry and hydrophilic surface [33,34], which makes MXene easy to bond to hydrophilic surfaces through hydrogen bonding. Consequently, to enhance the interface contact force, the surface of Si/SiO\(_2\) wafer should first be subjected to a hydrophilic treatment [35]. Through the water contact angle test, the surface hydrophilicity of hydrophilic-treated Si/SiO\(_2\) wafer is significantly improved (Fig. S1). Furthermore, through employing kapton tape as the mask and patterning the interdigitated electrode by direct UV (ultraviolet) laser cutting, the on-chip MSCs can be rapidly fabricated with low cost. This cold laser-cutting can effectively avoid high temperature damage to the edges and remarkably maximize the accuracy of the pattern. Besides, spin-coating was employed to deposit highly conductive Ti\(_3\)C\(_2\)T\(_x\) MXene on hydrophilically treated Si/SiO\(_2\) wafer, which is easy to operate and ensure fine uniformity of the MXene film. And along with PVA/H\(_2\)SO\(_4\) gel as the electrolyte, polydimethilsiloxane (PDMS) was utilized to package the on-chip MSCs. In a word, MXene-based on-chip MSCs can be massively fabricated through a treating-cutting-coating (TCC) approach, which is easy to operate, scalable and low-cost, and this may greatly facilitate the development of micro-scale energy device for next-generation CMOS applications.

Ti\(_3\)C\(_2\)T\(_x\) MXene was prepared via a mild etching method by HCl and LiF, and the exfoliated MXene sheets stay layered structure similar to their MAX precursor (Ti\(_3\)AlC\(_2\)), as shown in Fig. S2 (Supporting Information). To further prove that MXene was successfully etched, EDS and XRD analysis of Ti\(_3\)C\(_2\)T\(_x\) MXene film were also provided (Figs. S3–4, Supporting Information). It can be found that aluminium (Al) is completely removed, while O, F element occupies a certain proportion which derived from surface functional groups. In addition, similar to previous works, the (002) peaks for Ti\(_3\)C\(_2\)T\(_x\) MXene is located at around 7\(^{\circ}\), originating from the intercalation of a single layer of water molecules between MXene flakes [26]. The presence of –O functional groups and interlayer water can significantly promote the electrochemical capacity of Ti\(_3\)C\(_2\)T\(_x\) MXene [33,36].

Fig. 1. Schematic illustration of the fabrication of MSCs. (a) Digital photograph of the scalable MXene-based on-chip MSCs. (b) Preview of the on-chip MSCs integrated with other circuit components. (c) The detailed manufacturing process of on-chip MSCs. Kapton tape was used as a mask.
Fig. 2 shows the optical microscope photograph of the as-fabricated on-chip MSC devices, which consists of 6 interdigitated electrodes. The typical width and the gap between two electrodes is about 1.8 mm and 284 μm (Fig. 2b), respectively, while the length of the single micro-electrode is 10 mm. Through controlling the spin-coating times, the thickness of MXene film ranging from 100 to 600 nm can be easily obtained. Fig. 2c shows the layered structure of MXene film that facilitates rapid ion migration. And the thickness of 5 times spin-coating measured from the cross-section SEM is around 142 nm. To determine the thickness and edge shape of electrodes, atomic force microscopy (AFM) analysis is provided in Fig. 2d–e and Fig. S5 (Supporting Information). Due to the presence of the kapton tape mask during spin coating, the thickness of electrode edge is much higher than that of the middle portion. And the range of edge bulge is about 40 μm. The mean thickness with spin-coating times of 5, 10, 20, 30 is about 98, 162, 264, 521 nm, respectively. The surface of spin-coated MXene film is relatively uniform and some Ti3C2Tx sheets can be observed (Fig. S6, Supporting Information). And the robust interface combination between MXene film and Si/SiO2 wafer can be attributed to the hydrophilical pretreatment. Furthermore, according to the surface profiler, surface roughness of MXene electrode is 5.6 nm, revealing that the surface fluctuation caused by MXene sheets is only around 5.6 nm.

The electrochemical behavior of the on-chip MSCs were investigated by cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD) employing a PVA/H2SO4 gel electrolyte (Fig. 3a-b). As shown in Fig. 3a, CV curves of on-chip MSCs with different thickness including spin-coating for 5 (MSC-5), 10 (MSC-10), 20 (MSC-20), 30 times (MSC-30), were tested for comparison at a scan rate of 10 mV s⁻¹. Obviously, the areal capacitance increased with the increase of spin-coating times, while MSC-30 exhibited the largest areal capacitance, which can be attributed to the highest active material loading. The CV shapes of all devices are near rectangular, which means that Ti conversion in different valence states and establishment of fast ion adsorption can be easily achieved. Fig. 3b shows the GCD curves with a typical isosceles triangle shape for the on-chip MSCs. At the same current density of 1.0 μA cm⁻², MSC-30 exhibited the longest discharge time as well as the smallest voltage drop, further certificating that the areal capacitance increased with the increase of thickness. In addition, typical CV curves of MSC-30 displayed a good rectangular shape up to 100 mV s⁻¹ (Fig. 3c), indicating rapid charge storage property. Also, all the CV curves of these MSCs at different scan rates are provided in Fig. S7 (Supporting Information).

Calculated through the GCD curves at different current density (Fig. S8, Supporting Information), the corresponding areal and volumetric capacitances are shown in Fig. 3d and e. MSC-30 exhibits an areal capacitance of 470 μF cm⁻² at 1.0 μA cm⁻², and even the current density rapidly raises to 30 μA cm⁻², the capacitance retention is still 90.4% (425 μF cm⁻²). In contrast, MSC-5 possesses the lowest areal capacitance of only 111 μF cm⁻² and capacitance retention of 19.8% at 20 μA cm⁻² (Fig. 3d), which is consistent with the impedance variation of the devices (Fig. 3f). However, from MSC-30 to MSC-10, its volumetric capacitance remarkably increased (Fig. 3e), because the electrochemical performance of on-chip MSCs depends a lot on the thickness of MXene electrode, namely, as the thinner the thickness, the faster the ions transport [37,38]. This can be attributed to the formation of a compact inner layer in MXene film with increasing thickness. For MSC-30, the extraordinary rise of thickness is being caused by the hydrophilicity of MXene film (Fig. S1), which greatly reduced the volumetric capacitance. As shown in Fig. 3e, high volumetric capacitance of 21.4 F cm⁻³ at 1.0 μA cm⁻² is obtained for MSC-10, which has surpassed most MSCs based on other materials, such as graphene oxide (3.1 F cm⁻³) [39], graphene (17.9 F cm⁻³) [40], carbon nanotube fiber (13.3 F cm⁻³) [41]. But for MSC-5, the volumetric capacitance is only 11.3 F cm⁻³, which is much lower than other devices and not consistent with theoretical prediction. In fact, during the hydrophilic treatment of Si/SiO2 wafers by concentrated H2SO4 and H2O2, many concaves upon the surface of Si/SiO2 appeared. To understand it, surface profile images are shown in Fig. S6 (Supporting Information). There are too many concaves consisting in the surface of MSC-5, meaning that Ti3C2Tx MXene mainly fills in defects at the first few spin coating processes, so that the volumetric capacitance of

![Fig. 2. Morphology and structure of interdigitated MXene electrodes.](image-url)

Representative (a) Optical microscope image, (b) SEM and (c) Cross-section SEM images of the MXene electrodes. (d, e) AFM image of MSC-10 and the corresponding thickness of the MXene film is around 162 nm. (f) Surface profiler of MSC-10 indicates the uniform surface.
Fig. 3. Electrochemical properties of on-chip MSCs ranging from MSC-5 to MSC-30. (a) The corresponding CV curves at 10 mV s\(^{-1}\) and (b) the corresponding GCD curves at 1.0 \(\mu\)A cm\(^{-2}\) for these MSCs. (c) CV curves at the scan rates varying from 5 to 200 mV s\(^{-1}\) for MSC-30. (d, e) The areal and volumetric capacitances of on-chip MSCs with different MXene film thicknesses depend on different current densities. (f) The Nyquist plots of these four devices.

Fig. 4. Integration and power density characteristics of the as-fabricated MSCs. (a) CV curves at 10 mV s\(^{-1}\) and (b) the corresponding GCD curves when the devices are single, in series and in parallel connection, respectively. (c) The cycling performance of on-chip MSCs is measured under a current density of 10 \(\mu\)A cm\(^{-2}\). The inset shows the CV during cyclic test. (d) Ragone plot of on-chip MSCs. The comparison of energy and power density of MPG-MSCs with TG-MSCs, MPG-SSCs, lithium thin-film batteries, and conventional supercapacitors, demonstrating that MXene based on-chip MSCs exhibit exceptional electrochemical energy storage with simultaneous ultrahigh energy density and power density.
MSC-5 is much lower than theoretical prediction. In the process of increasing the spin coating times to 30, surface pits gradually decreased and eventually disappeared completely, corresponding to the changing trend of capacity (Figs. S8b–d, Supporting Information).

To further investigate the electrochemical capacitive behavior of on-chip MSCs, the electrochemical impedance spectroscopy (EIS) was conducted in the frequency range from 10⁵ to 10⁻² Hz, as shown in Fig. 3f. The ohmic resistance is around 200 Ω for all the MSCs in the high-frequency region. In contrast, at the high-to-medium frequency region, the interfacial charge transfer resistances (Rc) gradually decreased from 8350 to 810 Ω as the thickness of MXene electrodes increased. The significant impedance difference between the on-chip MSCs is corresponding to rate performance (Fig. 3d and e). Moreover, the nearly vertical line in the low-frequency region indicated the ideal capacitive behavior with prominent electrolyte ion propagation characteristics at the electrode/electrolyte interface [42,43].

The electrochemical behavior of Ti₃C₂Tx in H₂SO₄ is predominant pseudocapacitive that originate from the chemical reaction of Ti and –O species. Previous work indicated there was a clear change in Ti oxidation state from 2.33 to 2.43 over a 0.7 V window in H₂SO₄ electrolyte [44]. Indeed, limited by the electrolyte and the intrinsic properties of Ti₃C₂Tx, MXene, the working window of our on-chip MSCs is only 0–0.6 V, which cannot meet the demand of most occasions. Therefore, to expand the output voltage or the total capacitance, the on-chip MSCs should be integrated in series or in parallel. The corresponding CV and GCD curves of the on-chip MSCs can be improved from 0.0–0.6 V to 0.0–2.4 V with quasi-rectangular shape at a scan rate of 10 mV s⁻¹ (Fig. 4a). Besides, under the same current density, the discharge time of two MSCs in series was same to a single device MSC, while that of MSCs in parallel was two times of the single (Fig. 4b). Meanwhile, MXene-based on-chip MSCs exhibited excellent cycle stability, with 92.4% and 87.6% of initial areal capacitance preserved after 9000 and 10000 cycles, respectively (Fig. 4c).

The volumetric energy and power densities of MXene-based on-chip MSCs were compared with other micro-scale devices, as shown in Fig. 4d. The on-chip MSCs exhibited a high energy density of 1.1 mWh cm⁻³ with the corresponding power density of 189 mW cm⁻² and 0.53 mW h cm⁻² at a high power density of 11.96 W cm⁻³ (Fig. 4d). In fact, these values are higher than many other classes of electrode materials. For instance, the energy density of MSCs is about 0.68 mWh cm⁻² at 2.5 W cm⁻³ for reduced graphene oxide and carbon nanotube composites (GO-CNT) [45], and 0.54 mWh cm⁻² at 0.4 W cm⁻² for VN nanowires and carbon nanotubes (VN/CNT) [46], and 1 mWh cm⁻³ at 0.27 W cm⁻³ for polypropylene-coated paper (PPy) [47], etc.

The outstanding electrochemical performance of MXene-based on-chip MSCs is attributed to the unique properties of MXene (high conductivity, layered structure and rich functional groups, etc.), the digitized architecture constructed from TCC platform and the interface treating process [28,44]. Firstly, MXenes made the greatest contribution to the performance improvement for on-chip devices because of its high electrical conductivity, rapid ion intercalation between sheets, fast pseudocapacitive contribution, and hydrophilic surface. The presence of –O functional groups and interlayer water significantly promote the electrochemical capacity of Ti₃C₂Tx MXene. In addition, the easy treating-cutting-coating manufacture of on-chip MSCs, different from traditional micro/nano-fabrication technology which is complex and expensive, such as photolithography, inductively coupled plasma (ICP) etching technology, and physical/chemical deposition, can promote its large-scale production and greatly facilitate its commercial application. Especially, the kapton tape mask and the cold laser (355 nm) process can effectively reduce costs, decrease edge damage and improve the manufacture rate. Furthermore, the hydrophilic pretreatment greatly increases interface bonding between MXene and Si/SiO₂, ensuring the stability and uniformity of MXene film. More importantly, our work can be easily extended to other MXene materials, which will open up new avenues toward developing on-chip energy storage devices based on 2D materials.

3. Conclusion

In summary, we present a feasible treating-cutting-coating (TCC) manufacture process to fabricate MSCs on Si/SiO₂ wafer utilizing Ti₃C₂Tx MXene. Our approach is highly scalable and low-cost for silicon-based MSCs and facile to create high-energy MSCs. The on-chip MSCs with ultrathin MXene film exhibit exceptional electrochemical performance, including high areal capacitance and volumetric capacitance, high power and energy densities, in association with outstanding cycling stability. In addition, we have demonstrated that the on-chip MSCs can be easily fabricated in series and parallel connections. This TCC manufacture platform may open up new avenues toward developing on-chip energy storage devices based on 2D materials, which is beneficial to the next generation of semiconductor applications.

4. Experimental section

Preparation of water-stable MXene colloidal solution: The preparation of Ti₃C₂Tx MXene powder has been described in our previous study [48]. Typically, multilayer Ti₃C₂Tx powder was synthesized by etching MAX precursor phases of Ti₃AlC₂ (400 mesh, purchased from 11 Technology Co. Ltd.). After that, 1.0 g Ti₃C₂Tx powder was added into 100 ml deionized water, followed by sonication for 1 h. And the MXene colloidal solution was obtained after centrifugation at 3500 rpm for 1 h. To measure the concentration of specific amounts MXene solution, vacuum-assisted filtration through cellulose membrane with pore size of 0.2 μm was utilized to obtain the free-standing Ti₃C₂Tx films, followed by drying at 30 °C in vacuum drying oven for 1day. And the concentration of MXene colloidal solution is around 2 mg ml⁻¹.

Hydrophilic treatment of Si/SiO₂ wafers: In order to enhance the interfacial bonding between MXene colloidal solution and Si/SiO₂ wafers, hydrophilic treatment of Si/SiO₂ wafer is essential. The Si/SiO₂ wafer was cut into suitable size by laser marking machine, and then immersed in the mixture of 98% concentrated H₂SO₄ and 30% H₂O₂ with a volume ratio of 7:3. Then the mixture was placed in a water bath at 80 °C for 3 h. Furthermore, the as-treated Si/SiO₂ wafers were cleaned by ultrasonication in acetone, isopropanol, alcohol and DI water sequentially for 10 min each and then dried by flow gas.

Fabrication of MXene-based on-chip MSCs: The detailed fabrication procedure of MXene-based on-chip MSCs was shown as Fig. 1c. Kapton tape was first stuck on the surface of treated Si/SiO₂ wafer. And then, interdigitated patterns with specific area of 1.58 cm² were produced through ultraviolet laser marking technology (UV–3S, China, the laser beam size was 10 μm) and the remaining adhesive Kapton tape is retained as a mask. After that, MXene colloidal solution was spin-coated on Si/SiO₂ wafer drop by drop, which act as both the current collection and active materials. And the speed of spin-coating is 1500 rpm, 20 s at one time. Furthermore, the Kapton tape was directly stripped from the wafer. Finally, the electrode should be drying at room temperature for one night under vacuum.

The polyvinyl alcohol (PVA)/H₂SO₄ gel electrolyte was employed as the electrolyte for on-chip MSCs. To prepare the gel electrolyte, 8 g concentrated H₂SO₄ (98% mass concentration) was slowly add into 80 ml DI water. Then, 8 g PVA (Polyvinyl alcohol, 1799 type) was dissolved in the H₂SO₄ aqueous solution and stirred for 1 h in a water bath of 80 °C. Finally, put the gel electrolyte in fume hood until the solution cooled down to room temperature. The PVA/H₂SO₄ gel electrolyte was carefully dropped onto the interdigital pattern, followed by standing for 3 h to vaporize the excess water. At last, polydimethylsiloxane (PDMS) was dropped onto the electrodes to package the MSCs. After the PDMS module glue was fully solidified, on-chip MSCs were successfully obtained.

Characterizations: MAX phase powders and MXene film were
characterized by using a powder X-ray diffractometer (PANalytical X’Pert Powder diffractometer, Holland) with Cu Kα radiation over a 20 range of 5–60°. The surface morphology and microstructure of MXene powders and electrodes were imaged with a scanning electron microscope (SEM) (FEI QUANTA 250, American). The cyclic voltammetry (CV) tests were performed at a scan rate ranging from 10 to 200 mV s⁻¹ in the potential window of 0–0.6 V, while the Galvanostatic charge/discharge (GCD) tests were carried out in the range 1–30 μA cm⁻² in the same potential window. Electrochemical impedance spectroscopy (EIS) was performed at open circuit potential and frequencies ranging from 100 KHz to 0.1 Hz. In addition, an Arbin MSTAT4 multi-channel galvanostat/potentiotstat instrument (Arbin, USA) was used to measure the cycling stability for 10 000 cycles at 10 μA cm⁻².

Declaration of competing interest

The authors declare no competing financial interest.

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Appendix A. Supplementary data

Supporting Information is available from the Wiley Online Library or from the author.

Supplementary data to this article can be found online at https://doi.org/10.1016/j.nanoen.2019.104431.

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