Supporting Information

Binder-free bonding modularized MXene thin films into thick film electrodes for on-chip micro-supercapacitor with enhanced areal performance metrics

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Experimental

Preparation of multi-layered stacked Ti_3C_2Tx powders

Typically, 1.0 g of Ti_3AlC_2 MAX raw powders were first etched with a mixed solution consisting of 1.0 g lithium fluoride (LiF) and 20 ml 6 M hydrochloric acid (HCl) under agitation at 35 ℃ for 24 h to extract Al. Then, centrifuged the mixed solution and poured out the upper etching solution. The residual powders were washed with deionized (DI) water several times until the pH of the discarded upper liquid achieved 6. Finally, the multi-layered stacked Ti_3C_2Tx powders can be obtained through drying at room temperature.

Preparation of fully delaminated few-layered Ti_3C_2Tx flakes

First, 0.2 g as-obtained multi-layered stacked Ti_3C_2Tx powders were dispersed in 100 ml deionized water, followed by ultrasound exposure for 60 minutes in ice water bath. Then the unexploited multi-layered stacked Ti_3C_2Tx powders were removed by centrifugalization at 4000 rpm for 10 mins. Finally, a colloidal solution containing fully delaminated few-layered $Ti_3C_2T_x$ flakes (0.5 mg/ml) can be obtained.

Preparation of binder/conductive-additives free thick MXene film electrodes based on the modularized thin MXene films

First, the modularized thin MXene films with standard thickness were prepared through vacuum-assisted deposition of 20 ml as-prepared homogeneously colloidal suspension containing fully delaminated few-layered Ti_3C_2Tx flakes on Millipore filters (0.45 micron aperture). Then, a modularized thin MXene film was wetted with tiny amounts of deionized water, and covered with another modularized thin MXene film. After thoroughly drying, the two modularized thin films will fuse into a thick film and peeled off from the filter membrane, of which the thickness is twice as that of single modularized thin MXene film. By repeating the simple operation step, thicker MXene film electrodes with exponentially increased thickness can be prepared. All the prepared thick MXene film electrodes were followed by magnetron sputtering deposition (K550X) of an Au coating (80 nm) on top served as the current collector.

Fabrication of on-chip MSCs based on binder/conductive-additives free thick MXene film electrodes

First, interdigital-fingers-like circuit patterns were designed with AutoCAD software on a personal computer. Then, input the software into a laser cutting machine (TR-5030, professional CO_2 Universal Laser System, Shenzhen Triumph Industrial Co.,LTD). The laser power was set to 20% (10 W) and the speed was set to 200 mm s^{-1}, respectively. The Z-distance between the laser and the sample was 1.0 cm, while the laser beam size was about 100 μm. Finally, with the aid of the laser cutting, the designed coplanar interdigital electrodes based on the prepared binder/conductive-additives free thick MXene film electrodes can be fabricated. The polyvinyl alcohol (PVA)/sulfuric acid (H_2SO_4) gel electrolyte was used as the solid electrolytes, which was prepared through dissolving PVA powder (5 g) with H_2SO_4

aqueous solution (5 g H_2SO_4 into 50 ml DI water). The mixture was heated to 85 ℃ under vigorous stirring until the solution became clear. After cooling down, the gel solution was coated on the surface of interdigital electrodes. After the gel was solidified, the preparation of the on-chip MSCs based on binder/conductive-additives free thick MXene film electrodes built of modularized thin MXene film electrodes consisting of fully delaminated few-layered MXene flakes was finished.

The areal capacitance (mF cm^{-2}), areal energy density (mWh cm^{-2}), volumetric energy density (mWh cm^{-3}), and power density (W cm^{-3}) of the as-obtained MSCs were calculated from the charge-discharge curves according to the following equations:

$$C = Q/\Delta E = I\Delta t/\Delta E \quad (1)$$

$$Cs = C/S = I\Delta t/S\Delta E \quad (2)$$

$$Ws = 0.5C(\Delta E)^2/3600s \quad (3)$$

$$Wv = 0.5C(\Delta E)^2/3600v \quad (4)$$

$$Pv = Wv/\Delta t \quad (5)$$

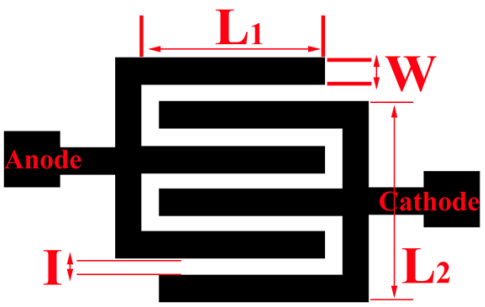
where C is the total capacitance, Q is the total charge, I is the discharge current, Δt is the discharge time, ΔE is the potential window during the discharge process after IR drop, and S is the total surface of the positive and the negative interdigital electrodes as shown in the Figure S1, V is the total volume of the positive and the negative interdigital electrodes.

Electrochemical Measurements

Electrochemical properties of all the fabricated devices were investigated in a two-electrode configuration. Two Cu wires were connected to the pad of each microelectrode using Ag paste to make a connection to the electrochemical instruments. CV, EIS, and GCD measurements of MSCs were carried out on an electrochemical workstation (CHI 660E, Chenhua, Shang-hai). Impedance spectroscopy measurements were performed at open circuit voltage with ±10 mV amplitude.

Material Characterization

The micromorphology and phase composition of all samples were characterized by Field-emission scanning electron microscopy (FE-SEM, S-4800, Hitachi, Japan), Transmission electron microscopy (TEM, JEM-2100, JEOL, Japan), and X-ray powder diffraction (XRD Bruker D8-ADVANCE) with an 18 kW advanced X-ray diffrac-tometer with Cu K_α radiation (λ=1.54056 Å). Sheet resistance of vacuum-assisted deposited MXene-based film on paper was measured by a standard four-point probe method (RST-9, Four-Probe Tech.). A Nikon D3100 digital single lens reflex camera was employed to take all the optical pictures.



MSCs	set parameters	actual parameters
L_1(um)	6500	6111
L_2(um)	7500	6940
W(um)	1500	1112
I (um)	500	345

Figure S1. The set and actual geometric parameters of as-fabricated interdigital electrodes through laser cutting.

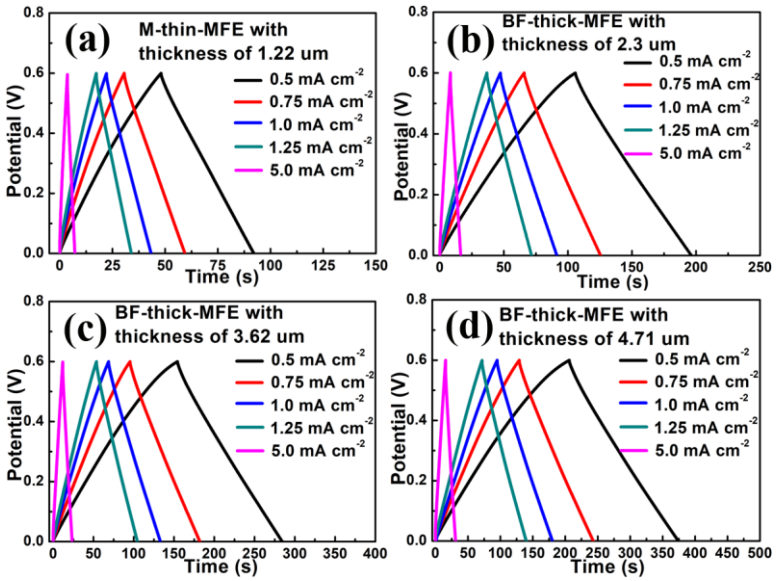


Figure S2. Galvanostatic charge-discharge curves of the as-fabricated on-chip MSCs based on BF-thick-MFEs with thickness from (a) 1.22 um, (b) 2.3 um, (c) 3.62 um, to (d) 4.71 um in the voltage range from 0 to 0.6 V at various current densities.