Supporting Information

Laser writing of TiVC film for high rate supercapacitors with ultrahigh capacitance

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Experimental Details

1. Synthesis of pristine TiVAlC

The TiVAlC MAX phase precursor was synthesized by a high-temperature solid-state reaction. Sponge titanium (Ti, Taobao, High purity), vanadium powder (V, Taobao, High purity), aluminum granules (Al, Taobao,0.5mm*0.5mm), and graphite powder (C, Taobao, High purity) were precisely weighed in a stoichiometric ratio of 1:1:1.2:1. First, titanium powder, vanadium powder, and graphite powder were mixed in a crusher for three cycles of 2 minutes each. Aluminum granules were then added, followed by additional crushing for 2 minutes to ensure a homogeneous precursor mixture. The mixed powder was loaded into an alumina crucible, which was then transferred to a tube furnace. Under a continuous argon flow, the temperature was raised at 3 °C/min to 1550 °C, held for 2 hours to complete the sintering reaction, and finally cooled down to room temperature inside the furnace. The resulting sintered product was mechanically crushed into MAX-phase powder. To remove excess aluminum metal impurities, 20 g of the MAX powder was immersed in 200 mL of 9 mol/L hydrochloric acid (HCl, industrial grade, 35–38%) for 48 hours. The solid product was collected by vacuum filtration and repeatedly washed with deionized water until the filtrate reached neutrality. The purified TiVAlC powder was finally dried in a vacuum oven at 70 °C for 8 hours.

2. Synthesis of pristine TiVC film

TiVC MXene was prepared by selectively etching aluminum from TiVAlC using an HCl+LiF etching system. Specifically, 30 mL of hydrochloric acid (HCl, industrial grade, 35–38%) was mixed with 2.8 g of LiF (Aladdin, 99%) and stirred at room temperature for 30 minutes. Then, 2 g of TiVAlC powder was gradually introduced into the solution maintained

at 40 °C and stirred at 600 rpm for 24 h. The resulting multilayer MXene suspension was collected and repeatedly centrifuged at 3500 rpm (5 min per cycle), followed by washing with deionized water until a stable TiVC colloidal solution was obtained.

3. *Laser irradiation of TiVC films*

A 1064 nm pulsed laser was employed to irradiate the TiVC films. The laser operated at a total output power of 20 W and a pulse repetition rate of 20 kHz. To preserve the structural integrity of the free-standing TiVC film, the power density was reduced using a 10 cm defocusing distance, as direct focusing under such high power would otherwise completely ablate the material. The laser scanning speed was set at 2 m/s.

4. Electrochemical measurements

Electrochemical tests were carried out in a Swagelok cell configuration using a three-electrode setup. The working electrodes were TiVC free-standing discs with a diameter of 5 mm, while over-capacitive activated carbon and a Hg/Hg_2SO_4 electrode served as the counter and reference electrodes, respectively. Both current collectors were made of glassy carbon. All measurements were conducted in 1 M H_2SO_4 electrolyte at room temperature using a VSP-3e electrochemical workstation. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed under these conditions. EIS measurements were recorded in the frequency range of 100 kHz to 0.1 Hz at the open-circuit potential (OCP) versus Hg/Hg_2SO_4, with an applied sinusoidal signal amplitude of 10 mV.

5. Electrochemical calculations

Gravimetric specific capacitance C_m (F/g) of electrode materials was calculated from the CV curves by integrating the discharge portion using the following equation:

$$C_m = \frac{1}{Vmv}\int idV \tag{1}$$

where i is the current (mA), V is the potential (V), v is the scan rate (mV/s) and m is the mass of the electrode (mg).

Supporting figures

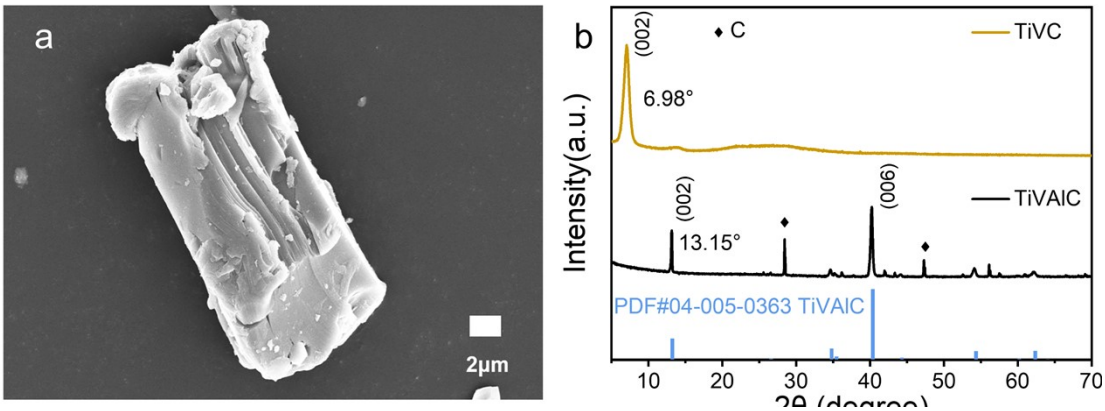

Fig. S1 (a) SEM of TiVAlC; (b) XRD of TiVAlC and TiVC.

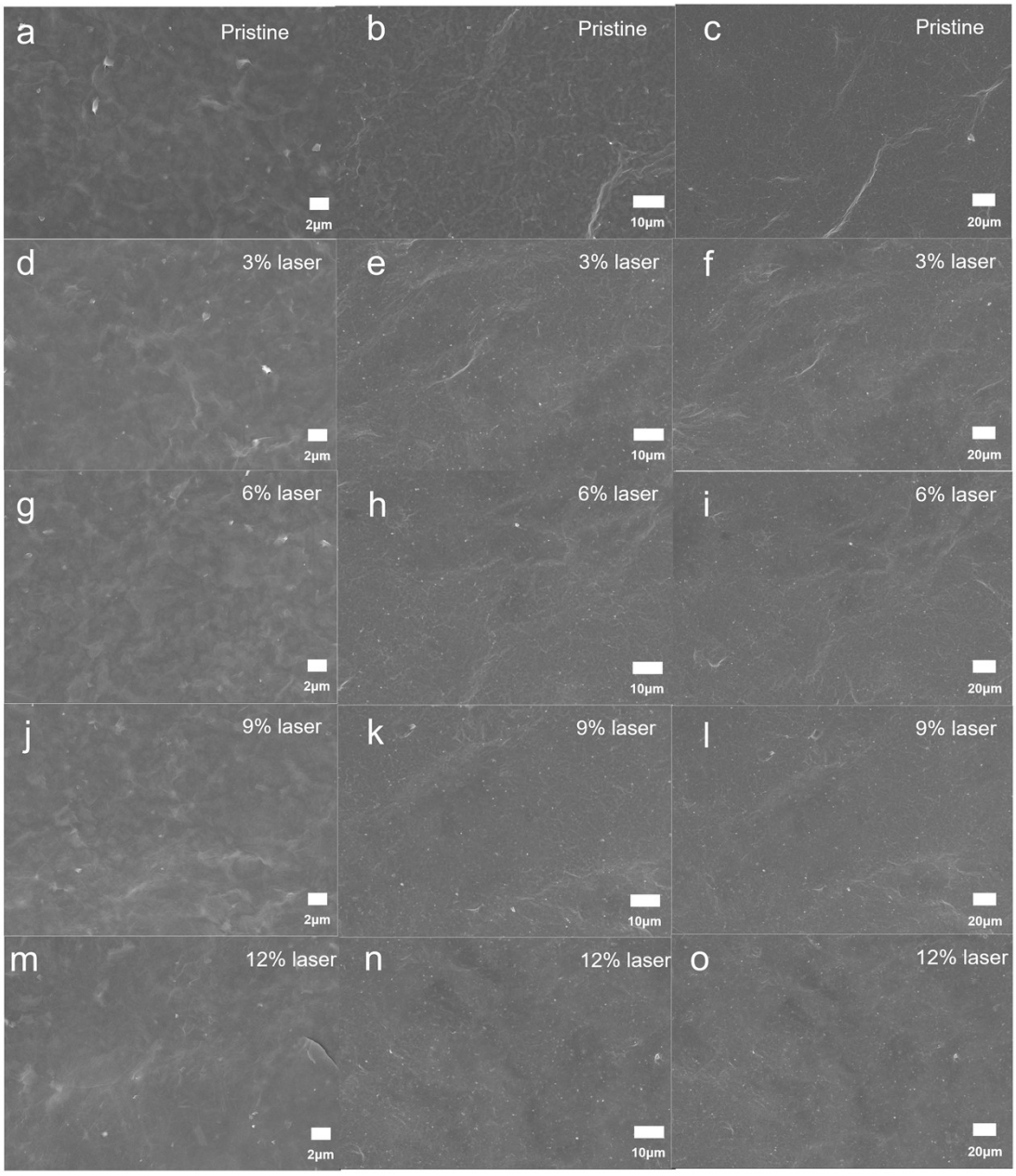

Fig. S2 Top view SEM images showing the TiVC films with different laser writing power ratios.

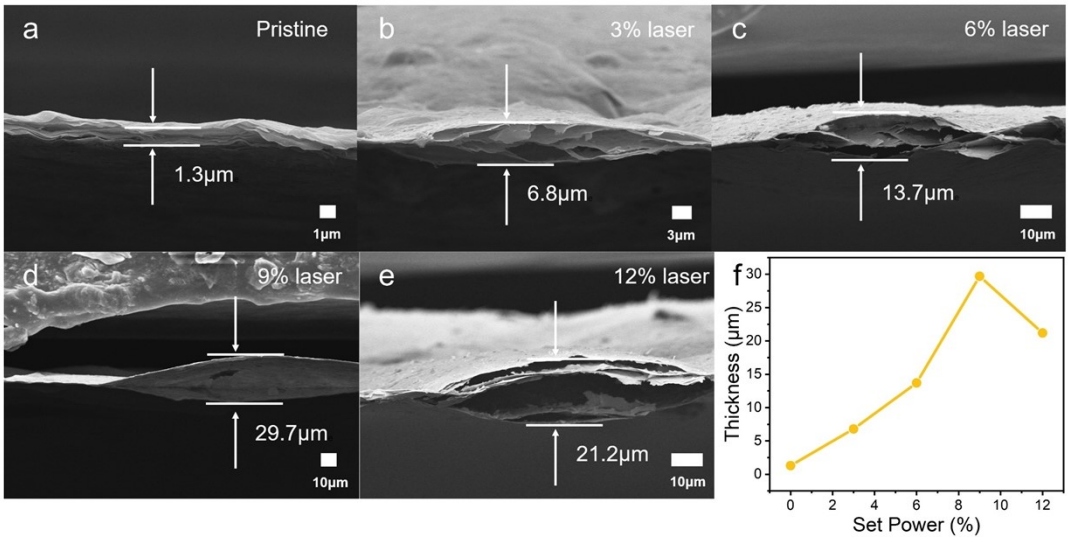

Fig. S3 (a-e) Cross-sectional SEM images showing the laser written TVC films with different laser writing power ratios; (f) The thickness of the laser written TiVC films varies with the intensity of laser writing power added.

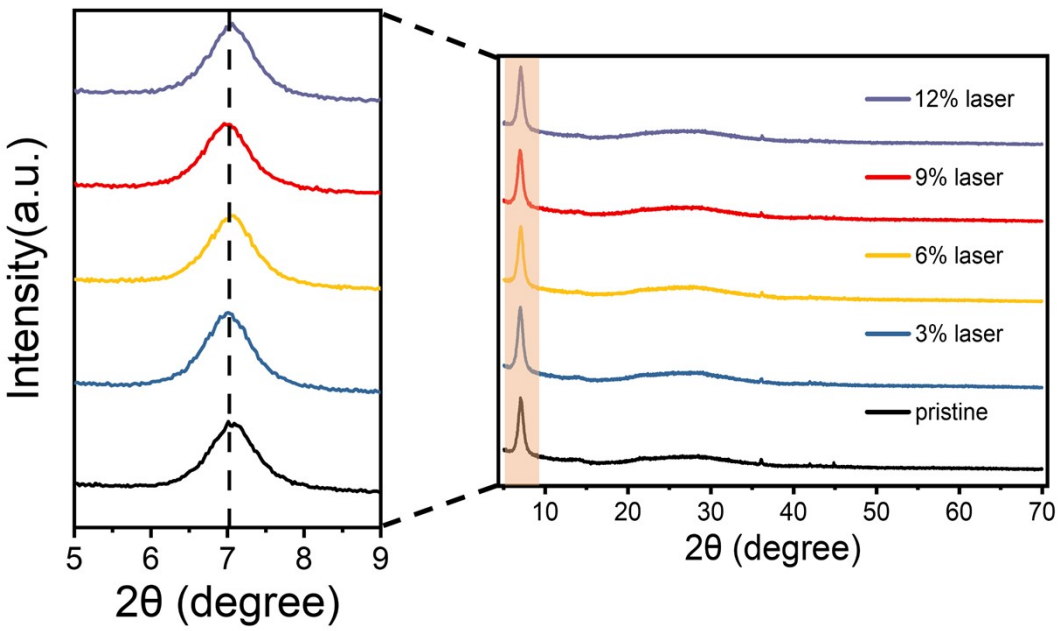

Fig. S4 XRD of TiVC films before and after laser writing power.

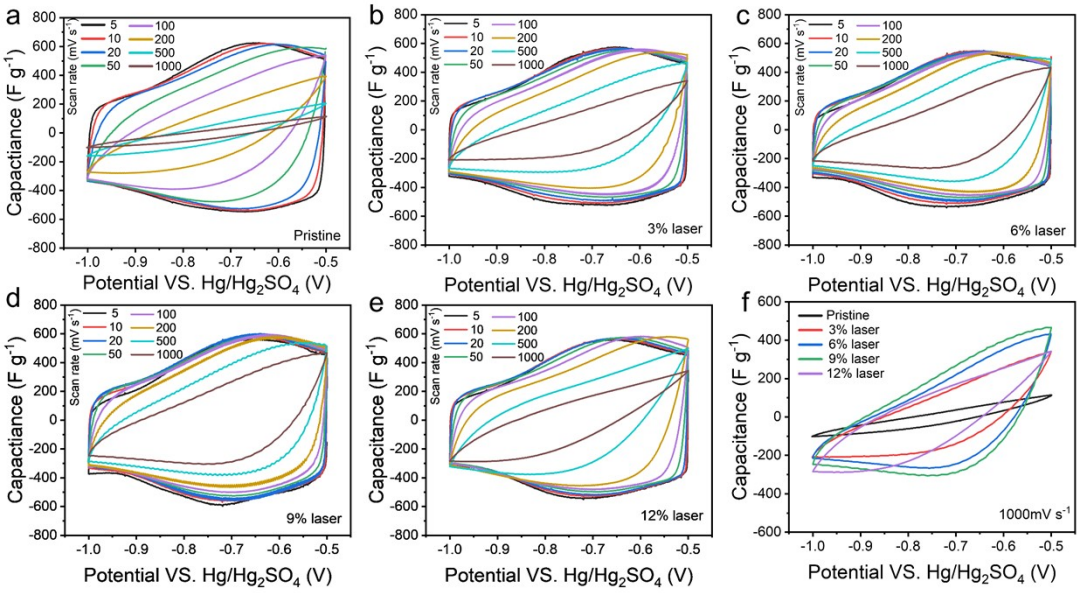

Fig. S5 (a-e) CV curves of the laser written TiVC films with different laser power ratios at various scan rates from 5 mV/s to 1000 mV/s; (f) CV curves of TiVC films at 1000 mV/s before and after laser writing.

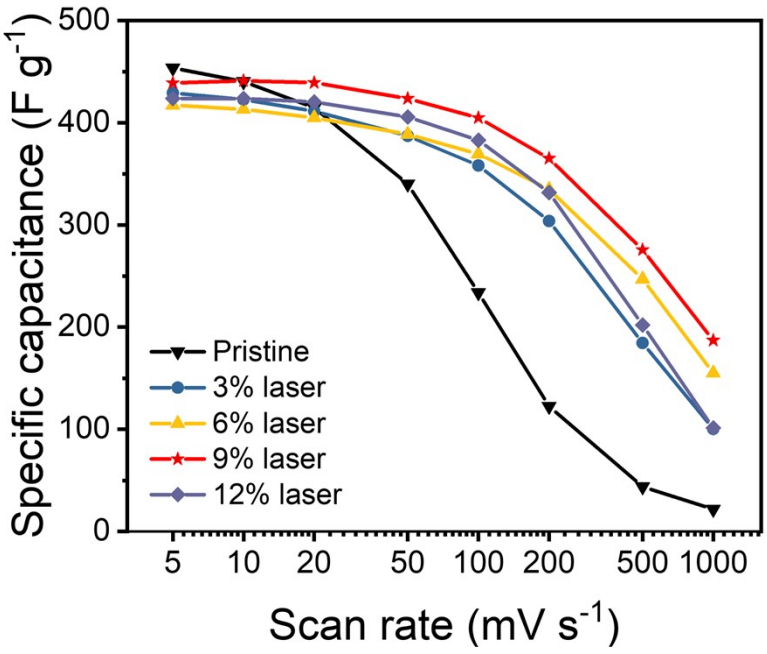

Fig. S6 Rate performance of the laser written TiVC films with different laser power ratios.

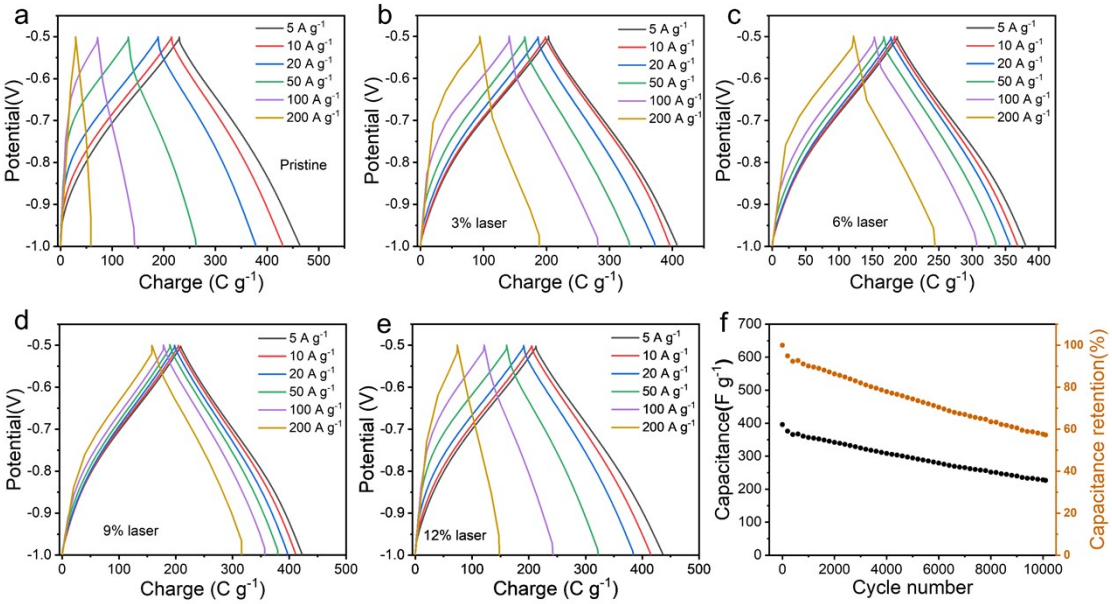

Fig. S7 (a-e) Charge-discharge curves of TiVC films at different current densities under varying laser power ratios; (f) Long-cycle performance of 9% laser TiVC films at a current density of 50 A/g.