

Supplementary Information

Light-Induced Electrostatic Lithography: Selective Discharge of Electrets by Utilizing Photothermal Conversion of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene

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Experimental Methods

TEM images were captured on a HT7700 electron microscope and corresponding EDS images were obtained on a field-emission. AFM measurements were performed on a Multi Mode 3 system (Bruker). The crystal structures of $\text{Ti}_3\text{C}_2\text{T}_x$ and $\text{Ti}_3\text{C}_2\text{T}_x@\text{PEI}$ nanosheets were characterized by X-ray diffraction (XRD, Bruker D8 Advance diffractometer) with a $\text{Cu K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). Raman spectra were collected on an XploRA laser Raman spectrometer with an excitation wavelength of 532 nm provided by an Ar laser. UV-vis spectra were measured with a UV-6100S instrument. NIR light was provided with an 808 nm high power multimode pump (Hite Optoelectronics). Infrared thermal imaging instrument (Fluke TiX 660, spectral range of 7.5-14.0 μm) with 0.95 as the emissivity was employed to record surface temperatures and thermal images of the photothermal agents. The surface temperatures of samples were measured at the same power density for five times and the error range was 0-7.8 °C. Kelvin probe force microscopy (KPFM) measurements were performed in amplitude modulation mode on a Multi Mode 3 system (Bruker). A Pt/Ir coated tip (SCM-PIT, Bruker) was used with 75 kHz resonant frequency, 2.8 N m^{-1} spring

constant and ~5.5 eV work function. The compensation voltage (V_{DC}) was applied to the sample during the KPFM measurement. The surface charge density (σ) on PMMA film can be calculated according to Gauss' Law

$$\sigma = \frac{\varepsilon_0 \Delta V_{CPD}}{h} \quad (1)$$

where ε_0 is the vacuum permittivity (8.854×10^{-12} F m⁻¹), ΔV_{CPD} is the contact potential difference change of PMMA film before and after contacting with irradiated $Ti_3C_2T_x@PEI$ pattern, and h is a KPFM lift height (20 nm).

Preparation of the dispersions of $Ti_3C_2T_x$ nanosheets: $Ti_3C_2T_x$ was prepared by etching Al layer of Ti_3AlC_2 powders according to the method previously reported.¹ Briefly, 1.0 g LiF was added to 20 mL hydrochloric acid (6 M) and reacted for 30 min. Then 1.0 g Ti_3AlC_2 MAX phase powders were slowly added to the above mixed acid solution. The reaction process was kept for 24 h at 35 °C to completely remove Al layer. Following, the suspension liquid was repeatedly rinsed with deionized water for 5 min at 3500 rpm until the pH value of the supernatant was about 6. Finally, $Ti_3C_2T_x$ powders were collected by freeze drying. $Ti_3C_2T_x$ nanosheets were prepared by adding $Ti_3C_2T_x$ powders to deionized water with a sonicating process for 1 h at room temperature.

Preparation of the $Ti_3C_2T_x@PEI$ ink: A $Ti_3C_2T_x$ dispersion (3 mL, 1 g L⁻¹) was dropwise added to a PEI aqueous solution (2 mL, 10 wt%) and the mixture was sonicated for 30 min. Then, the mixture solution was centrifuged at 10000 rpm for 30 min to obtain the $Ti_3C_2T_x@PEI$ ink after removing supernate.

Fabrication of $Ti_3C_2T_x@PEI$ pattern: The $Ti_3C_2T_x@PEI$ patterns were fabricated with a MIMIC procedure. A PDMS stamp with relief was adhered to a flat PDMS without

pattern. Then, $\text{Ti}_3\text{C}_2\text{T}_x@\text{PEI}$ ink filled channels between these two PDMS slices by capillarity. $\text{Ti}_3\text{C}_2\text{T}_x@\text{PEI}$ pattern with an inverted relief was obtained on the flat PDMS after removing the upper PDMS.

Patterning of charges on PMMA: The PMMA glass was rubbed with a silk cloth for several seconds to generate space charges. A $\text{Ti}_3\text{C}_2\text{T}_x@\text{PEI}$ pattern was exposed to an 808 nm NIR light at a power density of 1.7 W cm^{-2} for 20 seconds. The irradiated $\text{Ti}_3\text{C}_2\text{T}_x@\text{PEI}$ pattern was contacted with the charged PMMA glass for 5 seconds. Then dry carbon toner powders were blown on the PMMA glass. A 2.5% PMMA (dissolved in chlorobenzene) solution was spin-coated on a silicon wafer at 6000 rpm to form a thin nanofilm with a thickness of around 150 nm. The silicon substrates were cut into pieces with geometric area of 0.5 cm^2 . A piece of aluminum foil was coated on the film served as another electrode. Direct current was provided by a Keithley 2400 electrometer with a voltage of 10 kV cm^{-1} . After a current application ($\sim 1 \text{ mA}$) to the PMMA thin film for 20 seconds, the silicon wafer with charged PMMA nanofilm was removed and then put on the irradiated $\text{Ti}_3\text{C}_2\text{T}_x@\text{PEI}$ pattern for 5 seconds.

Reduction of metal ions: The PMMA nanofilms with electrostatic charge patterns were immersed into AgNO_3 and CuSO_4 ethanolic solutions (their concentrations were separately half of their saturated solutions in ethanol) for 20 seconds, respectively. Then, the PMMA electrets were quickly washed with ethanol to remove the loosed held parts.

Results and Discussion

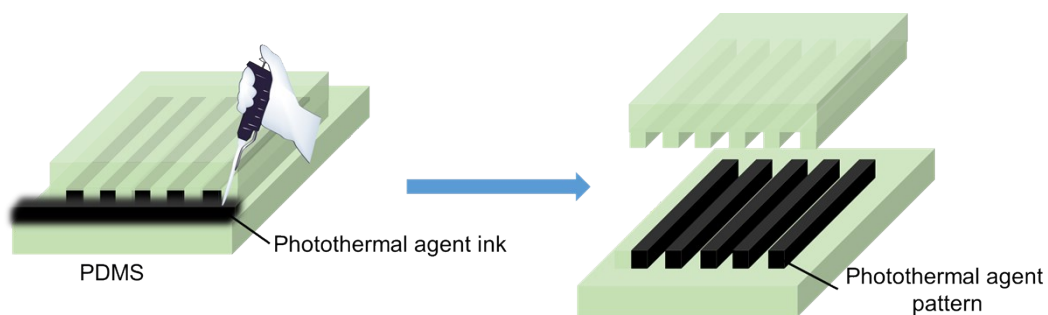


Fig. S1. Schematic illustration of the process of fabricating photothermal agent pattern on PDMS by a MIMIC technique. A PDMS stamp with relief is adhered to a flat PDMS. Photothermal agent ink fills channels between these two PDMS slices by capillarity. Photothermal agent pattern with an inverted relief is obtained on the bottom PDMS after removing the upper PDMS.

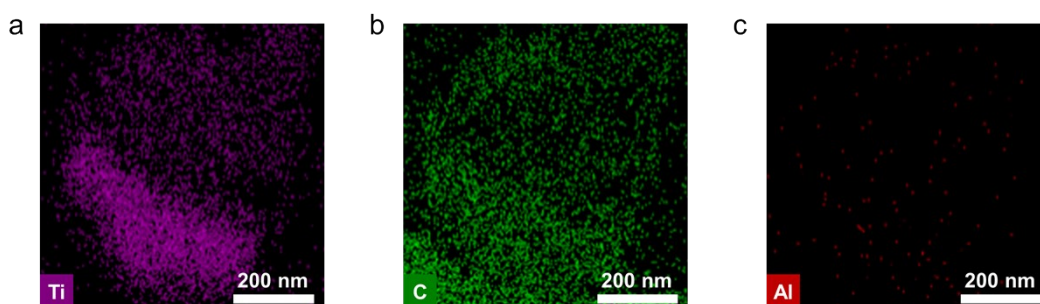


Fig. S2. EDS mapping images of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets.

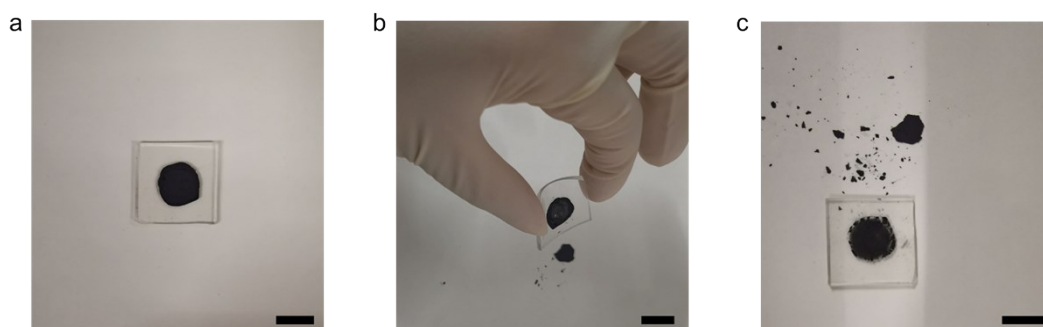


Fig. S3. Optical images of $\text{Ti}_3\text{C}_2\text{T}_x$ film painted on PDMS substrate before bending substrate (a), bending process (b) and after bending substrate (c). All the scale bars are 1.0 cm.

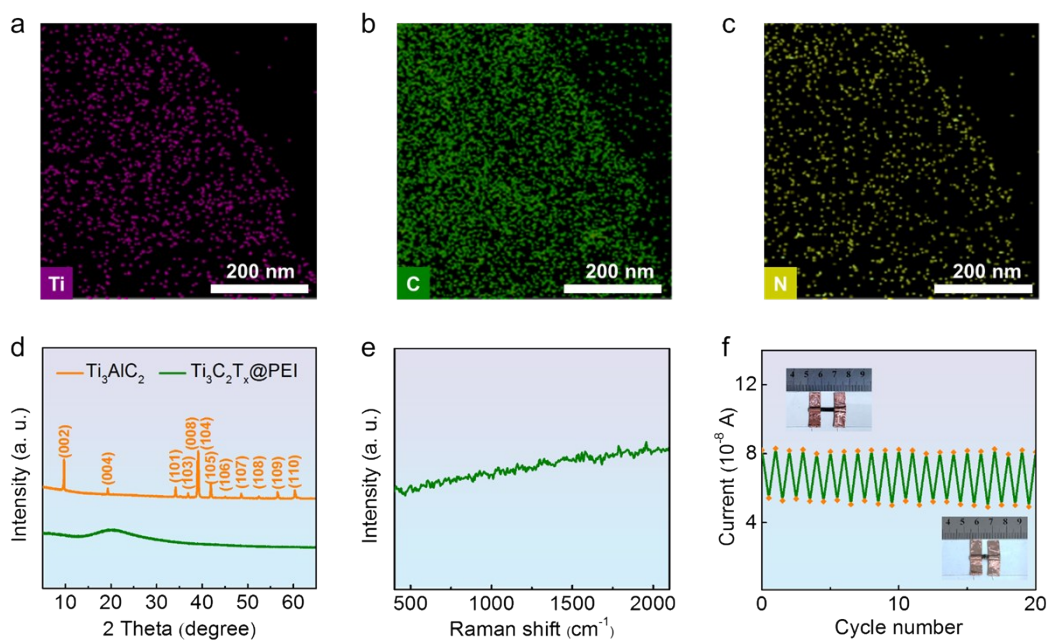


Fig. S4. (a-c) EDS mapping images of $\text{Ti}_3\text{C}_2\text{T}_x@PEI$ nanosheets. (d) XRD patterns of Ti_3AlC_2 powders, $\text{Ti}_3\text{C}_2\text{T}_x@PEI$ nanosheets. (e) Raman spectrum of $\text{Ti}_3\text{C}_2\text{T}_x@PEI$ nanosheets. (f) Stability performance test of $\text{Ti}_3\text{C}_2\text{T}_x@PEI$ film on PDMS with flat-bending cycling. Insets are optical images of $\text{Ti}_3\text{C}_2\text{T}_x@PEI$ film at flat state (top inset) and bending state (bottom inset), respectively.

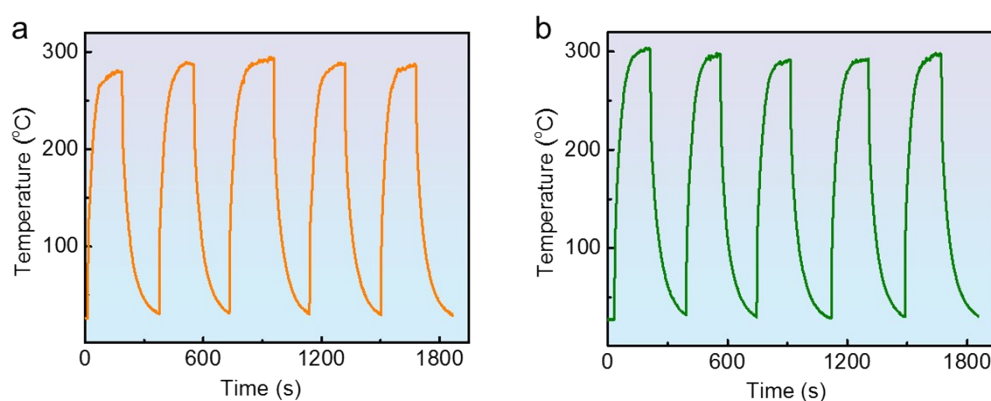


Fig. S5. On-off cycle responses of $\text{Ti}_3\text{C}_2\text{T}_x$ (a) $\text{Ti}_3\text{C}_2\text{T}_x@PEI$ film (b) on PDMS under 808 nm NIR light with a power density of 1.7 W cm^{-2} .

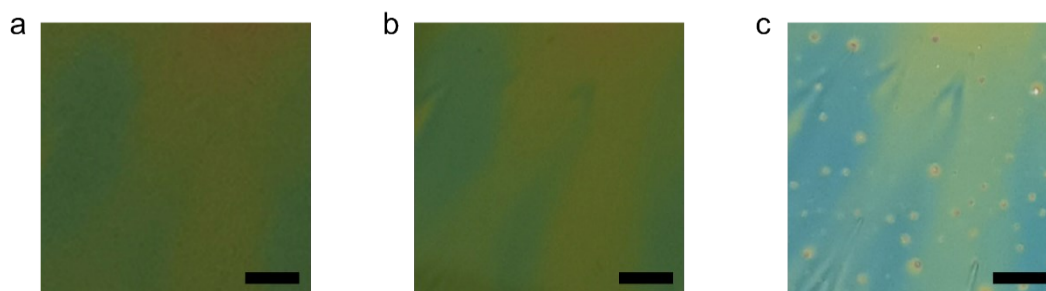


Fig. S6. Optical images of PMMA films without charged (a), positive charged (b) and negative charged (c) after contacting with AgNO_3 ethanolic solutions. All the scale bars are 2.5 mm.

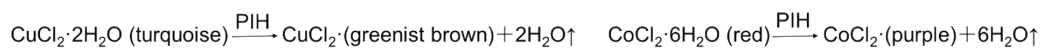
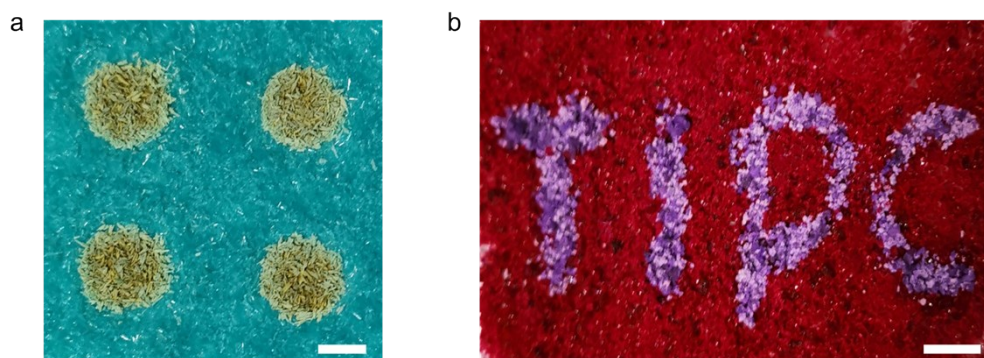


Fig. S7. Optical images of patterns produced by local thermal decomposition reaction of copper(II) chloride dihydrate (a) and cobalt(II) chloride hexahydrate (b) with photothermal-induced heat (PIH) $\text{Ti}_3\text{C}_2\text{T}_x$ @PEI film. All the scale bars are 0.5 cm.

Reference

- [1] M. Ghidui, M. R. Lukatskaya, M. Q. Zhao, Y. Gogotsi, M. W. Barsoum, *Nature*, 2014, **516**, 78.

Author Contributions

M. Xue, X. Zhang, and X. Ma initiated the project, conceived and supervised the experiments. H. Ma carried out the AFM, photothermal measurements and releasing charges experiments. H. Cheng and X. Zhang provided assistance with sample preparation and data analysis. X. Ma, S. Wang, Z. Zhou, Y. Chai, R. Chen, Y. He, Y. Wang, Y. Li, X. Wang, R. Li and N. Ma provided assistance with of materials characterization and data analysis. M. Xue and H. Ma analyzed the data and wrote the paper.