

Electronic Supplementary Information (ESI)

## **Near-infrared light-responsive hydrogels via peroxide-decorating MXene-initiated polymerization**

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### **Table of Contents**

#### **1. Experimental**

##### **1.1. Materials**

##### **1.2. Preparation of p-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> and conventional Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>**

##### **1.3. Preparation of PNIPAM-based nanocomposite (NC) polymer and hydrogel**

##### **1.4. Polymerization of different monomers initiated by p-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>**

##### **1.5. Preparation of pure PNIPAM and hydrogel**

##### **1.6. Acid sediment**

##### **1.7. Quantification of p-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> nanosheets by luminol assay**

##### **1.8. Electron paramagnetic resonance (EPR) spectra**

##### **1.9. Optical transmittance measurements**

##### **1.10. Scanning electron microscope (SEM)**

##### **1.11. Transmission electron microscope (TEM)**

##### **1.12. Atomic force microscope (AFM)**

##### **1.13. X-ray photoelectron spectrum (XPS)**

##### **1.14. X-ray diffraction (XRD)**

##### **1.15. <sup>1</sup>H-NMR spectroscopy**

##### **1.16. Absorbance spectra**

##### **1.17. Photothermal stability and calculation of photothermal conversion efficiency**

##### **1.18. Rheological measurements**

##### **1.19. Conductivity measurements**

##### **1.20. NIR-responsive applications**

#### **2. Supplementary Figures and Tables**

#### **References**

## 1. Experimental

### 1.1. Materials

Ti<sub>3</sub>AlC<sub>2</sub> powders (99.5% purity, 400 mesh) were purchased from Laizhou Kai Ceramic Material (Yantai, China). Lithium fluoride (LiF, 99.0%) and hydrochloric acid (HCl, 37%) were obtained from Sigma-Aldrich. Azobisisobutyronitrile (AIBN), ammonium persulfate (APS) and all monomers were purchased from Energy Chemical (Shanghai, China). N-isopropylacrylamide (NIPAM) was purified by recrystallization from petroleum ether and dried at 50 °C under vacuum. N,N-dimethylacrylamide (DMA), methyl methacrylate (MMA) and hydroxyethyl methacrylate (HEMA) were isolated by column chromatography filled with aluminum oxide to remove the polymerization inhibitor. All other chemicals were of analytical grade.

### 1.2. Preparation of p-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> and conventional Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>

p-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> nanosheet suspension was prepared from a modified procedure from previous minimally intensive layer delamination (MILD) etching method.<sup>1</sup> It was called the sonication-assisted MILD etching process, where delamination is simultaneously accomplished along with the etching process. Briefly, 0.125 g Ti<sub>3</sub>AlC<sub>2</sub> powders were immersed in the mixture of 0.2 g LiF and 2.5 mL 9 M HCl, and constantly stirred for 12 h at 35 °C. The resulting suspension was then delamination by sonication for 6 ~ 12 h without removing the etchants. After sonication, a dark suspension was observed and then washed by deionized water repeatedly. The solid was collected by centrifugation at 3500 rpm for 5 min until the pH of supernatant reached 5 ~ 6. Eventually, the clay-like sediment was redispersed in deaerated water, the final supernatant colloid (p-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> nanosheets) was collected at 12000 rpm for 10 min.

Conventional Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> nanosheets were prepared as a control according to the MILD etching process. Briefly, the precursor was mixed with etchant using (12 M LiF/9 M HCl) at 35 °C under continuous stirring for 24 h. Then, the powder was washed with deionized H<sub>2</sub>O via centrifugation (5 min per cycle at 3500 rpm), a supernatant slurry (conventional Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>) was obtained when the pH reached 5 ~ 6.

### 1.3. Preparation of PNIPAM-based nanocomposite (NC) polymer and hydrogel

Different amounts of NIPAM were dissolved in 1 mL p-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> nanosheets suspension and then aerated with pure nitrogen for 2 min to remove dissolved oxygen under ice-bath. The polymerization was easily detected by the increase of viscosity within minutes. At high concentration of monomer, the hydrogel was rapidly formed. Notably, the reaction vessel was finely protected against light during the whole N<sub>2</sub> purging and polymerization.

The monomer concentration to form the NC polymer dispersion is below 5 wt%. The NC polymer was prepared at 3 wt% NIPAM concentration unless specified otherwise. The monomer concentration to form the NC hydrogels is above 5 wt% (optimal selected: 80 mg mL<sup>-1</sup> NIPAM unless specified otherwise).

Generally, the p-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> concentration to initiate the polymerization is above 0.01 mg mL<sup>-1</sup>. More content of p-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> will produce more color of dark green, stronger photothermal effect and more sensitivity to electrons and/or photons. The NC hydrogel was prepared at 0.35 mg mL<sup>-1</sup> p-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> concentration unless specified otherwise.

### 1.4. Polymerization of different monomers initiated by p-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>

Different monomers (including acrylamide (AAm), DMA, MMA, HEMA) were added in 1 mL 0.35 mg mL<sup>-1</sup> p-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> nanosheets suspension and then aerated with pure nitrogen for 5 min to remove dissolved oxygen under ice-bath. Like NIPAM, AAm and DMA form hydrogels after the polymerization reaction at room temperature at 8 wt% concentration (Fig. S2). The others (MMA and HEMA) form insoluble white/grey aggregates after reaction at room temperature.

### 1.5. Preparation of pure PNIPAM polymer and hydrogel

To prepare pure PNIPAM polymer, NIPAM (4 g) and AIBN (1% mole ratio to monomer) were dissolved into *n*-hexane. After degassing, the reaction was heated to 70 °C for 6 h. Then the PNIPAM sample was purified by precipitation three times with acetone (8 : 1 related to *n*-hexane). Finally, the PNIPAM sample was dried in vacuum at 60 °C for 12 h.

To prepare pure PNIPAM hydrogel, N-isopropylacrylamide (160 mg) was dissolved in distilled water (2 mL), then APS (final concentration 1 mg mL<sup>-1</sup>) and TEMED (2 μL) were added with stirring. The resulting solution was reacted for 24 h at 4 °C.

### 1.6. Acid sediment

The acid stability of three p-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-containing solutions (p-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, physical mixture of PNIPAM and p-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, PNIPAM-based NC polymer) was measured by adding 20 μL 12 M HCl and then separating by centrifuge at 3500 rpm for 5 min. In the mixture and NC polymer, the concentration of PNIPAM or NIPAM and p-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> is about 30 and 1.0 mg mL<sup>-1</sup>, respectively.

### 1.7. Quantification of p-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> nanosheets by luminol assay

The luminol assay was prepared by the containing of 0.05 M NaOH solution and the concentration of luminol is 0.05 M. The fluorescence spectra were carried on a fluorescence spectrophotometer (Hitachi, F-4600) using a 2 mL quartz cell. Different concentrations of p-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> nanosheets were mixed with the luminol reagent. The fluorescence spectra were excited at 290 nm with the emission at 440 nm.

### 1.8. Electron paramagnetic resonance (EPR) spectra

EPR spectra of different samples were recorded on a Bruker A300 spectrometer (X-band) equipped with a Bruker ER4141VTM liquid N<sub>2</sub> system. Solution samples were loaded into 1 mm quartz EPR tubes (Blaubrand, 7087-33) and then measured at 290 K, with a frequency of 9.86 GHz, center field of 3500 G, sweep width of 120 G, microwave power 7.1 mW and modulation amplitude of 1.0 G. For •OH evaluation, both p-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> nanosheets suspension and APS (1 mM) were prepared in aqueous solution, 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) was applied as the spin-trapping agent for •OH.

### 1.9. Optical transmittance measurements

Transmittance spectra were recorded on a SHIMADZU UV 2600 spectrophotometer equipped with a temperature control system. A hydrogel prepared in an optical cuvette (1 cm width) was directly used for optical transmittance measurements. The mass concentrations of p-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> and NIPAM for hydrogel formation were 0.1 and 80 mg mL<sup>-1</sup>, respectively. The measurements

were in the range 20 ~ 50 °C with a heating rate of 1.0 °C min<sup>-1</sup>.

#### **1.10. Scanning electron microscope (SEM)**

Morphology of PNIPAM-based NC hydrogel was measured by scanning electron microscopy (SEM) through Nova NanoSEM230 (Czech). The NC hydrogel was freeze-dried, attached on conductive adhesives and then sputtered with gold for observation. The mass concentration of monomer for hydrogel formation was 8 wt%.

#### **1.11. Transmission electron microscope (TEM)**

TEM investigations were conducted on a FEI G20 (USA) microscope. The samples were prepared by dropping a diluted p-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> and PNIPAM-based NC polymer on a carbon-coated copper grid and drying in a desiccator containing silica gel. In addition, the staining technique by phosphotungstic acid was used to observe the structure of NC polymer under the transmission electron microscope (Tecnai G2 Spirit TWIN USA).

#### **1.12. Atomic force microscope (AFM)**

AFM images were collected on an atomic force microscope (Bruker instrument Dimension Icon) in tapping mode. The samples were prepared by dropping a diluted p-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> and NC polymer on a freshly cleaved mica and dried in a desiccator containing silica gel.

#### **1.13. X-ray photoelectron spectrum (XPS)**

X-ray photoelectron spectra (XPS) were carried out in a Thermo Fisher Scientific spectrometer (K-Alpha<sup>+</sup>) equipped with an Al K $\alpha$  X-ray source. All peaks are referenced to the signature of the C 1s peak for carbon at 284.8 eV. The samples were freeze-dried for the test. The spectra were acquired in the constant analyzer energy mode with pass energy of 100 eV for the survey. Narrow regions were collected with pass energy of 30 eV. Component peak fitting of XPS spectra was performed by using software XPS PEAK version 4.1. Prior to the peak fitting, the background contributions were subtracted using a Shirley function.

#### **1.14. X-ray diffraction (XRD)**

X-ray diffraction was performed on a Bruker diffractometer (Bruker AXS D8 Advance, Germany) with Cu K $\alpha$  radiation. The samples were freeze-dried for the test.

#### **1.15. <sup>1</sup>H-NMR spectroscopy**

<sup>1</sup>H-NMR spectra were recorded in DMSO-*d*<sub>6</sub> at 25 °C on Varian MERCURY plus-400 spectrometer, operating at 400 MHz. Monomer/p-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> mixture (before N<sub>2</sub> purging) was characterized after freeze-dried and redispersed in DMSO-*d*<sub>6</sub> for the test without further purification. The monomer conversion was calculated by dividing the integrated peak area of protons in the polymer backbone with the integrated peak area of protons in monomeric double bond and the polymer backbone.

In order to follow the kinetics, the monomer conversion *versus* reaction time and monomer concentration was monitored by <sup>1</sup>H-NMR spectroscopy. NIPAM was applied as an example of monomers. At the predetermined time, the reaction vessel is added with *p*-benzoquinone (final concentration 1.0 μM) to stop the reaction. The concentration of NIPAM is about 1.0 wt% for

the polymerization kinetics.

### 1.16. Absorbance spectra

Absorbance spectra of p-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> nanosheets and NC hydrogels were measured by UV-2450 Shimadzu UV-Vis-NIR spectrometer (Shimadzu, Japan). The NC polymer sample was prepared by 80 mg NIPAM monomer and 1 mL p-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> suspension with different concentration (0.05, 0.1, 0.15, 0.2 mg mL<sup>-1</sup>).

### 1.17. Photothermal stability and calculation of photothermal conversion efficiency

The photothermal effect of the NC hydrogels was measured by consecutively exposed to 808 nm laser at different powder density. The photothermal stability of the NC hydrogels was measured by consecutively exposed to 808 nm laser (1.0 W cm<sup>-2</sup>) for five cycles (Fig. S10). The NC hydrogel samples were prepared at 80 mg NIPAM monomer and 1 mL p-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> nanosheets suspension (0.35 mg mL<sup>-1</sup>).

According to the literature,<sup>2</sup> the photothermal conversion efficiency ( $\eta$ ) of PNIPAM-based NC hydrogel was determined by the following equations:

$$hS = \sum mC_p/\tau_s$$

$$\eta = hS (T_{\max} - T_{\max, \text{water}})/I(1 - 10^{-A})$$

where  $h$  is the heat transfer coefficient,  $S$  is the surface area of the container,  $m$  is the mass of hydrogel,  $\tau_s$  is the time constant,  $C_p$  is the specific heat capacity of water (4.2 J mol<sup>-1</sup>).  $\tau_s$  is obtained by applying the linear time data from the cooling period of the first cycles versus the negative natural logarithm of driving force temperature from Fig. S9 and S10.  $T_{\max}$  is the temperature of NC hydrogel (44.3 °C),  $T_{\max, \text{water}}$  is about 25.6 °C and the value of  $\tau_s$  is 238.86 s,  $hS = 0.0176$ .  $I$  is the laser power density (1.0 W cm<sup>-2</sup>), and  $A$  is the absorbance of NC hydrogel at 808 nm ( $A_{808 \text{ nm}} = 1.278$ ). The photothermal conversion efficiency ( $\eta$ ) is 34.7%.

### 1.18. Rheological measurements

Rheological properties of hydrogels were measured at 25 °C by using a rheometer (Anton Paar, MCR 302) with parallel plate geometry (25 mm diameter). The gap was set to be 1 mm. Storage moduli ( $G'$ ) and loss moduli ( $G''$ ) were measured on a strain sweep in a range of  $\gamma$  (0.1~1000%) at a fixed frequency ( $\omega = 6.28 \text{ rad s}^{-1}$ ). The alternate-step strain sweep is carried out. The high-magnitude strain of 800% holding 30 s, a low-magnitude strain (0.1%) for 3 min was used to detect the recovery of the hydrogel structure. The test was conducted for five cycles to demonstrate the recovering property of NC hydrogels.

### 1.19. Conductivity measurements

A round-shape disk PNIPAM-based NC hydrogel (diameter of 5 mm) was measured by electrochemical impedance spectroscopy (EIS) using CHI 660E (Chenhua, Shanghai) electrochemical workstation. The NC hydrogel sample was prepared at 80 mg NIPAM monomer and 1 mL p-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> nanosheets suspension (1.0 mg mL<sup>-1</sup>). The test was performed at open circuit potential, amplitude of 10 mV, the frequency ranging from 100000 to 0.01 Hz. The conductivity ( $\sigma$ ) is calculated from the following formula.

$$\sigma = L/(R \times S)$$

where  $L$  represents the thickness,  $S$  is the area of the film, and  $R$  is the resistance.

### 1.20. NIR-responsive applications

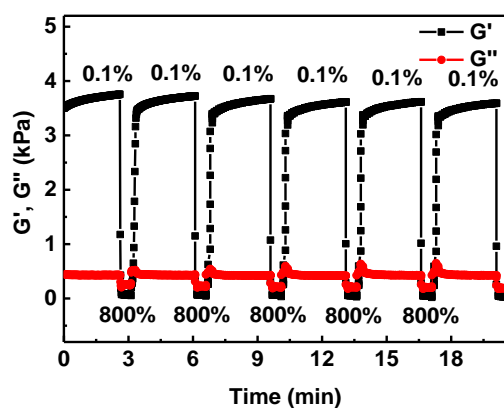
*“Smart” window application:* The NC hydrogel sample was prepared in a plastic cuvette at 80 mg NIPAM monomer and 1 mL p-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> nanosheets suspension (0.1 mg mL<sup>-1</sup>). Transparent NC hydrogel changed to opaque by being consecutively exposed to 808 nm laser (0.375 W cm<sup>-2</sup>) for 5 min.

*Fluidic valve application:* The NC hydrogel was filled in a glass tube. The NC hydrogel blocked the flow of the two solutions (left: an aqueous solution with diluted rhodamine B (red color); right: colorless deaerated water). When the microfluidic hydrogel was irradiated by the 808 nm laser (1.0 W cm<sup>-2</sup>) for 30 s, the NC hydrogel shrunk, leading the red rhodamine B solutions passed through the valve.

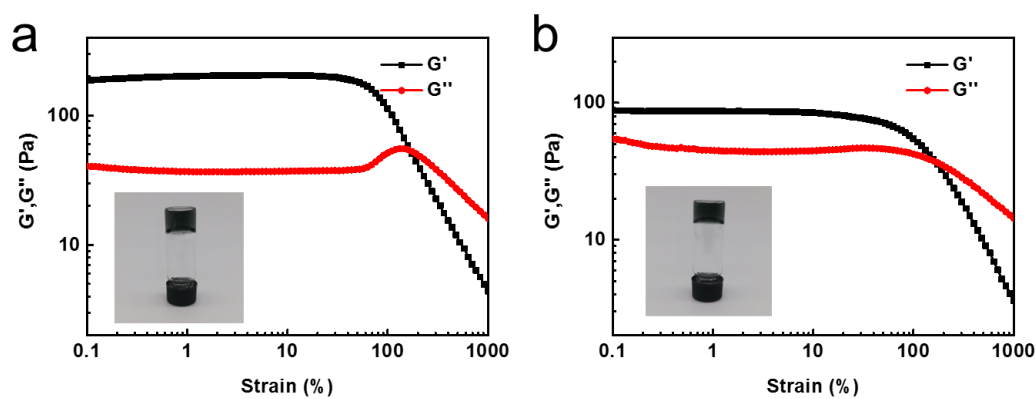
*Circuit application:* The NC hydrogel sample was prepared at 80 mg NIPAM monomer and 1 mL p-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> nanosheets suspension (1.0 mg mL<sup>-1</sup>). A simple electric circuit with a power supply with an output voltage of 1.5 V is connected with the NC hydrogel, and the LED lamp glows when the circuit is closed.

*Photodetector application:* To characterize the electrical performance of NC hydrogel, the hydrogel was tested by semiconductor analyzer (Keithley 4200-SCS) and a computer-controlled stepping motor. The hydrogel sample was prepared by 320 mg NIPAM monomer, 2 mL p-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> nanosheets suspension (1.0 mg mL<sup>-1</sup>) and 60 mg clay (hectorite “Laponite XLG” [Mg<sub>5.34</sub>Li<sub>0.66</sub>Si<sub>8</sub>O<sub>20</sub>(OH)<sub>4</sub>]Na<sub>0.66</sub>) to improve the strength of NC hydrogel. The hydrogel was irradiated by 808 nm laser (1.0 W cm<sup>-2</sup>) for 3 s and then turned off for five cycles.

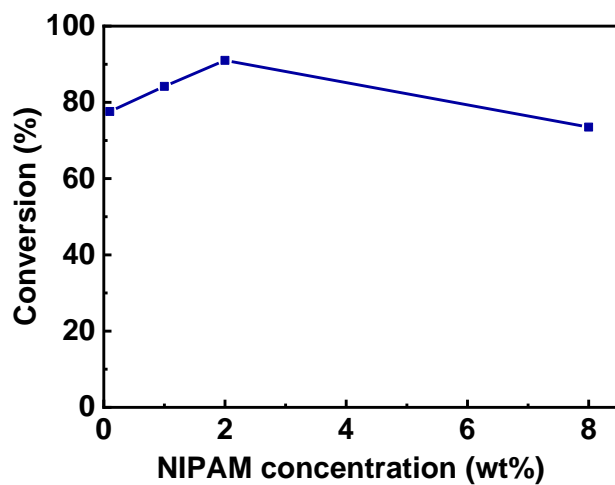
## Supplementary Figures and Tables.



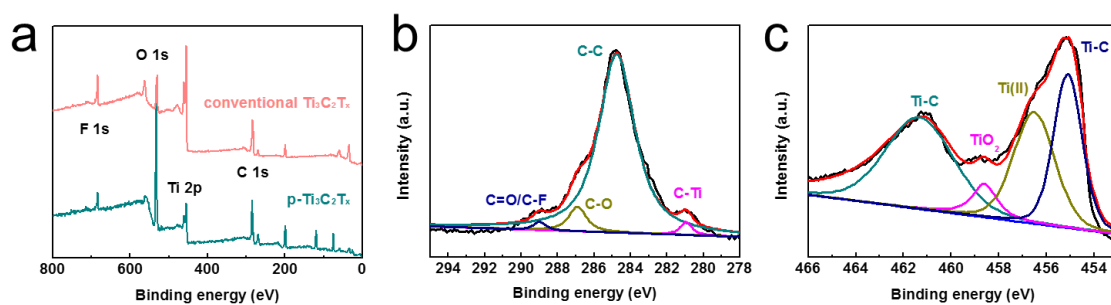
**Fig. S1** The recovering property of PNIPAM-based NC hydrogel measured by alternate-step strain sweeps.



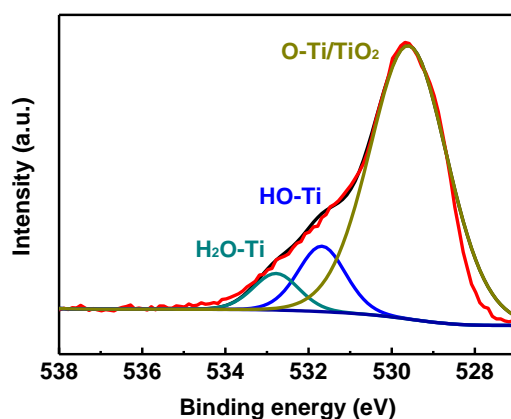
**Fig. S2** The storage and loss moduli of (a) PAAm-based and (b) PDMA-based NC hydrogels by continuous strain sweep at 25 °C. The concentration of AAm and DMA for the NC hydrogel preparation is 8 wt%.



**Fig. S3** Conversion of NIPAM to polymer at different monomer concentrations. All samples were polymerized at 0.35 mg/mL  $\text{Ti}_3\text{C}_2\text{T}_x$  nanosheets for 24 h.

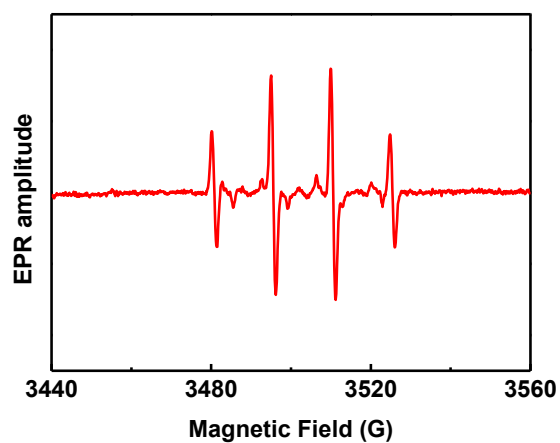


**Fig. S4** (a) XPS survey spectra of p- $\text{Ti}_3\text{C}_2\text{T}_x$  and conventional  $\text{Ti}_3\text{C}_2\text{T}_x$ . High-resolution XPS spectra of p- $\text{Ti}_3\text{C}_2\text{T}_x$  nanosheets in the C 1s region (b) and Ti 2p region (c).

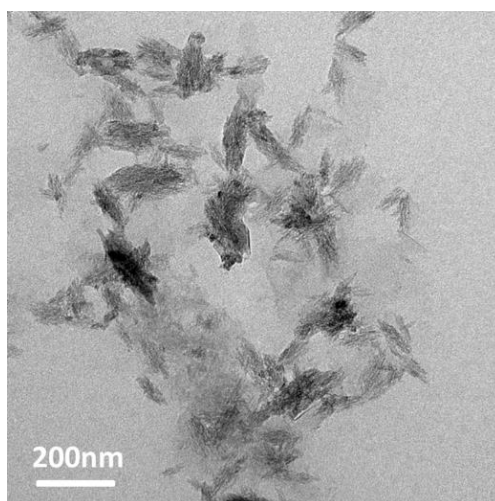


**Fig. S5** High-resolution XPS spectra of  $\text{Ti}_3\text{C}_2\text{T}_x$  nanosheets after being stored over one week at 4 °C in the O 1s region.

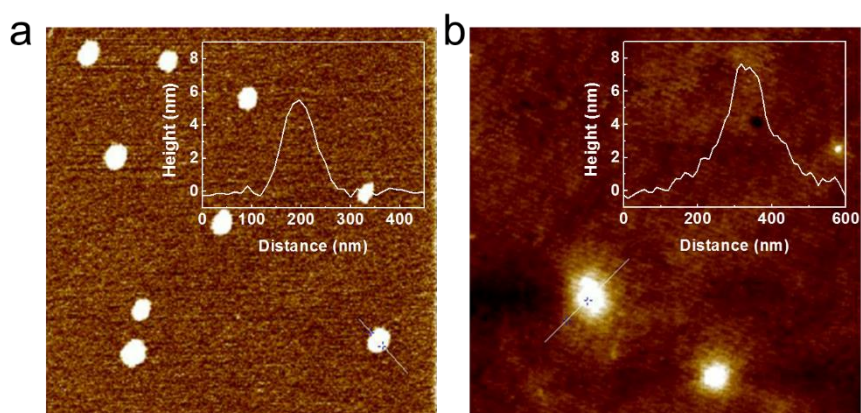




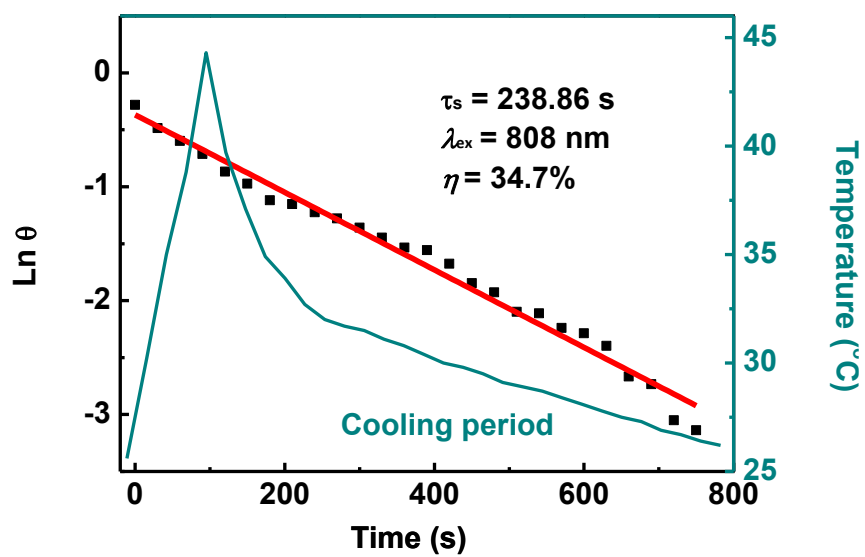
**Fig. S6** EPR spectrum of ammonium persulfate (APS) by DMPO trapping for  $\bullet\text{OH}$  characterization.



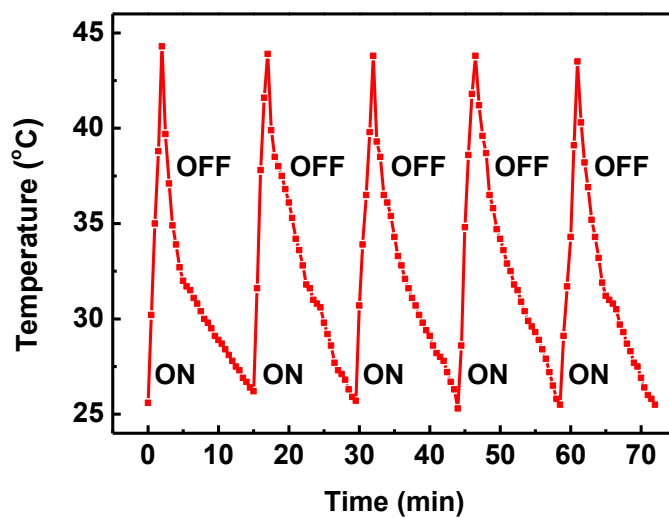
**Fig. S7** TEM image of PNIPAM-based NC polymer.



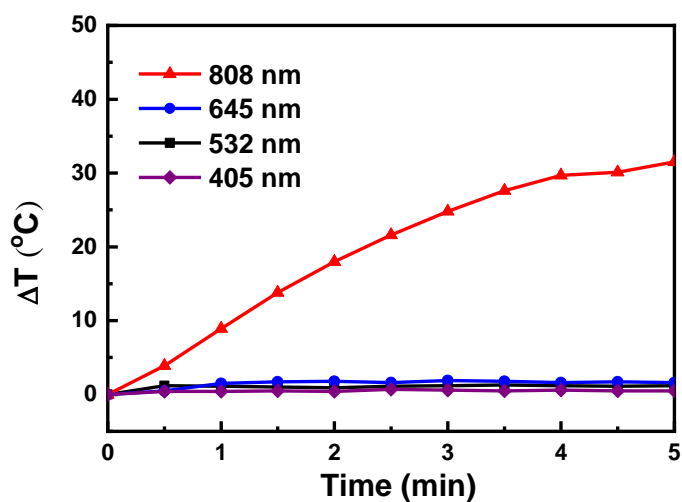
**Fig. S8** AFM images of  $p\text{-Ti}_3\text{C}_2\text{T}_x$  nanosheets (a) and PNIPAM-based NC polymer (b).



**Fig. S9** Calculation of photothermal conversion efficiency using the cooling period in the first photothermal cycle of PNIPAM-based NC hydrogel.



**Fig. S10** Photothermal stability of NC hydrogel by 808 nm irradiation at  $1.0 \text{ W cm}^{-2}$  for 5 cycles.



**Fig. S11** Photothermal property of NC hydrogel under the light irradiation at different wavelengths and  $1.0 \text{ W cm}^{-2}$ .

**Table S1** List of different monomer structures and their polymerization initiated by  $p\text{-Ti}_3\text{C}_2\text{T}_x$ .<sup>a</sup>

Entry	1	2	3	4	5
Monomer	AAm	DMA	NIPAM	MMA	HEMA
Structure					
Monomer concentration	1 wt%	1 wt%	1 wt%	8 wt%	1 wt%
Monomer conversion <sup>b</sup>	84.2%	77.8%	84.2%	73.7%	97.4%

<sup>a</sup> Reaction conditions: The sample was prepared by mixing the monomer with  $0.35 \text{ mg mL}^{-1}$   $p\text{-Ti}_3\text{C}_2\text{T}_x$  nanosheets dispersion and then aerated with pure nitrogen for 5 min to remove dissolved oxygen under ice-bath. The  $^1\text{H}$  NMR spectra of AAm, DMA, NIPAM, MMA and HEMA were recorded in  $\text{DMSO-}d_6$  at  $25 \text{ }^\circ\text{C}$ , shown in Fig. 2b.

<sup>b</sup> The monomer conversions are obtained at reaction 24 h.

## References

- 1 M. Alhabeab, K. Maleski, B. Anasori, P. Lelyukh, L. Clark, S. Sin and Y. Gogotsi, *Chem. Mater.*, 2017, **29**, 7633-7644.
- 2 C. Sun, L. Wen, J. Zeng, Y. Wang, Q. Sun, L. Deng, C. Zhao and Z. Li, *Biomaterials*, 2016, **91**, 81-89.