Electronic Supplementary Material

Silver decorated MXene Nanosheet as a Radical Initiator for Polymerization and Multifunctional Hydrogel

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Experimental Sections

Materials

Ti_3AlC_2 powders (99.5% purity, 400 mesh) were purchased from Laizhou Kai Ceramic Material (Yantai, China). Lithium fluoride (LiF, 99.0%) was obtained from Sigma-Aldrich. Hydrochloric acid (HCl, 37.0%) was purchased from Chron Chemicals (Chengdu, China). Silver nitrate was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Gelatin (CP grade) was obtained from Sangon Biotech Co., Ltd. (Shanghai, China). All monomers and crosslinker N,N'-methylenebisacrylamide (MBA) 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) was isolated by column chromatography filled with aluminum oxide to remove the polymerization inhibitor. Methacrylic acid (MAA), acrylamide (AAm), and acrylic acid (AAc) were used directly. All other chemicals were of analytical grade.

Preparation of $Ag/Ti_3C_2T_x$

Conventional multi-layered MXene nanosheets were prepared using the MILD etching process as previously reported.[1] Briefly, the precursor Ti_3AlC_2 MAX was mixed with an etchant (12 M LiF/9 M HCl) at 35 °C under continuous stirring for 48 h. Then, the powder was washed with deionized H_2O via centrifugation (3500 rpm) for several cycles, a supernatant slurry was obtained when the pH reached 5 ~ 6. The slurry was further delaminated by sonication under N_2 for 30 min and separated from the sediment via centrifugation at 3500 rpm for 30 min. The supernatant of conventional $Ti_3C_2T_x$ was collected and freeze-dried. The $Ti_3C_2T_x$ powder was dispersed in deionized water under sonication for 5 min before use.

$Ag/Ti_3C_2T_x$ was prepared by adding $AgNO_3$ aqueous solution (1 mL, 7.9 mg mL^{-1}) dropwise slowly into the conventional $Ti_3C_2T_x$ dispersion (4 mL, 2.5 mg mL^{-1}) under stirring in the air for at least 10 min. $Ag/Ti_3C_2T_x$ (containing 2 mg mL^{-1} $Ti_3C_2T_x$) was directly used without further purification for initiation of polymerization.

Polymerization of different monomers initiated by $Ag/Ti_3C_2T_x$

Different monomers (including DMA, MAA, AAc, NIPAM, AAm) (0.02 mL for DMA, 0.04 mL for MAA, 0.02 mL for AAc, 40 mg for NIPAM, 53 mg for AAm) were added in 1 mL $Ag/Ti_3C_2T_x$ suspension (containing 2 mg mL^{-1} $Ti_3C_2T_x$) and then bubbled with pure nitrogen for 5 min to remove the dissolved oxygen under an ice-bath. Then, the mixture was kept overnight at room temperature to complete the polymerization.

Preparation of $Ag/Ti_3C_2T_x@gelatin/PAAm$ hydrogel

First, 0.23 g/mL gelatin solution was completely dissolved by magnetically stirring in a water bath at 45 °C. Second, an AAm/MBA mixture solution (4 mmol monomers with a crosslinker-to-monomer molar ratio of 0.000225) was added to 0.655 mL gelatin solution, followed by vortex mixing for 60 s. Then, 0.335 mL $Ag/Ti_3C_2T_x$ hybrid colloidal solution (containing 6 mg mL^{-1} $Ti_3C_2T_x$) was added to the above mixture solution, followed by vortex mixing, and was further deoxygenated with nitrogen. Finally, the reactants were polymerized at room

temperature for 12 h to form a PAAm network and cooled down to 4 °C to form a gelatin network.

Photothermal performance

The photothermal effect of the Ag/Ti$_3$C$_2$T$_x$@gelatin/PAAm hydrogels (containing 2 mg/mL Ti$_3$C$_2$T$_x$) was measured by exposure to 808 nm laser at different power density (0.5 W/cm^2, 1.0 W/cm^2, 1.5 W/cm^2, 2.0 W/cm^2, 2.5 W/cm^2, 3.0 W/cm^2). The photothermal cycling stability of the Ag/Ti$_3$C$_2$T$_x$@gelatin/PAAm hydrogel was measured by exposure to 808 nm laser (1.0 W/cm^2) for 4 min and then cooled down to room temperature for five cycles.

Shape memory under near-infrared (NIR) irradiation

The shape memory experiments were performed using Ag/Ti$_3$C$_2$T$_x$@Gelatin/PAAm hydrogel with/without NIR irradiation, according to the literature.[2] A hydrogel strip of 42 mm × 3.5 mm × 2.5 mm was curled into a tight spiral after being immersed in an 80 °C water bath for 30 s. Then, the sample was immersed in ice water for 60 s to quickly fix the temporary shape. The hydrogel sample in the temporary shape was irradiated from the top to down by NIR laser (3 W/cm^2, 808 nm) for 24 s, and the shape recovery process was simultaneously recorded with a video camera.

Characterization

Absorbance spectra of Ag/Ti$_3$C$_2$T$_x$ solution (containing 0.0375 mg/mL Ti$_3$C$_2$T$_x$) and conventional Ti$_3$C$_2$T$_x$ solution (0.0375 mg/mL Ti$_3$C$_2$T$_x$) were measured by Shimadzu UV 2600 spectrophotometer.

Electron paramagnetic resonance (EPR) spectra of different samples were recorded on a Bruker A300 spectrometer (X-band) equipped with a Bruker ER4141VTM liquid N$_2$ 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, a center field of 3500 G, a sweep width of 120 G, a microwave power 7.1 mW, and a modulation amplitude of 1.0 G. 5,5-Dimethyl-1-pyrroline-N-oxide (DMPO) was applied as the spin-trapping agent for •OH and •O$_2^-$ detection. X-ray diffraction (XRD) was performed on a Bruker diffractometer (Bruker AXS D8 Advance, Germany) with Cu Kα radiation.

X-ray photoelectron spectra (XPS) were carried out in a Thermo Fisher Scientific spectrometer (K-Alpha+) equipped with an Al Kα X-ray source. All peaks are referenced to the C 1s peak at 284.8 eV. The spectra were acquired in the constant analyzer energy mode with a pass energy of 100 eV for the survey. The high-resolution spectra were collected with a pass energy of 30 eV. Data fitting of XPS spectra was performed by using software XPS PEAK version 4.1. Prior to the fitting, the background contributions were subtracted using a Shirley function. The Ti 2p core level was fitted with four doublets (Ti 2p 2p$_{3/2}$ – Ti 2$p_{1/2}$) with a fixed area ratio of 2:1 and a doublet separation of 5.7 eV. The Ag 3d core level was fitted with two doublet peaks (Ag 3d 3d$_{5/2}$ – Ag 3$d_{3/2}$) with a fixed area ratio of 3 : 2 and a doublet separation of 6.0 eV.

Morphology of Ag/Ti$_3$C$_2$T$_x$ was observed by scanning electron microscopy (SEM) through JSM-7610FPlus (JEOL). Ag/Ti$_3$C$_2$T$_x$ nanosuspension was dropped to a silicon wafer and freeze-dried, and then sputtered with gold for observation. ^{1}H NMR spectra were recorded on

a spectrometer (AVANCE III 400 MHz, Bruker, Germany). The kinetics of the polymerization of DMA was monitored by ^{1}H NMR spectroscopy. At the predetermined polymerization time, the reaction was stopped with the addition of p-benzoquinone (final concentration 1.0 μM). The products were then freeze-dried and dispersed in deuterated solvent for the test without further purification. The concentration of DMA was 0.5 wt% for the polymerization kinetics. The monomer conversion to polymer was calculated by dividing the integrated peak area of protons in the polymer backbone by the integrated peak area of protons in the monomeric double bond and the polymer backbone. The protons in the monomeric double bonds are denoted by a and b, while the protons in the polymer backbone are denoted by a' and b' in Fig. 2a in the maintext.

The product (PAAm) of AAm polymerization was added to ethanol to precipitate, then washed with ethanol, and finally dried in vacuum at 50 °C for 24 h for ^{1}H NMR characterization. The product (PAAc) of AAc polymerization was dialyzed against water for 3 days and finally freeze-dried for ^{1}H NMR characterization. The product (PNIPAM) of NIPAM polymerization was directly freeze-dried and dispersed in a deuterated solvent for ^{1}H NMR characterization without further purification. The product (PMAA) of MAA polymerization was directly used for ^{1}H NMR characterization without further purification.

Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) equipped with a column (Shodex GPC KD-806M) and a refractive index detector (Elite, SOP-W5100) (set at 25 °C). The eluent was DMF at a flow rate of 1.0 mL/min. The product (PDMA) of DMA polymerization was lyophilized, dissolved in DMF, and filtered through a 0.22 μm nylon membrane before the test.
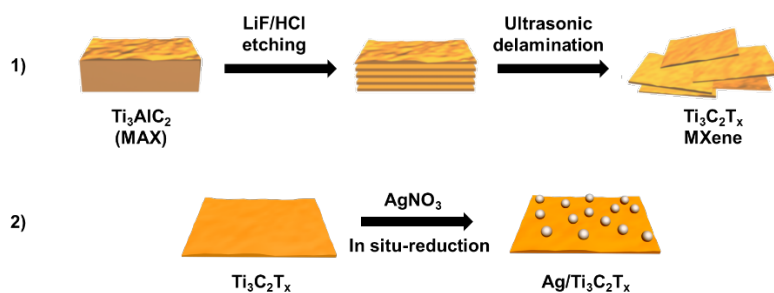
Supplementary Figures and Tables

Fig. S1 Preparation of pristine $Ti_3C_2T_x$ and $Ag/Ti_3C_2T_x$ nanosheets.
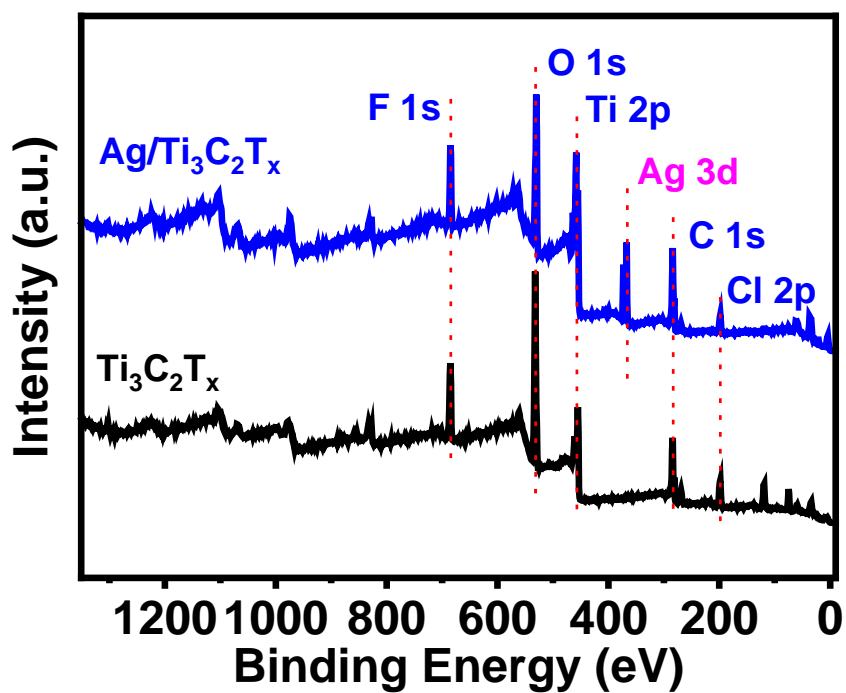
Fig. S2 XPS survey spectra of $Ag/Ti_3C_2T_x$ and pristine $Ti_3C_2T_x$.
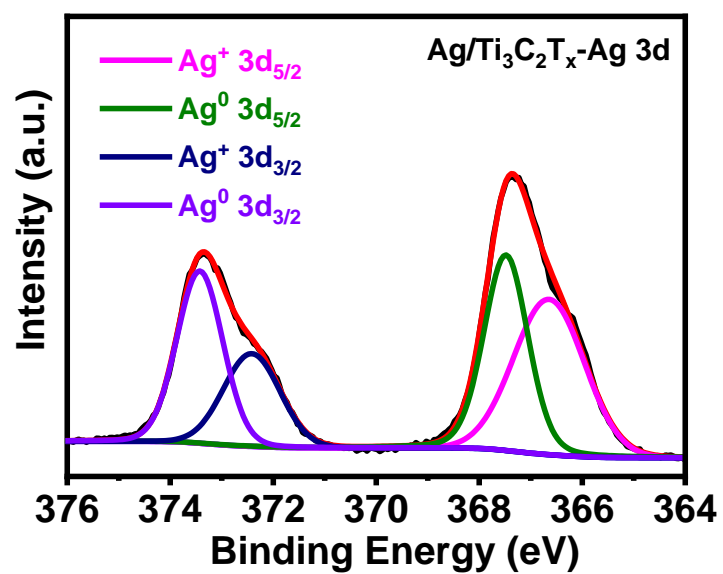
Fig. S3 High-resolution XPS spectra in the Ag $3d$ region of Ag/Ti$_3$C$_2$T$_x$.
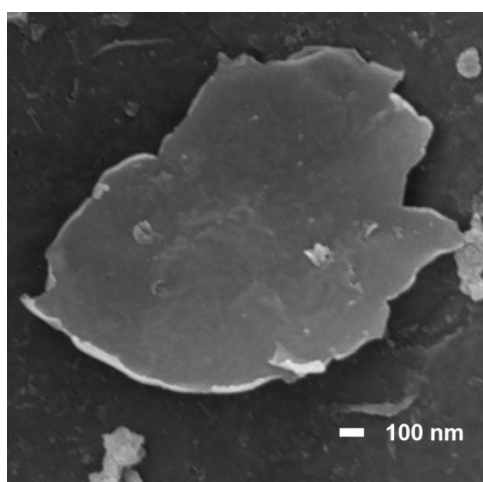
Fig. S4 SEM image of Ti$_3$C$_2$T$_x$ nanosheets.
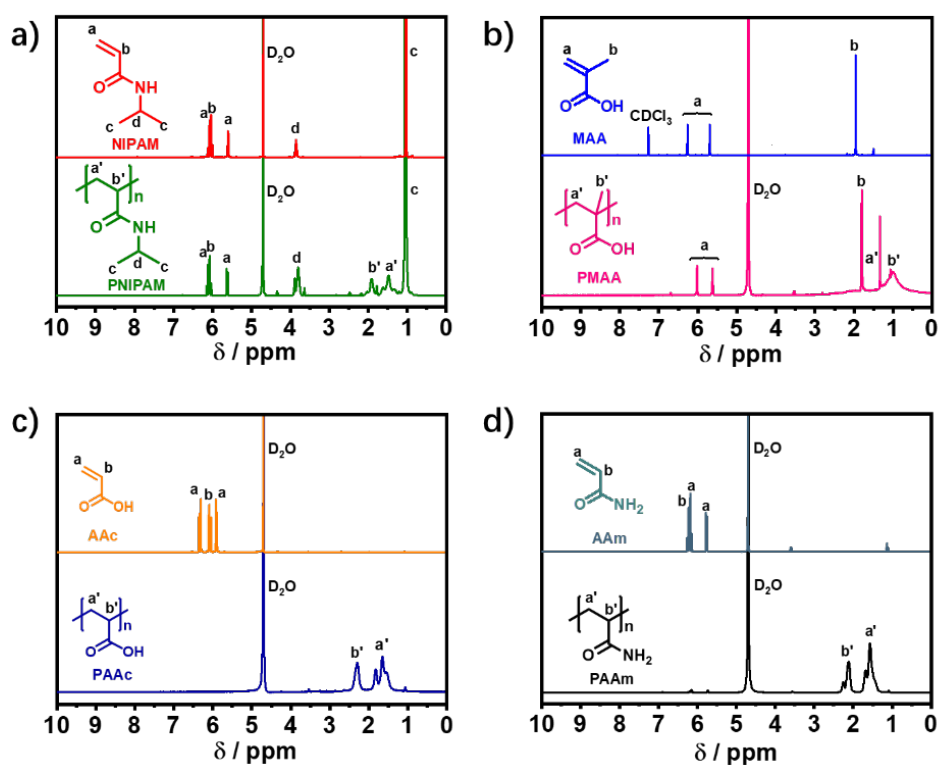
Fig. S5 ^{1}H NMR spectra of PNIPAM, PMAA, PAAc, and PAAm initiated by Ag/Ti$_3$C$_2$T$_x$.

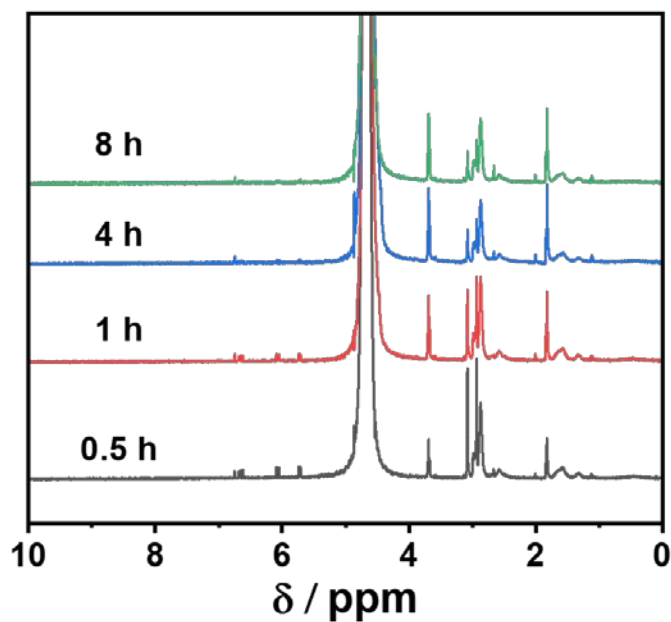**Fig. S6** ^{1}H NMR spectra of the polymerization of DMA initiated by Ag/Ti$_3$C$_2$T$_x$ at different reaction times. The conversion of DMA to its polymer at 0.5, 1, 4, and 8 h is 82.7%, 90.9%, 96.7% and 97.5%, respectively.
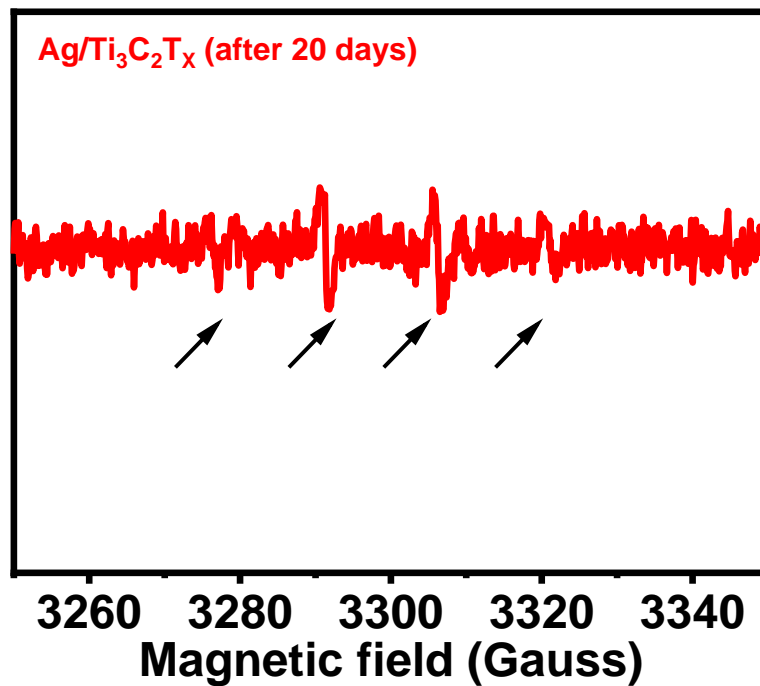
Fig. S7 EPR spectrum of Ag/Ti$_3$C$_2$T$_x$ aqueous solution after storage at 4 °C for 20 days. The spectrum was obtained by using DMPO as a spin-trapping reagent.
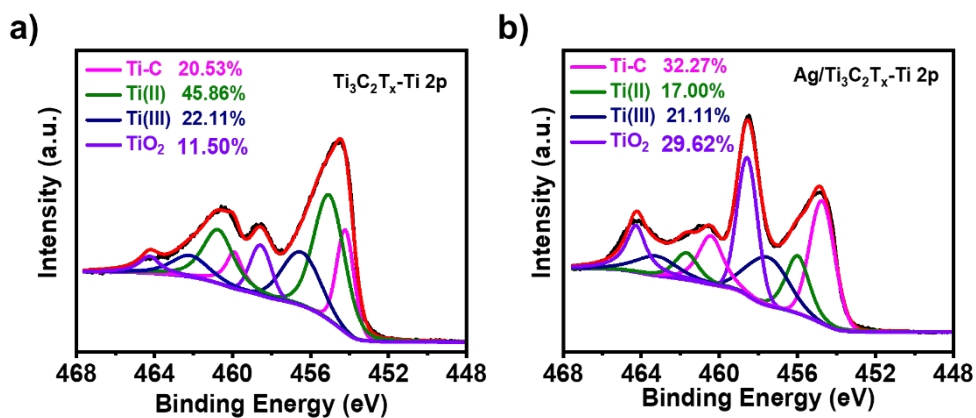

Fig. S8 High-resolution XPS spectra of Ti$_3$C$_2$T$_x$ (a) and Ag/Ti$_3$C$_2$T$_x$ nanosheets (b) in the Ti 2p region.
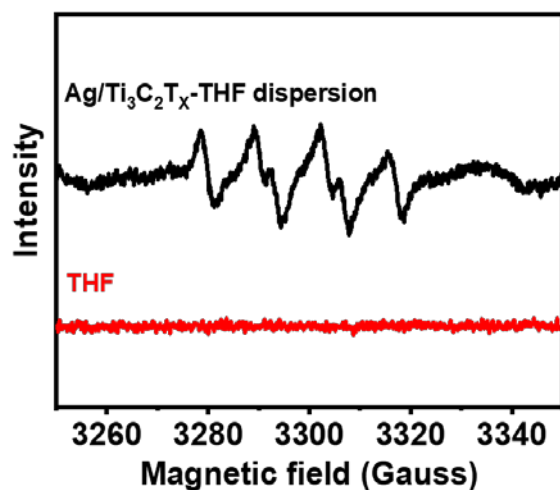
Fig. S9 EPR spectra of Ag/Ti$_3$C$_2$T$_x$-tetrahydrofuran (THF) dispersion and pure tetrahydrofuran solution obtained by DMPO trapping.
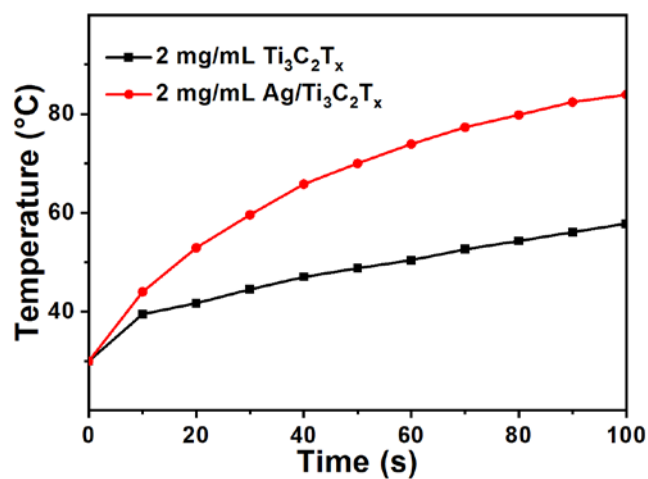

Fig. S10 Photothermal property of Ag/Ti$_3$C$_2$T$_x$ and pristine Ti$_3$C$_2$T$_x$ (808 nm, 1.0 W/cm^2).
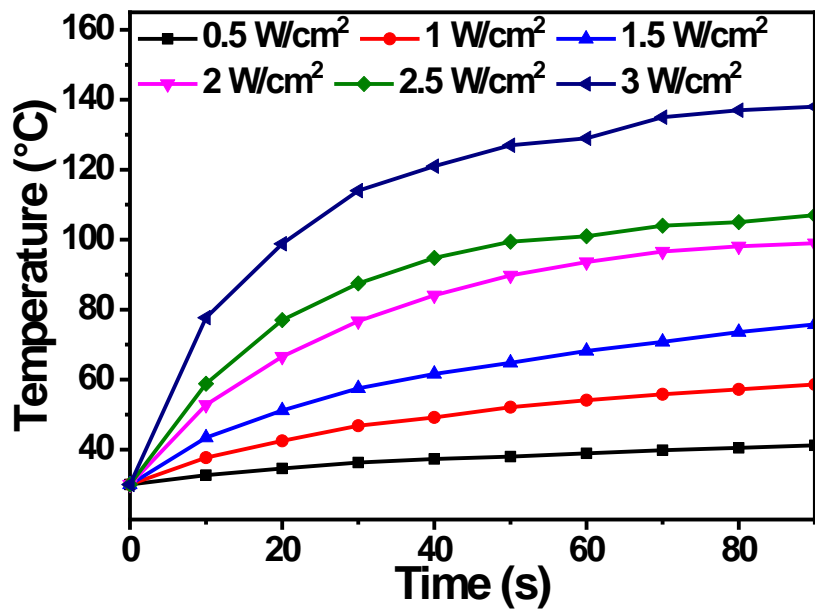
Fig. S11 Temperature evolution of the Ag/Ti$_3$C$_2$T$_x$@gelatin/PAAm hydrogels under 808 nm irradiation at different power densities.
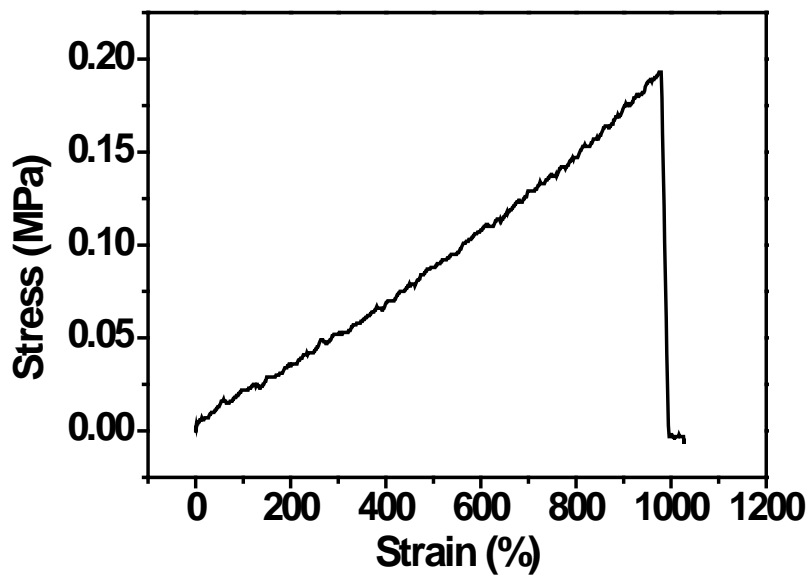

Fig. S12 Stress-strain curve of Ag/Ti$_3$C$_2$T$_x$@gelatin/PAAm hydrogel.
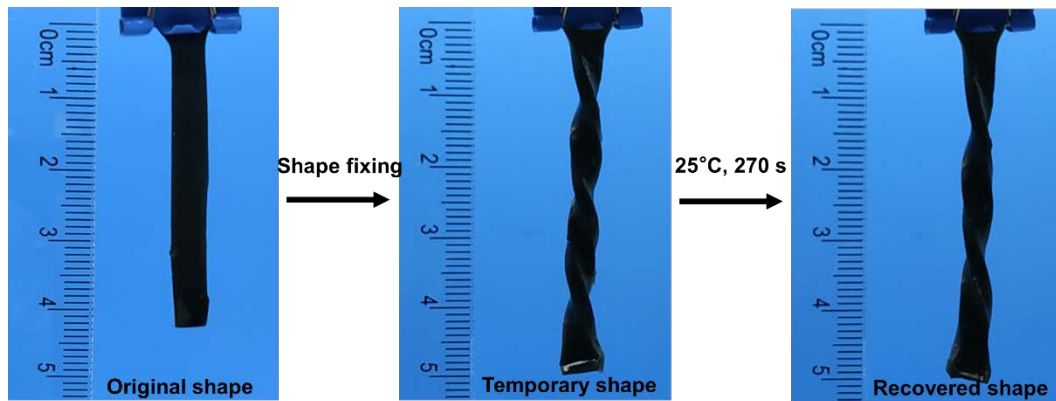
Fig. S13 Original shape, fixed temporary shape, and recovered shape of the control Ag/Ti$_3$C$_2$T$_x$@gelatin/PAAm hydrogel without NIR irradiation.

Table S1. Parameters for deconvolution of XPS spectra of pristine $Ti_3C_2T_x$ and $Ag/Ti_3C_2T_x$.

Sample	Position/eV	FWHM	Area	Ascription	Fraction
MXene ($Ti_3C_2T_x$)	528.89	0.89	14426.26	$O_{absorbed}$	3.59%
	530.08	1.61	47788.43	O-Ti	11.89%
	531.82	1.78	216245.5	HO-Ti	53.82%
	532.65	2.3	123365.5	H_2O-Ti	30.70%
Ag/MXene ($Ag/Ti_3C_2T_x$)	529.4	1.36	74676.27	O-Ag	24.07%
	530	1.37	106057.3	O-Ti	34.18%
	531.26	2.25	73330.73	HO-Ti	23.63%
	532.36	2.3	56229.63	H_2O-Ti	18.12%

Table S2. Comparison of pristine multi-layered $Ti_3C_2T_x$, $Ag/Ti_3C_2T_x$ and p-$Ti_3C_2T_x$.

Materials		$Ti_3C_2T_x$	p-$Ti_3C_2T_x$ [3]	$Ag/Ti_3C_2T_x$
MXene Structure		multi-layered	few-layered	multi-layered
MXene Preparation	sonication	< 1 h	> 6 h	< 1h
	yield	higher	lower	higher
Property	photothermal performance	yes	yes	better than $Ti_3C_2T_x$
	initiation-active for polymerization	no	yes	yes
	mechanism for radical generation	n. a.	decomposition of peroxyl group	pseudo-Fenton reaction
	antibacterial	no	no	excellent[4]

References

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