

www.acsnano.org

Plasmonic Ti₃C₂T_x MXene Enables Highly Efficient Photothermal Conversion for Healable and Transparent Wearable Device

Xiangqian Fan,^{†,⊥} Yan Ding,^{†,⊥} Yang Liu,[†] Jiajie Liang,^{*,†,‡,§}[®] and Yongsheng Chen^{†,‡}[®]

[†]School of Materials Science and Engineering, National Institute for Advanced Materials, Nankai University, Tianjin 300350, People's Republic of China

[‡]Key Laboratory of Functional Polymer Materials of Ministry of Education, College of Chemistry, Nankai University, Tianjin 300350, People's Republic of China

[§]Tianjin Key Laboratory of Metal and Molecule-Based Material Chemistry and Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University, Tianjin 300350, People's Republic of China

Supporting Information

ABSTRACT: Skin-mountable and transparent devices are highly desired for next-generation electronic applications but are susceptible to unexpected ruptures or undesired scratches, which can drastically reduce the device lifetime. Developing wearable and transparent materials with healable function that can recover their original functionality after mechanical damage under mild and noninvasive repairing operation is thus imperative. Herein, we demonstrate that the incorporation of ultrasmall quantities of plasmonic silver nanoparticle (AgNP)@MXene nanosheet hybrids to serve as photothermal fillers in waterborne elastic polyurethane enables high transparency as well as effective light-triggered healing capabilities for wearable composite coatings. The AgNP@MXene hybrid functions as a highly effective photon captor, energy transformer, and molecular heater due to the amalgamation of (1)



ultrahigh photothermal conversion efficiency, high thermal conductivity, and structural properties of MXene, (2) the outstanding plasmonic effect of AgNPs, and (3) the synergistic effects from their hybrids. The resulting wearable composite coating with ultralow loading of plasmonic AgNP@MXene hybrids (0.08 wt % or 0.024 vol %) can produce a significant temperature increase of $\sim 111 \pm 2.6$ °C after the application of 600 mW cm⁻² light irradiation for 5 min, while maintaining a high optical transmittance of ~83% at a thickness of ~60 μ m. This local temperature increase can rapidly heal the mechanical damage to the composite coating, with a healing efficiency above 97%.

KEYWORDS: MXene, photothermal conversion, plasmonic effect, light-triggered healing, wearable and transparent device

T he Earth receives approximately 4.4×10^{14} megajoules of renewable solar energy per hour, a quantity greater than the worldwide consumption of energy in an entire year.^{1,2} Because of these astronomical values, significant effort has been dedicated to the development of advanced green technologies, including photovoltaics,³ photocatalysis,⁴ artificial photosynthesis,⁵ and photothermal conversion,⁶ processes that can capture and convert this renewable energy into sustainable power. In particular, solar-to-heat conversion has received increasing interest in recent years, due in part to its relatively simple operation and high energy conversion efficiency when compared to other solar energy harvesting technologies.⁷ This technology has been used in a wide variety of applications including steam generation, water desalination,

photothermal therapy, and light-triggered self-healing materials.⁸⁻¹⁴

Parallel to the development of advanced green technology, the field of wearable and transparent devices has also experienced extreme growth in recent years.¹⁵⁻¹⁸ While stretchable devices have been perceived as an alternative technology for the realization of next-generation electronics, the emergence of wearable devices that combine elasticity with high optical transparency offers opportunities for many more exciting applications.¹⁹ High optical transparency would enable the integration of optical components and allow more emission

Received: April 24, 2019 Accepted: June 19, 2019 Published: June 19, 2019

from or absorption to the wearable optoelectronics, would make the conformal devices invisible on some uncovered areas of the human body such as the face and neck during daily activities, would not obstruct the wearer's view when the wearable devices are used as contact lenses, and would bring additional valuable and fashionable effects on the wearable devices.^{19,20} Representative potential applications enabled by the stretchable and transparent form factors include skinmountable physical and chemical sensors,^{21–23} smart contact lenses,^{24,25} wearable heaters or textiles,^{26,27} neural interfa-ces,^{28,29} and wearable or fashionable display or lighting systems.^{30,31} However, like other conventional wearable electronics, wearable and transparent devices usually work in harsh environments; one prevailing issue thus remains: the susceptibility of the wearable and transparent devices to failure after experiencing unexpected ruptures or undesired scratches, which inevitably drastically reduces the device lifetime and safety.³² In efforts to mitigate this limitation, much work has been put forth in developing healable materials capable of recovering their original functionality after experiencing mechanical damage. In general, healable materials or devices are automatically or non-automatically repaired via an internal or external trigger, respectively.33 Within these classes of healing mechanisms, light-driven processes are regarded as one of the most promising trigger mechanisms, as they allow for noncontact remote manipulation and precise control.³⁴ These attributes are particularly useful for wearable and transparent devices, which typically require ambient, rapid, and noninvasive repairs.³

In recent years, light-triggered, healable polymeric composites with photothermal fillers embedded into a polymer matrix have been extensively explored.^{36,37} Generally, the healing efficiencies of these materials are determined by three factors of the photothermal fillers: photothermal efficiency, thermal conductivity, and specific structural properties.³⁸⁻⁴⁰ To achieve high photothermal efficiency, the photothermal fillers must both exhibit high light absorption in broadband wavelengths and be capable of effective light-to-heat conversion. High thermal conductivity of the photothermal fillers enables rapid thermal transportation throughout the entire composite material and minimizes heat loss. Finally, large aspect ratios and good compatibility with the matrix facilitate rapid and uniform heat transportation even at low loadings of the photothermal fillers, which is able to reduce the production cost and increase the optical transparency of the healable polymeric composites. Given these requirements, two predominant categories of photothermal fillers have arisen for applications in light-powered, healable polymeric composites: carbon-based effective photon captors and molecular heaters, such as graphene and carbon nanotubes,^{41,42} and plasmonic nanoparticles, such as Ag, Au, and Al nanoparticles or nanorods.^{7,43-46} Graphene nanosheets and carbon nanotubes with sufficiently large aspect ratios exhibit excellent photothermal efficiency and high thermal conductivity due in part to their large π -conjugated system. However, perfect graphene and carbon nanotubes with the integrity of a graphitic network are insoluble in any aqueous and organic solvent, which inevitably leads to rather poor dispersibility of these carbonbased photothermal fillers in a healable polymer matrix.⁴¹ Although chemical functionalization has been widely employed to improve dispersion of graphene and carbon nanotube-based materials in a polymer matrix, the damage to the sp^2 carbon network structure would adversely affect their photothermal

efficiency and thermal conductivity.^{41,47,48} Thus, there exists a dichotomy between functionality and processability for materials based on graphene and carbon nanotubes. On the other hand, plasmonic particles exhibit outstanding intrinsic light-to-heat conversion but narrow absorption bandwidths and small aspect ratios, which usually necessitates high filler loadings in polymer composites.^{49,50} This in turn results in high production costs and loss of transparency, an unintended consequence particularly for wearable devices. Thus, a photothermal filler that is simultaneously capable of possessing broadband absorption, having high light-to-heat conversion and high thermal conductivity, possessing a large aspect ratio, and being easily processed, is still highly required for the development of healable, wearable, and transparent devices.

Recently, a family of 2D layered materials termed MXene has been the subject of intense investigations.^{51–55} This class of material can be denoted by the general formula $M_{n+1}X_nT_{x'}$ wherein M is an early transition metal, X is either carbon or nitrogen, T represents surface terminations (-O, -OH, and/ or -F), and x is the number of functional termination groups and is obtained by etching away the A-group element from its MAX phase (Ti_3AlC_2).^{56–58} MXene has been reported to exhibit nearly 100% internal light-to-heat conversion efficiency⁷ and has high thermal conductivity.⁵⁹ Moreover, abundant surface functional terminations enable MXene to be solution processed without disrupting its desirable intrinsic physical properties.⁶⁰ These attributes make MXene a promising candidate for photothermal fillers for a variety of light-responsive applications.^{61–63}

Herein, we report on a wearable and transparent composite coating with effective light-powered healing capabilities through hybridizing plasmonic silver nanoparticle (AgNP)@ MXene nanosheets with waterborne elastic polyurethane (PU). The hybridization of MXene and AgNPs (Table S1) results in high photothermal conversion due to the combination of the plasmonic properties of AgNPs in conjunction with the photothermal effects and thermal conductivity of the 2D MXene nanosheets. As a result, the thermal energy generated via photothermal conversion from low loadings (0.08 wt %) of the AgNP@MXene hybrid results in significant temperature increases of approximately 111 ± 2.6 °C after applying light irradiation for 5 min, even with a low-power visible-infrared (vis-IR) light source. This temperature increase allows for fusion of the elastic PU matrix and rapid repairing of damaged composite coatings, with a healing efficiency exceeding 97%. Moreover, the low loadings of photothermal fillers enable a high optical transmittance of ~75% at a thickness of 100 μ m. As a result, our wearable composite coating can achieve effective photothermal conversion and rapid healing properties while maintaining high transparency. As a proof of concept, this healable AgNP@MXene-PU composite was employed as a transparent, skin-mountable, and sun-powered worn coating in order to demonstrate its feasibility for applications in wearable and transparent devices.

RESULTS AND DISCUSSION

The fabrication process of the wearable and transparent AgNP@MXene-PU composite coating is illustrated in Figure S1. Briefly, the AgNP@MXene hybrid is synthesized *via* an *in situ* self-reduction and hybridization method,^{64–66} with the delaminated $Ti_3C_2T_x$ MXene nanosheets obtained by acid etching of the aluminum layers in the MAX phase followed by ultrasonication.^{51,67} The large aspect ratio of the resulting



Figure 1. (a) Low-resolution TEM images of the AgNP@MXene hybrid. (b) High-resolution TEM images of the AgNP@MXene hybrid. (c) EDS elemental mapping images of Ti, C, O, and Ag for the AgNP@MXene hybrid. (d) XRD patterns for pure MXene nanosheets and the AgNP@MXene hybrid. (e) FTIR spectra of pure MXene nanosheets and the AgNP@MXene hybrid. (f) XPS survey spectra of the delaminated MXene nanosheets and AgNP@MXene hybrid. (g) High-resolution XPS spectrum of Ag 3d for the AgNP@MXene hybrid. (h) UV-vis spectra of aqueous solutions of pure MXene and the AgNP@MXene hybrid.

MXene nanosheets can be observed through transmission electron microscopy (TEM) and atomic force microscopy (AFM) images, and selected area electron diffraction (SAED) patterns indicate a well-defined hexagonal crystal symmetry structure (Figure S2a and b), in line with previous reports.⁶ The MXene nanosheets are approximately 1.5 nm thick with a lateral length of ~3 μ m and a lateral width of ~1.5 μ m (Figure S2b), indicating that the aspect ratio of the $Ti_3C_2T_x$ nanosheets is larger than 1000. To introduce AgNPs, aqueous silver nitrate (AgNO₃) was added dropwise into the uniformly dispersed $Ti_3C_2T_x$ MXene aqueous solution under continuous stirring. The Ag⁺ in the mixture system could adsorb onto the surface of MXene through electrostatic interaction between Ag⁺ and the negatively charged -OH functional groups on MXene. Thereafter, the adsorbed Ag⁺ received an electron from MXene via electron transfer, which experiences a redox reaction. Since the bond with the -OH functional group is strong, these MXene-Ag dimeric complexes then undergo a further reduction and form stable (Ag⁰) nanoclusters.⁶⁵ This nanocluster formation further leads to the nucleation and subsequent growth of AgNPs onto the surface of MXene nanosheets. This in situ self-reduction method guarantees strong interaction between the plasmonic AgNPs and hydrophilic MXene nanosheet and thus leads to the fabrication of AgNP@MXene hybrids with AgNPs uniformly and firmly

anchored on the MXene nanosheets. To maximize the photothermal conversion of the hybrid, plasmonic AgNPs with diameters ranging from 20 to 50 nm were introduced and hybridized with the 2D $Ti_3C_2T_x$ MXene nanosheets. The silver loading in the AgNP@MXene hybrid was controlled by the initial concentration of $\mathrm{Ag}^{\scriptscriptstyle +}$ and MXene, and the initial mass ratio between Ag^+ and MXene in their raw mixture solution is optimized to 0.25:1 in this work.^{64–66} The obtained AgNP@ MXene hybrid is subsequently incorporated into commercial waterborne PU elastomers to fabricate wearable composite coatings through full solution-based blending and coating processes (Figure S1b). Following solution preparation, composite coatings with low AgNP@MXene hybrid loadings of 0.05, 0.08, and 0.16 wt % (corresponding to 0.015, 0.024, and 0.048 vol %, respectively) were prepared. As a baseline, composite coatings with pure MXene or AgNP alone as the photothermal filler were also prepared to the same loadings.

Various characterization techniques were employed to elucidate the architecture of the AgNP@MXene hybrid. TEM images shown in Figure 1a and b were obtained to visualize the morphology and distribution of the AgNPs on the MXene nanosheets. The low-resolution TEM image of the AgNP@MXene hybrid in Figure 1a illustrates that the AgNPs are attached to the surface of MXene nanosheets and that their shapes are approximately spherical, with diameters ranging



Figure 2. Optical transmittance spectra of the AgNP@MXene-PU composite coatings with AgNP@MXene hybrid loadings of (a) 0.05 wt %, (b) 0.08 wt %, and (c) 0.16 wt % for a variety of coating thicknesses. Inset photographs show a series of AgNP@MXene-PU composite coatings with increasing thickness from 20 to 100 μ m on glass substrates. (d) Temperature change as a function of time for 100 μ m thick MXene-PU (left) and AgNP@MXene-PU (right) composite coatings with different photothermal filler loadings under 600 mW cm⁻² vis–IR light irradiation. (e) Temperature increase (ΔT) versus the irradiated power density for 100 μ m thick MXene-PU and AgNP@MXene-PU composite coatings with 0.08 wt % photothermal fillers after an irradiation time of 5 min. (f) Surface temperature of 100 μ m thick AgNP@ MXene-PU composite coatings with different AgNP@MXene loadings recorded by an infrared thermal imager as a function of time under 600 mW cm⁻² vis–IR light irradiation.

from 20 to 50 nm. The corresponding high-resolution images in Figure 1b indicate that the AgNPs have a constant interplanar distance of ~0.209 nm, corresponding to the (111) crystallographic planes of the metallic silver. These results further validate the successful attachment of AgNPs to the surface of the MXene nanosheets. In addition, energydispersive X-ray spectroscopy (EDS) elemental mapping (Figure 1c) of the TEM image shows a uniform distribution of Ti, C, O, and Ag, further verifying the homogeneous dispersion of AgNPs on the MXene nanosheets.

Following TEM and EDS mapping, X-ray diffraction (XRD) analysis was used to confirm the formation and crystalline nature of the AgNPs in the AgNP@MXene hybrid, with the diffraction patterns of the MXene and AgNP@MXene hybrid depicted in Figure 1d. The two diffraction peaks at 38.17° and 44.33° can be attributed to the (111) and (200) crystallographic planes of the face-centered cubic structure of metallic silver, which is consistent with the aforementioned TEM

analysis. However, the characteristic peak of MXene shifts from 7.5° in pure MXene to 6.6° in the AgNP@MXene hybrid, which suggests the expansion of the d-spacing of MXene nanosheets.^{64,68} This expansion of *d*-spacing further indicates that the AgNPs can firmly anchor on the MXene nanosheets and the anchored AgNPs can prevent the restacking of MXene nanosheets and expand the interlayer spacing of MXene nanosheets in their hybrids.⁶⁹⁻⁷² The successful adhesion of AgNPs to the MXene nanosheets in the hybrid was further demonstrated using Fourier transform infrared spectroscopy (FTIR) (Figure 1e). The pure MXene spectrum exhibits the typical peaks for the -OH hydroxyl stretching mode at 3433 cm^{-1} , -OH bending vibration in the plane at 1445 cm^{-1} , C-F bonds at 1045 cm⁻¹, and Ti-O bonds at 550 cm⁻¹. In the AgNP@MXene hybrid, the bending vibration of -OH is shifted from 1445 cm⁻¹ to ~1426 cm⁻¹, suggesting a possible bonding interaction between $Ti-(OH)_x$ of the MXene nanosheets and AgNPs.^{60,64}



Figure 3. Schematic of the photothermal effects produced from the AgNP@MXene hybrids in the AgNP@MXene-PU composite coating when irradiated with light.

To analyze the adhesion of silver nanoparticles to the surface of the MXene nanosheets, X-ray photoelectron spectroscopy (XPS) was employed to analyze the pure MXene and AgNP@ MXene hybrid. As shown in Figure 1f, the wide survey scan spectrum of the fabricated MXene and AgNP@MXene hybrid exhibits peaks corresponding to C 1s, O 1s, Ti 2p, Ti 3p, and F 1s. Of particular note is the presence of the band located near 368 eV in the AgNP@MXene hybrid. This particular band is associated with the characteristic peak of Ag 3d, but is absent in the pure MXene spectrum. Figure 1g shows the Ag 3d core level XPS spectrum of the AgNP@MXene hybrid. The two characteristic peaks located at 367.75 and 373.76 eV correspond to the binding energy of Ag $3d_{5/2}$ and Ag $3d_{3/2}$ respectively, indicating the self-reduction of the silver. In addition, the spin energy separation between the 3d doublet of Ag is approximately 6.0 eV, which further confirms the formation of metallic AgNPs on the MXene nanosheets.^{65,73} Finally, ultraviolet and visible (UV-vis) spectra for MXene and the AgNP@MXene hybrid are shown in Figure 1h. In the AgNP@MXene hybrid, there is a stronger absorption band in the range of \sim 400 to \sim 650 nm in the visible region, and in particular at 470 nm, which indicates the successful formation of AgNPs in the AgNP@MXene hybrid.^{64,74} The combination of these various characterization techniques conclusively confirms the incorporation and strong anchor of AgNPs onto MXene nanosheets in the hybrid.

Following material characterization, the optical and photothermal properties of the coatings were measured. Figure 2a–c show the optical transmittance of the AgNP@MXene-PU composite coatings with different AgNP@MXene hybrid loadings as a function of the coating thickness. Though there exists variation of transmittance as a function of thickness, all composite coatings exhibit a high transmittance across the entirety of the visible range. Specifically, the optical transmittance of the AgNP@MXene-PU composite coatings with all three hybrid loadings (0.05, 0.08, and 0.16 wt %) exceeds 80% at 550 nm for coating thicknesses of less than 40 μ m. When looking at varying the thickness, the AgNP@MXene-PU composite coating with 0.08 wt % hybrid loading exhibits an optical transmission of 83% and 75% at 550 nm at a film thicknesses of 60 and 100 μ m, respectively. The insets of Figure 2a–c show optical photographs of the corresponding AgNP@MXene-PU composite coatings with increasing thicknesses from 20 to 100 μ m, wherein the background logo can be seen clearly through all coatings regardless of thickness. This high transparency is critical for applications in wearable and transparent devices.

To investigate the photothermal performance of the transparent composite coatings, pure PU, AgNP-PU, MXene-PU, and AgNP@MXene-PU composite coatings were exposed to vis-IR light, and their surface temperatures as a function of time were measured using an IR camera. When exposed to 600 mW cm⁻² light irradiation for 5 min, the surface temperatures for the AgNP-PU, MXene-PU, and AgNP@MXene-PU composite coatings increase significantly, whereas the temperatures of the pure PU coating show only moderate increases (Figure 2d and Figure S3). This discrepancy in temperature increase stems from the incorporation of AgNP, MXene, or hybridized AgNP@MXene photothermal fillers into the PU matrix, which enables the system to efficiently convert incoming light to thermal energy. In addition to the difference in temperature increase, the overall temperature of the AgNP@ MXene-PU composite coatings was also consistently higher than that of the AgNP-PU and MXene-PU composite coatings under the same conditions. As an illustration, the surface temperature of the 0.16 wt % AgNP@MXene-PU composite coating reached about 145 °C, while that of the 0.16 wt % AgNP-PU and MXene-PU composite coatings reached only 100 °C (Figure S3) and 134 °C after 5 min of 600 mW cm⁻² light irradiation. The photothermal conversion efficiency of composites containing the AgNP@MXene hybrid is superior to that of those containing MXene nanosheets or AgNP alone due to the synergistic interactions between AgNPs and MXene nanosheets within the AgNP@MXene hybrid as discussed below.

The surface temperature change (ΔT) of 100 μ m thick 0.08 wt % MXene-PU and 0.08 wt % AgNP@MXene-PU composite coatings was also measured as a function of irradiation intensity, as illustrated in Figure 2e. For light intensities of 600 and 800 mW cm⁻², the ΔT of the AgNP@MXene-PU



Figure 4. Optical micrographs showing the healing process of the cracked (a) pure PU and (b) 0.05 wt %, (c) 0.08 wt %, and (d) 0.16 wt % AgNP@MXene-PU composite coatings as a function of time under 600 mW cm⁻² vis–IR light irradiation. Right images in (d) show 3D topography images of the healing process of the 0.16 wt % AgNP@MXene-PU composite coating. The thickness for all coatings is approximately 100 μ m.

composite coatings are as high as 111 ± 2.6 and 148 ± 5.1 °C, respectively. To visualize the surface temperature change of the composite coatings, IR thermal imaging was used to capture thermal images of the AgNP@MXene-PU composite coatings at varied AgNP@MXene filler contents as a function of time under 600 mW cm⁻² light irradiation. The resulting thermal images depicted in Figure 2f align well with the data presented in Figure 2d. Furthermore, the optical transmittance of this composite coating is above 75% at 550 nm (Figure 2b), highlighting the ability to simultaneously achieve high photothermal conversion and high transparency.

The rapid and substantial temperature increase of the transparent AgNP@MXene-PU composite coatings even at low photothermal filler loadings is largely attributed to the combination of the physical and structural properties of the MXene nanosheets, the plasmonic effect of the AgNPs, and the synergistic effects when combining the two materials (Figure 3). The hydrophilic nature of the MXene nanosheets enables the AgNP@MXene hybrid to be uniformly distributed within the waterborne PU matrix, allowing for homogeneous thermal behavior. When the system is irradiated with light, the broadband light-absorption property and high light-to-heat conversion efficiency of MXene can lead to effective heat production from the MXene and AgNP@MXene hybrids.^{7,61} Moreover, the plasmonic AgNPs can absorb more light in the wavelength ranging from 400 to 650 nm due to the dipole resonance coupling with incident light (Figure 1h) and convert the incident light into more heat based on the plasmonic effect.^{75,76} The heat produced outside of the AgNPs can be subsequently transferred to the hybridized MXene nanosheets due to the close proximity between the AgNPs and MXene nanosheets, in addition to the high intrinsic thermal conductivity of AgNPs.⁷⁷ Finally, the high thermal conductivity and large aspect ratio of the MXene nanosheets ensure effective heat transfer throughout the polymer matrix, allowing localized heating of the AgNP@MXene hybrid to raise the temperature of the entire composite coating.^{14,78}

To evaluate and quantify the photothermal stability and sensitivity of the AgNP@MXene-PU composite coatings, five

light on/off cycles were conducted for composite coatings with various loadings (Figure S4). Within each cycle, the temperatures of the AgNP@MXene-PU composite coatings were recorded when subjected to irradiation at a power density of 600 mW cm⁻² for 10 s followed by a 10 s cooling period. It was observed that the maximum light-induced temperature increased sharply with increasing AgNP@MXene hybrid loading. With regard to repeatability, the peak photothermal temperature showed no deterioration upon cycling, high-lighting not only the sensitive response but also the fatigue-free photothermal effects of the AgNP@MXene hybrid. The high optical absorption properties and excellent thermal conductivity of the AgNP@MXene hybrid enable rapid, consistent temperature increases in polymer composites.

After characterization of optical transmittance and photothermal efficiency, the self-healing properties of the AgNP@ MXene-PU composite coatings were investigated. Microscopic cracks approximately 10 μ m wide and 90 μ m deep were intentionally cut on the surface of 100 μ m thick pure PU and composite coating samples using a surgical blade. Following this manual crack generation, the cracked pure PU coating was first scribbled on the surface of the hot plate whose temperature was kept at 100 and 120 °C, respectively, to verify the thermal-triggered healing process of the thermoplastic and elastic polymer matrix used in this work. Crack healing in the thermoplastic PU has several stages, namely, surface rearrangement, surface approach, wetting, diffusion, and randomization.⁷⁹ Thus, once the cracked PU was heated to the temperature above its melting temperature of ~95 °C (Figure S5), the dynamic PU chains became movable and started to wet the crack interface. By the end of the wetting stage, potential barriers associated with the inhomogeneities at the crack interface disappear and the PU chains are free to move across the crack interface in the following stages of diffusion and randomization, which can subsequently heal the crack.^{41,42} Obviously, higher temperature leads to faster polymer chain diffusion and randomization, thus resulting in shorter healing time. As shown in Figure S6, the cracks on the surface of PU coatings fully disappeared after about 12 and 8



Figure 5. Stress-strain curves of AgNP@MXene-PU composite coatings during the healing process of composites with (a) 0.08 wt % and (b) 0.16 wt % AgNP@MXene hybrids.



Figure 6. (a) Photograph of a ~100 μ m thick 0.08 wt % AgNP@MXene-PU composite coating attached on the hand of a volunteer. IR thermal images of (b) a hand with attached coating before solar irradiation and (c) after solar irradiation for 1 min.

min of heating at a temperature of 100 and 120 $^{\circ}$ C, respectively. Moreover, choosing a thermoplastic PU with lower melting temperature as the polymer matrix can further reduce the healing temperature.

Next, to characterize the light-triggered healing process, the coatings were exposed to 600 mW cm⁻² irradiation under vis-IR light, with the crack closure process recorded using optical microscopy, as shown in Figure 4. The crack on the surface of the pure PU coating exhibits no visible change after 15 min (Figure 4a). In contrast, the cracked 0.05 wt % AgNP@ MXene-PU composite coating demonstrates gradual healing: the crack on the surface is observed to narrow within 5 min and disappears fully after 10 min (Figure 4b), indicating that the composite coating can completely heal over short durations of time, even at such low filler loadings. When the content of the hybridized AgNP@MXene photothermal fillers is increased to 0.08 and 0.16 wt %, the composite coatings exhibit faster healing behavior, with the width of the crack shrinking significantly within 3 min and vanishing completely after only 5 min of irradiation (Figure 4c and d). This shortened time frame indicates that the healing ability of the composite coatings is strongly dependent on the loading of the AgNP@ MXene hybrids. When the AgNP@MXene-PU composite is irradiated with light, the AgNP@MXene hybrids that are well dispersed in the PU matrix can absorb the light, convert it into thermal energy, and transfer it to the PU matrix. The surface temperature of the 0.05, 0.08, and 0.16 wt % AgNP@MXene-PU composite coatings reached about 118, 127, and 139 °C after 3 min of 600 mW cm⁻² light irradiation (Figure 2d). Obviously, only 0.08 wt % loading under 3 min irradiation can generate a large localized photothermal temperature increase, which is much higher than the melting temperature of PU (95 °C), to allow for fast fusion of the polymer matrix and rapid healing of the damage. At this concentration, the AgNP@ MXene-PU composite coating exhibits light transmittance up to 75% at 550 nm, demonstrating that self-healing properties

and high optical transmittance are not mutually exclusive. It is also important to note that compared to MXene-PU composite coating, AgNP@MXene-PU composite coating produces higher surface temperature (Figure 2d) and thus exhibits a faster light-triggered healing process under the same filler loading and irradiation conditions (Figure S7).

An optical profiler was also used to characterize the selfhealing process of the 0.16 wt % AgNP@MXene-PU composite coating. The surface topographies of the cracked coating were recorded visually under the aforementioned conditions for 5 min, with the resulting images displayed on the right side of Figure 4d. The results from the optical profile were found to be in agreement with the optical microscope measurements. The crack on the coating surface gradually diminishes and closes with increasing radiation time, and there is no trace line left on the surface of the composite coating after complete healing.

In order to characterize the self-healing properties more quantitatively, strain-stress tests were conducted to evaluate the recovery of mechanical properties in the AgNP@MXene-PU composite coatings upon healing. The healing efficiency is defined as the ratio of the tensile strength of the healed sample to that of the original sample, according to eq 1:⁸⁰

healing efficiency (%) =
$$\frac{\text{tensile stress}_{\text{healed}}}{\text{tensile stress}_{\text{original}}} \times 100\%$$
 (1)

The stress-strain curves for the virgin, cracked, and healed 0.08 and 0.16 wt % AgNP@MXene-PU composite coatings after 3 and 5 min irradiation treatment times are shown in Figure 5, and the corresponding mechanical properties including tensile strength and elongation at break are given in Table S2. For both composite coatings, the tensile strength and elongation at break of the cracked coatings increase with increasing irradiation time (Figure 5a and b). Equation 1 was used to quantify the healing efficiency after an irradiation time

of 5 min. These values were calculated to be 97% and 98% for the 0.08 and 0.16 wt % AgNP@MXene-PU composites, respectively, illustrating that the mechanical properties of the cracked coatings are virtually fully recovered after only 5 min of photothermal healing.

To demonstrate the practical feasibility of the self-healing AgNP@MXene-PU composite coating as a transparent and skin-mountable heating device, the temperature of a hand with an attached coating was measured. A freestanding, wearable, and transparent 0.08 wt % AgNP@MXene-PU composite coating with a thickness of ~100 μ m was attached onto the skin of a volunteer's hand (Figure 6a), and the surface temperature of the hand was monitored using an IR thermal imager. The experiment was conducted outdoors in winter at approximately -12 °C, and the surface temperature of the hand was initially measured to be 18.3 °C (Figure 6b). Upon exposure to sunlight for about 1 min, the temperature of the composite coating increased by 6 °C to 24.3 °C, while the temperature of other parts of the hand increased by only 0.5 $^{\circ}C$ (Figure 6c). These results highlight the efficacy of the 0.08 wt % AgNP@MXene-PU composite coating in transforming sunlight into heat in practical applications. This demonstration on a human hand in a cold outdoor environment demonstrates the potential of the AgNP@MXene-PU composite coating to be used as a skin-mountable, sunlight-powered heating material for wearable and transparent devices.

CONCLUSIONS

A strategy is proposed to construct healable, wearable, and transparent composite coatings based on the green technology of photothermal conversion. The in situ hybridization of plasmonic AgNPs with 2D MXene nanosheets combines the outstanding plasmonic effects of AgNPs with the thermal properties and structural features of MXene nanosheets. The resulting AgNP@MXene hybrids are effective photon captors, energy transformers, and molecular heaters. When integrated into wearable AgNP@MXene-PU composite coatings, significant temperature increases under mild light irradiation can be realized even with low (0.08 wt %) loadings of the AgNP@ MXene hybrid. These attributes endow the coatings with a rapid and effective light-triggered healing functionality while simultaneously retaining high transparency. As a proof of concept, the composite coating was directly applied as a transparent and skin-mountable warming material to demonstrate its applicability for wearable and transparent devices. This facile strategy to construct wearable and transparent materials with effective photothermal and remotely triggered healing features represents an important step toward producing safe, long-lifetime skin-mountable devices, such as wearable physical and chemical sensors, smart contact lenses, wearable heaters or textiles, neural interfaces, wearable or fashionable display or lighting systems, and so on.

EXPERIMENTAL SECTION

Raw Materials. Silver nitrate $(AgNO_3)$ was purchased from Beijing Innochem Co., Ltd. Waterborne polyurethane (Impranil DL1380) was obtained from Shanghai Yuanhe Chemical Co., Ltd. Lithium fluoride (LiF) was acquired from Chemart (Tianjin) Chemical Technology Co., Ltd. Sodium citrate dehydrate was obtained from Alfa Aesar. Hydrochloric acid (HCl) was purchased from Tianjin Bohua Chemical Reagent Co., Ltd. All chemicals were used without further purification.

Synthesis of Ti₃C₂T_x MXene Nanosheets. Ti₃C₂T_x was synthesized by selective etching of a Ti₃AlC₂ MAX phase in LiF with HCl. A minimally intensive layer delamination (MILD) method was used to delaminate the resulting bulk materials. A 2 g amount of LiF was added to 20 mL of 9 M HCl and sonicated for 30 min, after which 2 g of Ti₃AlC₂ was gradually added at 35 °C, and the solution was stirred for 24 h. Afterward, the solution was centrifuged at 3500 rpm several times to allow the pH of the supernatant to reach ~7, followed by vibration for 30 min, and the supernatant was collected and freeze-dried to isolate the delaminated MXene nanosheets.

Preparation of the AgNP@MXene Hybrid. A 10 mg amount of $Ti_3C_2T_x$ MXene nanosheets was dispersed uniformly in 10 mL of distilled water under vibration. A 1 mL amount of aqueous AgNO₃ with 3.94 mg of AgNO₃ was added dropwise into the MXene solution under continuous stirring to reach an initial mass ratio of 0.25:1 between Ag and MXene. The obtained hybrid solution was sonicated for 12 min and centrifuged at 10 000 rpm for 10 min. This centrifugation process was repeated twice. The resultant precipitate was redispersed in deionized water and then sonicated for 5 min, yielding a 1 mg mL⁻¹ uniform AgNP@MXene hybrid solution.

Preparation of MXene-PU and AgNP@MXene-PU Composite Coatings. The MXene colloidal solution or the AgNP@MXene hybrid solution was mixed with waterborne elastic polyurethane to achieve loadings of MXene or AgNP@MXene hybrid in PU of 0.05, 0.08, and 0.16 wt %. The resulting mixture was dispersed uniformly under vibration and sonication. The composite coatings were subsequently prepared by coating the solution onto a glass substrate and drying at 50 °C for 2 h. The thickness of the composite coating can be controlled *via* simply tuning the concentration of photothermal filler and PU in their solution.

Preparation of AgNP-PU Composite Coatings. The AgNP-PU composite coatings were prepared according to the previously reported method.⁸¹ Briefly, 1 mL of aqueous AgNO₃ (3.9 mg mL⁻¹) was mixed with different amounts of waterborne PU under stirring to achieve loadings of Ag in PU of 0.05, 0.08, and 0.16 wt % and then sonicated for 10 min. Then the mixture was heated to 90 °C under stirring in an oil bath. After that, 1 mL of aqueous sodium citrate (0.048 wt %) was introduced into the above AgNO₃–PU solution. The reaction was allowed to proceed for 1 h to obtain a beige solution, which indicates the formation of AgNPs in PU emulsions. Then the resulting mixture was dispersed uniformly further under vibration and sonication, and the composite coatings were subsequently prepared by coating the solution onto a glass substrate and drying at 50 °C for 2 h.

Characterization. Ultraviolet-visible absorbance spectra were measured using a Shimadzu UV-2600 spectrophotometer. Optical microscope and TEM images were obtained using an upright metallurgical microscope (Leica DM750 M) and a transmission electron microscope (JEM-2800, Japan), respectively. AFM images were captured using a MultiMode 8 system from Bruker. XPS spectra were obtained using an ESCALAB 250Xi system from Thermo Scientific. XRD patterns were recorded using a Rigaku D/max 2200 pc diffractometer using Cu K α radiation. FTIR spectra were acquired using a Bruker TENSOR27 FTIR spectrometer in the range of 400 to 4000 cm⁻¹. Vis–IR light was produced using a vis–IR bulb (HW220-275W-E27), with the surface temperature of the coatings measured using an infrared thermal imager (Testo 869, Testo SE & Co. KGaA). The mechanical properties of the AgNP@MXene-PU composite coatings were tested using a tensile testing machine (Shimadzu AGS-X) at a crosshead speed of 100 mm min⁻¹ at room temperature. The composite coatings were cut into rectangular samples and their exact sizes measured using a micrometer thickness gauge (0.001 mm/ 0.00005"AICE)

The emissivity of all AgNP@MXene-PU and MXene-PU composite coatings was measured and calibrated. The composite coating was scribbled on the surface of the hot plate whose temperature was kept at 70 °C. The surface temperature of the composite coating was recorded through both a thermal couple and IR camera. The emissivity of the composite coating was calculated

based on the temperatures read from the thermal couple and the IR camera. The emissivity of the 0.05, 0.08, and 0.16 wt % AgNP@ MXene-PU composite coatings was measured to be 0.93, 0.94 and 0.94, and the emissivity of the 0.05, 0.08, and 0.16 wt % MXene-PU composite coatings was measured to be 0.93, 0.94 and 0.94.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.9b03161.

Schematic illustrations for the preparation of the AgNP@MXene hybrid and AgNP@MXene-PU composite coatings; TEM and AFM images of $Ti_3C_2T_x$ MXene nanosheets; photothermal effect of the AgNP-PU composite; cycling heating profiles of the AgNP@ MXene-PU composite coatings; DSC curves of pure PU; thermoinduced healing process of pure PU; light-triggered healing process of MXene-PU composite; tables of physical properties of Ag and $Ti_3C_2T_x$ Mxene; tensile strength and elongation at break of the AgNP@MXene-PU composite coatings initially and after 0, 3, and 5 min healing times after being cut (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail (J. Liang): liang0909@nankai.edu.cn. ORCID ©

Jiajie Liang: 0000-0003-2112-6721 Yongsheng Chen: 0000-0003-1448-8177

Author Contributions

 $^{\perp}$ X.F. and Y.D. contributed equally.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The work reported here was supported by NSFC (51872146, 51673099, 91633301, 21421001), the "Fundamental Research Funds for the Central Universities", Nankai University (63191520), and MoST (2016YFA0200200).

REFERENCES

(1) Morton, O. A New Day Dawning: Silicon Valley Sunrise. *Nature* **2006**, 443, 19–22.

(2) Lawlor, D. W.; Ke, B. Photosynthesis: Photobiochemistry and Photobiophysics. *Ann. Bot.* **2003**, *91*, 106.

(3) Stranks, S. D.; Snaith, H. J. Metal-Halide Perovskites for Photovoltaic and Light-Emitting Devices. *Nat. Nanotechnol.* **2015**, *10*, 391–402.

(4) Tan, C. F.; Su Su Zin, A. K.; Chen, Z.; Liow, C. H.; Phan, H. T.; Tan, H. R.; Xu, Q.-H.; Ho, G. W. Inverse Stellation of CuAu-ZnO Multimetallic-Semiconductor Nanostartube for Plasmon-Enhanced Photocatalysis. *ACS Nano* **2018**, *12*, 4512–4520.

(5) Tachibana, Y.; Vayssieres, L.; Durrant, J. R. Artificial Photosynthesis for Solar Water-Splitting. *Nat. Photonics* **2012**, *6*, 511–518.

(6) Li, D.; Han, D.; Qu, S.-N.; Liu, L.; Jing, P.-T.; Zhou, D.; Ji, W.-Y.; Wang, X.-Y.; Zhang, T.-F.; Shen, D.-Z. Supra-(Carbon Nanodots) with A Strong Visible to Near-Infrared Absorption Band and Efficient Photothermal Conversion. *Light: Sci. Appl.* **2016**, *5*, e16120.

(7) Li, R.; Zhang, L.; Shi, L.; Wang, P. MXene Ti_3C_2 : An Effective 2D Light-to-Heat Conversion Material. ACS Nano 2017, 11, 3752–3759.

(8) Ghasemi, H.; Ni, G.; Marconnet, A. M.; Loomis, J.; Yerci, S.; Miljkovic, N.; Chen, G. Solar Steam Generation by Heat Localization. *Nat. Commun.* **2014**, *5*, 4449.

(9) Xu, N.; Hu, X.; Xu, W.; Li, X.; Zhou, L.; Zhu, S.; Zhu, J. Mushrooms as Efficient Solar Steam-Generation Devices. *Adv. Mater.* **2017**, *29*, 1606762.

(10) Zhou, L.; Tan, Y.; Wang, J.; Xu, W.; Yuan, Y.; Cai, W.; Zhu, S.; Zhu, J. 3D Self-Assembly of Aluminium Nanoparticles for Plasmon-Enhanced Solar Desalination. *Nat. Photonics* **2016**, *10*, 393–398.

(11) Lyu, Y.; Fang, Y.; Miao, Q.; Zhen, X.; Ding, D.; Pu, K. Intraparticle Molecular Orbital Engineering of Semiconducting Polymer Nanoparticles as Amplified Theranostics for *In Vivo* Photoacoustic Imaging and Photothermal Therapy. *ACS Nano* **2016**, *10*, 4472–4481.

(12) Ma, Y.; Liang, X.; Tong, S.; Bao, G.; Ren, Q.; Dai, Z. Gold Nanoshell Nanomicelles for Potential Magnetic Resonance Imaging, Light-Triggered Drug Release, and Photothermal Therapy. *Adv. Funct. Mater.* **2013**, *23*, 815–822.

(13) Chen, S.; Tang, F.; Tang, L.; Li, L. Synthesis of Cu-Nanoparticle Hydrogel with Self-Healing and Photothermal Properties. *ACS Appl. Mater. Interfaces* **2017**, *9*, 20895–20903.

(14) Hu, Z.; Shao, Q.; Huang, Y.; Yu, L.; Zhang, D.; Xu, X.; Lin, J.; Liu, H.; Guo, Z. Light Triggered Interfacial Damage Self-Healing of Poly(*P*-Phenylene Benzobisoxazole) Fiber Composites. *Nanotechnol*ogy **2018**, *29*, 185602.

(15) Wang, X.; Liu, Z.; Zhang, T. Flexible Sensing Electronics for Wearable/Attachable Health Monitoring. *Small* 2017, *13*, 1602790.
(16) Zheng, Z. Q.; Yao, J. D.; Wang, B.; Yang, G. W. Light-Controlling, Flexible and Transparent Ethanol Gas Sensor Based on

ZnO Nanoparticles for Wearable Devices. *Sci. Rep.* **2015**, *5*, 11070. (17) Wu, C.; Kim, T. W.; Li, F.; Guo, T. Wearable Electricity Generators Fabricated Utilizing Transparent Electronic Textiles Based on Polyester/Ag Nanowires/Graphene Core-Shell Nanocomposites. *ACS Nano* **2016**, *10*, 6449–6457.

(18) Yun, T. G.; Park, M.; Kim, D.-H.; Kim, D.; Cheong, J. Y.; Bae, J. G.; Han, S. M.; Kim, I.-D. All-Transparent Stretchable Electrochromic Supercapacitor Wearable Patch Device. *ACS Nano* **2019**, *13*, 3141–3150.

(19) Kim, K.; Park, Y.-G.; Hyun, B. G.; Choi, M.; Park, J.-U. Recent Advances in Transparent Electronics with Stretchable Forms. *Adv. Mater.* **2019**, *31*, 1804690.

(20) Roh, E.; Hwang, B.-U.; Kim, D.; Kim, B.-Y.; Lee, N.-E. Stretchable, Transparent, Ultrasensitive, and Patchable Strain Sensor for Human-Machine Interfaces Comprising a Nanohybrid of Carbon Nanotubes and Conductive Elastomers. *ACS Nano* **2015**, *9*, 6252–6261.

(21) Maiti, R.; Gerhardt, L.-C.; Lee, Z. S.; Byers, R. A.; Woods, D.; Sanz-Herrera, J. A.; Franklin, S. E.; Lewis, R.; Matcher, S. J.; Carré, M. J. *In Vivo* Measurement of Skin Surface Strain and Sub-Surface Layer Deformation Induced by Natural Tissue Stretching. *J. Mech. Behav. Biomed. Mater.* **2016**, *62*, 556–569.

(22) Kim, D.-H.; Lu, N.; Ma, R.; Kim, Y.-S.; Kim, R.-H.; Wang, S.; Wu, J.; Won, S. M.; Tao, H.; Islam, A.; Yu, K. J.; Kim, T.-i.; Chowdhury, R.; Ying, M.; Xu, L.; Li, M.; Chung, H.-J.; Keum, H.; McCormick, M.; Liu, P.; Zhang, Y.-W.; Omenetto, F. G.; Huang, Y.; Coleman, T.; Rogers, J. A. Epidermal Electronics. *Science* **2011**, 333, 838–843.

(23) Liu, Y.; Pharr, M.; Salvatore, G. A. Lab-on-Skin: A Review of Flexible and Stretchable Electronics for Wearable Health Monitoring. *ACS Nano* **2017**, *11*, 9614–9635.

(24) Park, J.; Kim, J.; Kim, S.-Y.; Cheong, W. H.; Jang, J.; Park, Y.-G.; Na, K.; Kim, Y.-T.; Heo, J. H.; Lee, C. Y.; Lee, J. H.; Bien, F.; Park, J.-U. Soft, Smart Contact Lenses with Integrations of Wireless Circuits, Glucose Sensors, and Displays. *Sci. Adv.* **2018**, *4*, eaap9841. (25) Kim, J.; Kim, M.; Lee, M.-S.; Kim, K.; Ji, S.; Kim, Y.-T.; Park, J.; Na, K.; Bae, K.-H.; Kyun Kim, H.; Bien, F.; Young Lee, C.; Park, J.-U. Wearable Smart Sensor Systems Integrated on Soft Contact Lenses for Wireless Ocular Diagnostics. *Nat. Commun.* **2017**, *8*, 14997.

(26) An, B. W.; Gwak, E.-J.; Kim, K.; Kim, Y.-C.; Jang, J.; Kim, J.-Y.; Park, J.-U. Stretchable, Transparent Electrodes as Wearable Heaters Using Nanotrough Networks of Metallic Glasses with Superior Mechanical Properties and Thermal Stability. *Nano Lett.* **2016**, *16*, 471–478.

(27) Jang, J.; Hyun, B. G.; Ji, S.; Cho, E.; An, B. W.; Cheong, W. H.; Park, J.-U. Rapid Production of Large-Area, Transparent and Stretchable Electrodes Using Metal Nanofibers as Wirelessly Operated Wearable Heaters. *NPG Asia Mater.* **2017**, *9*, e432.

(28) Zhang, J.; Liu, X.; Xu, W.; Luo, W.; Li, M.; Chu, F.; Xu, L.; Cao, A.; Guan, J.; Tang, S.; Duan, X. Stretchable Transparent Electrode Arrays for Simultaneous Electrical and Optical Interrogation of Neural Circuits *In Vivo. Nano Lett.* **2018**, *18*, 2903–2911.

(29) Cardin, J. A.; Carlén, M.; Meletis, K.; Knoblich, U.; Zhang, F.; Deisseroth, K.; Tsai, L.-H.; Moore, C. I. Targeted Optogenetic Stimulation and Recording of Neurons *In Vivo* Using Cell-Type-Specific Expression of Channelrhodopsin-2. *Nat. Protoc.* **2010**, *5*, 247–254.

(30) Liang, J.; Li, L.; Niu, X.; Yu, Z.; Pei, Q. Elastomeric Polymer Light-Emitting Devices and Displays. *Nat. Photonics* **2013**, *7*, 817–824.

(31) Liang, J.; Li, L.; Tong, K.; Ren, Z.; Hu, W.; Niu, X.; Chen, Y.; Pei, Q. Silver Nanowire Percolation Network Soldered with Graphene Oxide at Room Temperature and Its Application for Fully Stretchable Polymer Light-Emitting Diodes. *ACS Nano* **2014**, *8*, 1590–1600.

(32) Fang, Y.; Du, X.; Du, Z.; Wang, H.; Cheng, X. Light- and Heat-Triggered Polyurethane Based on Dihydroxyl Anthracene Derivatives

for Self-Healing Applications. J. Mater. Chem. A 2017, 5, 8010-8017. (33) Hager, M. D.; Greil, P.; Leyens, C.; van der Zwaag, S.; Schubert, U. S. Self-Healing Materials. Adv. Mater. 2010, 22, 5424-5430.

(34) Han, B.; Zhang, Y.-L.; Zhu, L.; Li, Y.; Ma, Z.-C.; Liu, Y.-Q.; Zhang, X.-L.; Cao, X.-W.; Chen, Q.-D.; Qiu, C.-W.; Sun, H.-B. Plasmonic-Assisted Graphene Oxide Artificial Muscles. *Adv. Mater.* **2018**, *31*, 1806386.

(35) Kang, H. S.; Kim, H.-T.; Park, J.-K.; Lee, S. Light-Powered Healing of a Wearable Electrical Conductor. *Adv. Funct. Mater.* 2014, 24, 7273–7283.

(36) Du, W.; Jin, Y.; Lai, S.; Shi, L.; Fan, W.; Pan, J. Near-Infrared Light Triggered Shape Memory and Self-Healable Polyurethane/ Functionalized Graphene Oxide Composites Containing Diselenide Bonds. *Polymer* **2018**, *158*, 120–129.

(37) Zhang, H.; Zhao, Y. Polymers with Dual Light-Triggered Functions of Shape Memory and Healing Using Gold Nanoparticles. *ACS Appl. Mater. Interfaces* **2013**, *5*, 13069–13075.

(38) Yang, X.; Guo, Y.; Luo, X.; Zheng, N.; Ma, T.; Tan, J.; Li, C.; Zhang, Q.; Gu, J. Self-Healing, Recoverable Epoxy Elastomers and Their Composites with Desirable Thermal Conductivities by Incorporating BN Fillers *via In-Situ* Polymerization. *Compos. Sci. Technol.* **2018**, *164*, 59–64.

(39) Noack, M.; Merindol, R.; Zhu, B.; Benitez, A.; Hackelbusch, S.; Beckert, F.; Seiffert, S.; Mülhaupt, R.; Walther, A. Light-Fueled, Spatiotemporal Modulation of Mechanical Properties and Rapid Self-Healing of Graphene-Doped Supramolecular Elastomers. *Adv. Funct. Mater.* **2017**, *27*, 1700767.

(40) Altuna, F. I.; Antonacci, J.; Arenas, G. F.; Pettarin, V.; Hoppe, C. E.; Williams, R. J. J. Photothermal Triggering of Self-Healing Processes Applied to the Reparation of Bio-Based Polymer Networks. *Mater. Res. Express* **2016**, *3*, 045003.

(41) Huang, L.; Yi, N.; Wu, Y.; Zhang, Y.; Zhang, Q.; Huang, Y.; Ma, Y.; Chen, Y. Multichannel and Repeatable Self-Healing of Mechanical Enhanced Graphene-Thermoplastic Polyurethane Composites. *Adv. Mater.* **2013**, *25*, 2224–2228.

(42) Pu, W.; Fu, D.; Wang, Z.; Gan, X.; Lu, X.; Yang, L.; Xia, H. Realizing Crack Diagnosing and Self-Healing by Electricity with a Dynamic Crosslinked Flexible Polyurethane Composite. *Adv. Sci.* **2018**, *5*, 1800101.

(43) Wu, M.; Li, Y.; An, N.; Sun, J. Applied Voltage and Near-Infrared Light Enable Healing of Superhydrophobicity Loss Caused by Severe Scratches in Conductive Superhydrophobic Films. *Adv. Funct. Mater.* 2016, 26, 6777–6784.

(44) Chen, L.; Si, L.; Wu, F.; Chan, S. Y.; Yu, P.; Fei, B. Electrical and Mechanical Self-Healing Membrane Using Gold Nanoparticles as Localized "Nano-Heaters. *J. Mater. Chem. C* **2016**, *4*, 10018–10025. (45) Hribar, K. C.; Metter, R. B.; Ifkovits, J. L.; Troxler, T.; Burdick,

J. A. Light-Induced Temperature Transitions in Biodegradable Polymer and Nanorod Composites. *Small* **2009**, *5*, 1830–1834.

(46) Lecarme, O.; Sun, Q.; Ueno, K.; Misawa, H. Robust and Versatile Light Absorption at Near-Infrared Wavelengths by Plasmonic Aluminum Nanorods. *ACS Photonics* **2014**, *1*, 538–546.

(47) Xiang, Z.; Zhang, L.; Li, Y.; Yuan, T.; Zhang, W.; Sun, J. Reduced Graphene Oxide-Reinforced Polymeric Films with Excellent Mechanical Robustness and Rapid and Highly Efficient Healing Properties. *ACS Nano* **2017**, *11*, 7134–7141.

(48) Wang, C.; Liu, N.; Allen, R.; Tok, J. B. H.; Wu, Y.; Zhang, F.; Chen, Y.; Bao, Z. A Rapid and Efficient Self-Healing Thermo-Reversible Elastomer Crosslinked with Graphene Oxide. *Adv. Mater.* **2013**, *25*, 5785–5790.

(49) Chong, X.; Jiang, N.; Zhang, Z.; Roy, S.; Gord, J. R. Plasmonic Resonance-Enhanced Local Photothermal Energy Deposition by Aluminum Nanoparticles. J. Nanopart. Res. **2013**, *15*, 1678.

(50) Zhang, H.; Xia, H.; Zhao, Y. Optically Triggered and Spatially Controllable Shape-Memory Polymer-Gold Nanoparticle Composite Materials. J. Mater. Chem. 2012, 22, 845–849.

(51) Naguib, M.; Kurtoglu, M.; Presser, V.; Lu, J.; Niu, J.; Heon, M.; Hultman, L.; Gogotsi, Y.; Barsoum, M. W. Two-Dimensional Nanocrystals Produced by Exfoliation of Ti₃AlC₂. *Adv. Mater.* **2011**, 23, 4248–4253.

(52) Naguib, M.; Mochalin, V. N.; Barsoum, M. W.; Gogotsi, Y. 25th Anniversary Article: MXenes: A New Family of Two-Dimensional Materials. *Adv. Mater.* **2014**, *26*, 992–1005.

(53) Mashtalir, O.; Naguib, M.; Mochalin, V. N.; Dall'Agnese, Y.; Heon, M.; Barsoum, M. W.; Gogotsi, Y. Intercalation and Delamination of Layered Carbides and Carbonitrides. *Nat. Commun.* **2013**, *4*, 1716.

(54) Naguib, M.; Mashtalir, O.; Carle, J.; Presser, V.; Lu, J.; Hultman, L.; Gogotsi, Y.; Barsoum, M. W. Two-Dimensional Transition Metal Carbides. *ACS Nano* **2012**, *6*, 1322–1331.

(55) Ghidiu, M.; Lukatskaya, M. R.; Zhao, M.-Q.; Gogotsi, Y.; Barsoum, M. W. Conductive Two-Dimensional Titanium Carbide 'Clay' with High Volumetric Capacitance. *Nature* **2014**, *516*, 78–81.

(56) Halim, J.; Kota, S.; Lukatskaya, M. R.; Naguib, M.; Zhao, M.-Q.; Moon, E. J.; Pitock, J.; Nanda, J.; May, S. J.; Gogotsi, Y.; Barsoum, M. W. Synthesis and Characterization of 2D Molybdenum Carbide (MXene). *Adv. Funct. Mater.* 2016, 26, 3118–3127.

(57) Alhabeb, M.; Maleski, K.; Anasori, B.; Lelyukh, P.; Clark, L.; Sin, S.; Gogotsi, Y. Guidelines for Synthesis and Processing of Two-Dimensional Titanium Carbide ($Ti_3C_2T_x$ MXene). *Chem. Mater.* **2017**, *29*, 7633–7644.

(58) Shahzad, F.; Alhabeb, M.; Hatter, C. B.; Anasori, B.; Man Hong, S.; Koo, C. M.; Gogotsi, Y. Electromagnetic Interference Shielding with 2D Transition Metal Carbides (MXenes). *Science* **2016**, 353, 1137–1140.

(59) Li, Z.; Zhang, H.; Han, J.; Chen, Y.; Lin, H.; Yang, T. Surface Nanopore Engineering of 2D MXenes for Targeted and Synergistic Multitherapies of Hepatocellular Carcinoma. *Adv. Mater.* **2018**, *30*, 1706981.

(60) Wang, H.; Wu, Y.; Yuan, X.; Zeng, G.; Zhou, J.; Wang, X.; Chew, J. W. Clay-Inspired MXene-Based Electrochemical Devices and Photo-Electrocatalyst: State-of-the-Art Progresses and Challenges. *Adv. Mater.* **2018**, *30*, 1704561.

(61) Yang, C.; Xu, D.; Peng, W.; Li, Y.; Zhang, G.; Zhang, F.; Fan, X. $Ti_2C_3T_x$ Nanosheets as Photothermal Agents for Near-Infrared Responsive Hydrogels. *Nanoscale* **2018**, *10*, 15387–15392.

(62) Tang, W.; Dong, Z.; Zhang, R.; Yi, X.; Yang, K.; Jin, M.; Yuan, C.; Xiao, Z.; Liu, Z.; Cheng, L. Multifunctional Two-Dimensional Core-Shell MXene@Gold Nanocomposites for Enhanced Photo-

Radio Combined Therapy in the Second Biological Window. ACS Nano 2019, 13, 284-294.

(63) Lin, H.; Wang, X.; Yu, L.; Chen, Y.; Shi, J. Two-Dimensional Ultrathin MXene Ceramic Nanosheets for Photothermal Conversion. *Nano Lett.* **2017**, *17*, 384–391.

(64) Pandey, R. P.; Rasool, K.; Madhavan, V. E.; Aïssa, B.; Gogotsi, Y.; Mahmoud, K. A. Ultrahigh-Flux and Fouling-Resistant Membranes Based on Layered Silver/MXene $(Ti_3C_2T_x)$ Nanosheets. J. Mater. Chem. A **2018**, 6, 3522–3533.

(65) Satheeshkumar, E.; Makaryan, T.; Melikyan, A.; Minassian, H.; Gogotsi, Y.; Yoshimura, M. One-step Solution Processing of Ag, Au and Pd@MXene Hybrids for SERS. *Sci. Rep.* **2016**, *6*, 32049.

(66) Han, X.-W.; Meng, X.-Z.; Zhang, J.; Wang, J.-X.; Huang, H.-F.; Zeng, X.-F.; Chen, J.-F. Ultrafast Synthesis of Silver Nanoparticle Decorated Graphene Oxide by a Rotating Packed Bed Reactor. *Ind. Eng. Chem. Res.* **2016**, *55*, 11622–11630.

(67) Anasori, B.; Lukatskaya, M. R.; Gogotsi, Y. 2D Metal Carbides and Nitrides (MXenes) for Energy Storage. *Nat. Rev. Mater.* **2017**, *2*, 16098.

(68) Ran, J.; Gao, G.; Li, F.-T.; Ma, T.-Y.; Du, A.; Qiao, S.-Z. Ti_3C_2 MXene Co-Catalyst on Metal Sulfide Photo-Absorbers for Enhanced Visible-Light Photocatalytic Hydrogen Production. *Nat. Commun.* **2017**, *8*, 13907.

(69) Li, H.; Li, X.; Liang, J.; Chen, Y. Hydrous RuO₂-Decorated MXene Coordinating with Silver Nanowire Inks Enabling Fully Printed Micro-Supercapacitors with Extraordinary Volumetric Performance. *Adv. Energy Mater.* **2019**, *0*, 1803987.

(70) Cao, W.-T.; Chen, F.-F.; Zhu, Y.-J.; Zhang, Y.-G.; Jiang, Y.-Y.; Ma, M.-G.; Chen, F. Binary Strengthening and Toughening of MXene/Cellulose Nanofiber Composite Paper with Nacre-Inspired Structure and Superior Electromagnetic Interference Shielding Properties. ACS Nano 2018, 12, 4583–4593.

(71) Xu, M.; Lei, S.; Qi, J.; Dou, Q.; Liu, L.; Lu, Y.; Huang, Q.; Shi, S.; Yan, X. Opening Magnesium Storage Capability of Two-Dimensional MXene by Intercalation of Cationic Surfactant. ACS Nano 2018, 12, 3733–3740.

(72) Ling, Z.; Ren, C. E.; Zhao, M.-Q.; Yang, J.; Giammarco, J. M.; Qiu, J.; Barsoum, M. W.; Gogotsi, Y. Flexible and Conductive MXene Films and Nanocomposites with High Capacitance. *Proc. Natl. Acad. Sci. U. S. A.* **2014**, *111*, 16676.

(73) Jiang, B.; Wu, Q.; Zhang, L.; Zhang, Y. Preparation and Application of Silver Nanoparticle-Functionalized Magnetic Graphene Oxide Nanocomposites. *Nanoscale* **2017**, *9*, 1607–1615.

(74) Li, C.-Y.; Meng, M.; Huang, S.-C.; Li, L.; Huang, S.-R.; Chen, S.; Meng, L.-Y.; Panneerselvam, R.; Zhang, S.-J.; Ren, B.; Yang, Z.-L.; Li, J.-F.; Tian, Z.-Q. Smart" Ag Nanostructures for Plasmon-Enhanced Spectroscopies. *J. Am. Chem. Soc.* **2015**, *137*, 13784–13787.

(75) Ding, X.; Liow, C. H.; Zhang, M.; Huang, R.; Li, C.; Shen, H.; Liu, M.; Zou, Y.; Gao, N.; Zhang, Z.; Li, Y.; Wang, Q.; Li, S.; Jiang, J. Surface Plasmon Resonance Enhanced Light Absorption and Photothermal Therapy in the Second Near-Infrared Window. J. Am. Chem. Soc. **2014**, 136, 15684–15693.

(76) Chen, M.; He, Y.; Huang, J.; Zhu, J. Synthesis and Solar Photo-Thermal Conversion of Au, Ag, and Au-Ag Blended Plasmonic Nanoparticles. *Energy Convers. Manage.* **2016**, *127*, 293–300.

(77) Baby, T. T.; Ramaprabhu, S. Synthesis and Nanofluid Application of Silver Nanoparticles Decorated Graphene. *J. Mater. Chem.* **2011**, *21*, 9702–9709.

(78) An, X.; Wang, W.; Wang, J.; Duan, H.; Shi, J.; Yu, X. The Synergetic Effects of Ti_3C_2 MXene and Pt as Co-Catalysts for Highly Efficient Photocatalytic Hydrogen Evolution over G-C₃N₄. *Phys. Chem. Chem. Phys.* **2018**, *20*, 11405–11411.

(79) Kim, Y. H.; Wool, R. P. A Theory of Healing at a Polymer-Polymer Interface. *Macromolecules* **1983**, *16*, 1115–1120.

(80) Lin, C.; Sheng, D.; Liu, X.; Xu, S.; Ji, F.; Dong, L.; Zhou, Y.; Yang, Y. A Self-Healable Nanocomposite Based on Dual-Crosslinked Graphene Oxide/Polyurethane. *Polymer* **2017**, *127*, 241–250.

(81) Li, Y.; Zhao, X.; Zhang, P.; Ning, J.; Li, J.; Su, Z.; Wei, G. A Facile Fabrication of Large-Scale Reduced Graphene Oxide-Silver Nanoparticle Hybrid Film as a Highly Active Surface-Enhanced Raman Scattering Substrate. J. Mater. Chem. C 2015, 3, 4126–4133.