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Full paper

Electricity generation based on a photothermally driven $Ti_3C_2T_x$ MXene nanofluidic water pump

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ABSTRACT

A popular method to harvest solar power is to convert light to heat, then to the kinetic energy of water, and finally to electricity, so-called concentrating solar power. However, it requires highly bulky components, limiting the applications. In this study, we present a miniaturized nanofluidic version—simply placing a MXene film on ionic solution and exposing part of the film to light. The distinguished photothermal property of MXene converts the asymmetric light irradiation to a water evaporation gradient, pumping water through the nanofluidic channels in the film, which transports cations and results in an ionic current. We expect this study to inspire more studies to explore the possibility of nanofluidic photothermal electricity as an alternative solar electricity technology for dispatched electricity generation and powering microfluidic/nanofluidic devices.

1. Introduction

Photothermal effect is used to convert light to electricity by focusing light with concentrating mirrors, boiling water, and driving a steam engine connected to an electrical power generator, so-called concentrating solar power [1]. Concentrating solar power is one of most popular solar electricity technologies, only second to photovoltaic solar cells. Compared to photovoltaic solar cells, it has the advantage of being compatible with cheap thermal storage technologies, enabling electricity generation at night. However, the complex structure of concentrating solar power makes it highly bulky and cost-ineffective, severely limiting its applications, especially for dispatched electricity generation and powering miniaturized devices. Removing the bulky components such as concentrating mirrors and the mechanical engine will potentially mitigate this problem. The concept of converting light to heat, then to water movement, and finally to electricity is still appealing, because in theory, all these steps can reach high efficiency. In addition, numerous strategies have been developed to harvest the energy of almost all forms of water movement, for example, pressure-driven flow in nanofluidic channels [2,3], moisture flow [4], rain [5], and water evaporation [6]. These forms of water movement could be exploited to replace water steam, so that concentrating mirrors and steam engine can both be removed. Herein, we demonstrate the nanofluidic photothermal electricity generation that realizes similar energy conversion steps to that of concentrating solar power. The configuration is extremely simple: after placing a layered film of MXene on top of ionic solution, photothermal electricity is generated upon asymmetric light irradiation. We reveal that MXene converts the asymmetric light irradiation to a temperature gradient due to its distinguished photothermal property [7], which induces an asymmetric evaporation of water through the nanofluidic channels in the MXene film. This evaporation gradient drives the water flow across the channel, converting thermal energy to the kinetic energy of water. Due to the negatively charged MXene, this water flow transports cations within the electric double layer, resulting in a streaming current [2].

2. Result and discussion

MXene is a family of two-dimensional (2D) materials consisting of transition metal carbide and nitride [8]. It attracted great interest in

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energy harvesting such as triboelectricity [9–12]. In this study, we chose $Ti_3C_2T_x$, where T represent terminal groups such as –OH and –F (Fig. S1 and Fig. S2), because it has exceptionally high photothermal conversion efficiency [7]. It was prepared by etching bulk Ti_3AlC_2 with concentrated hydrochloric acid and lithium fluoride, and then exfoliate with ultrasonication (Inset in Fig. 1a) [13–15]. After dispersed in water, it was washed and vacuum-filtrated to form a laminar film (Fig. 1a) with a typical thickness of 5 μm. The massive interlayer spacings of the film form interconnected nanofluidic channels [16], with a channel size of ~0.7 nm (Fig. S3) when the film is hydrated, allowing the transport of simple ions.

The film was then cut into a rectangular shape with a size of 0.5 cm × 2 cm, and the two ends were connected to silver electrodes. The connecting part was sealed with polydimethylsiloxane (PDMS) and black insulating tape to prevent from light irradiation. Then it was placed on ionic solution (1 M NaCl in water. Fig. 1b and Fig. S4). For mechanistic study, we irradiated the right end of the film with 808 nm laser light which is within the solar spectrum, using a power density of 100 mW/cm^2. The light spot size is ~0.15 cm^2, with its center 0.6 cm away from the film center. Upon light irradiation, a current of ~12 μA was detected (Fig. 1c). We also tested gold electrodes, which are expected to be more stable in electrolyte. The result is shown in Fig. S5, the device can generate a current of ~10 μA and maintained this value after one day. Here positive sign represents the direction from the left to the right side of the film (Fig. 1b). Infrared image shows that the irradiation established a temperature gradient of ~10 °C across the film, indicating the role of photothermal effect for the electricity generation.

We note that many 2D materials exhibit photo current effect [17–20]. In our experiment, the intrinsic photo current effect of 2D materials does not play a key role. Fig. S6 shows that a MXene film suspended in air generates ~2 μA current under the same light irradiation, even though the temperature gradient (~25 °C, Fig. S6) is much higher than the film floating on solution. The mechanism of this 2 μA of the dry MXene film should be photothermoelectric effect, which is a widely know property of dry 2D materials including graphene [21] and graphene-like materials such as MoS_2 [22], WSe_2 [23] and GaTe [24].

We propose the nanofluidic photothermal electricity generation mechanism as illustrated in Fig. 2a. When light is on, the irradiated part of the film is rapidly heated up due to the exceptionally high photothermal conversion efficiency of MXene, evaporating the water confined in the nanofluidic channels. The asymmetric light irradiation causes a temperature gradient across the film (infrared image in Fig. 1b), and thereby a water evaporation gradient. The water in the slow evaporation region (left) is then forced to flow to the fast evaporation region (right) to compensate the water loss. This directional water flow in the nanochannels transports cations within the electric double layer at the negatively charged channel walls (*i.e.* MXene nanosheets), resulting in a net current. The negative surface charge of MXene is suggested by its negative zeta potential (Fig. 2b). This water flow induced ionic current is a generic phenomenon in micro/nanochannels named streaming current [25].

To validate the above mechanism, several experiments were carried out. First, we measured the evaporation rate of water through the nanochannels under varying light power density, which shows an increasing trend with the increase of light power density (Fig. 2c). This rationalizes that asymmetric light irradiation should induce asymmetric evaporation. Furthermore, to confirm the effect of thermal gradient, a hot plate was placed above on one end of the membrane with a small gap in between for asymmetric heating of the MXene while not stopping the evaporation, and the ionic transport current was demonstrated in Fig. S7. A current was also detected. The current (~1 μA) is, however, much smaller than the photo induced current, presumably because the hot plate inevitably affects evaporation. Second, to verify that the current is driven by the evaporation, we sealed the whole film with a thin layer (10 μm) of transparent PDMS, which allows light transmission but prohibits water evaporation. A temperature gradient of ~20 °C is generated under the same asymmetric light irradiation, but the current drops to around 0.4 μA (Fig. 2d) which we attribute to the intrinsic photo current effect of MXene. In addition, we sealed half of the film with the right side exposed to air, and measured the current under darkness. This should also cause an evaporation asymmetry even without light irradiation. Indeed, a small current of 3.4 μA was detected (Fig. 2e). Furthering experiments were carried out with different humidity and wind, which can directly affect the water evaporation. The same half-sealed device was placed in different relative humidity (RH), and the response current decreased with increasing RH (Fig. S8a), due to the decreased evaporation rate in higher humidity. Besides, in windy environment, the current can also increase in a few seconds (Fig. S8b). These experiments confirm the key role of evaporation for current generation.

Finally, to confirm that water flow can induce ionic current, we forced the water to flow by placing a droplet of ionic solution (1 M NaCl) on a film (0.5 cm × 5 cm), and moving it along the film. Part of the water permeated into the nanochannels would also be dragged to move, together with the counter-ions in the electric double layer (Fig. 2f). When the droplet moves at a velocity of about 0.5 cm/s, a current of 1.6 μA is generated (Fig. 2g). When the droplet stops moving, the current drops to zero quickly (Fig. 2g). Importantly, when the droplet moving velocity increases, the current also increases linearly (Fig. 2h). It is worth noting that a pseudocapacitor mechanism was also proposed to explain a similar droplet-moving-induced-electricity phenomenon on single layer graphene [26], but the current direction was opposite to ours, and thereby their mechanism is not applicable here. All the above experiments strongly support our mechanism.

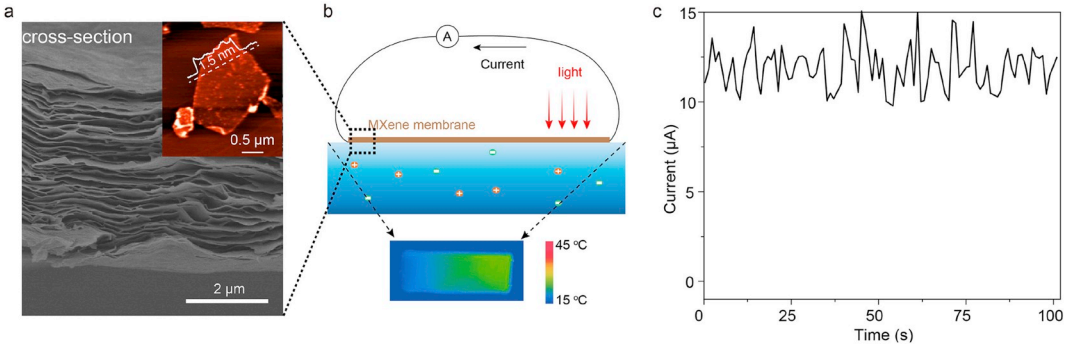

Fig. 1. Nanofluidic photothermal electricity generation. a) SEM image of the cross-section of MXene film (Inset: AFM image of an exfoliated nanosheet with a thickness of 1.5 nm). b) Current is generated when a MXene film is placed on ionic solution (1 M NaCl) with one end exposed to light irradiation. The top-view infrared image (bottom) shows the temperature distribution of MXene film when the right end is irradiated. c) The generated current under 100 mW/cm^2 light irradiation.

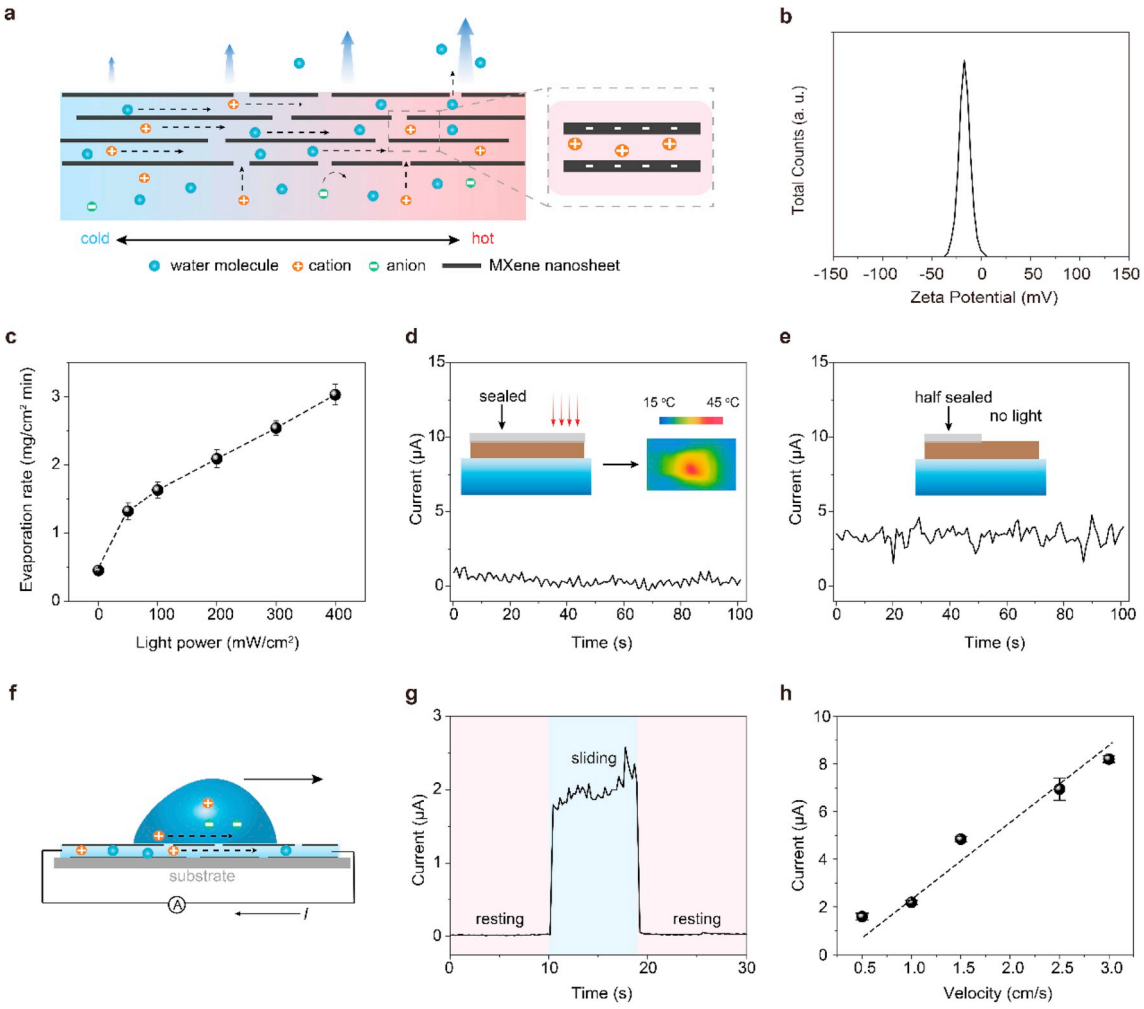

Fig. 2. Mechanism of the current generation. a) Schematic illustration of the mechanism. Briefly, asymmetric light irradiation on the film induces a temperature gradient, and thereby a water evaporation gradient. Water in the slow evaporation region (here left side, when the right end is irradiated) is forced to flow to the fast evaporation region (right side) to compensate the water loss, which transports cations within the electric double layer of the negatively charged MXene sheets. This directional transport of cations results in a net current. b) Negative zeta potential of MXene nanosheets, confirming its negative surface charge. c) Water evaporation increases with the increase of light power for a uniformly irradiated film, rationalizing that asymmetric irradiation induces asymmetric evaporation. d) A sealed film (inset scheme) generated merely 0.4 μA current, even though a temperature gradient of ~20 °C (inset infrared image) is established. e) A half sealed film generates ~3 μA current without light irradiation. The above results confirm that evaporation plays key role in the current generation. To further validate that current originates from water flow, f) a droplet of ionic solution was moved along MXene film. g) only when the droplet moves, current is generated. h) the generated current scales linearly with the droplet moving velocity.

We further investigated the effect of various parameters on the electricity generation. First, the response current should be strongly dependent on the asymmetry of light irradiation. When the center of the MXene film is irradiated, water will flow from both ends to the center, resulting in zero net current. When the irradiation is switched from the right to the left side, the current direction should also be reversed. Such behavior was indeed observed when we moved the light from the left end to the center and then to the right end of the film (Fig. 3a). Furthermore, we measured the current for different irradiation positions. The film center position is marked as zero. The results show that the current is symmetric to film center, and its absolute magnitude increases when the irradiation asymmetry increases (Fig. 3b and Fig. S9 shows the same trend for different ionic concentrations), as expected. We then changed the light power density from 50 to 400 mW/cm^2. The response current increases approximately linearly with the light power density, from 10.1 μA to 44.0 μA (Fig. 3c), due to the fact that the evaporation rate of water increases with the light power density (Fig. 2d). To elucidate the effect of ionic concentration, we varied the NaCl concentration of the bulk solution from 10^{-6} M–1 M. It is observed that the current increases from 0.4 μA to 12.0 μA (Fig. 3d). Considering the 6 orders of magnitude change in concentration, the change in current is not dramatic, which is close to what Helmholtz-Smoluchowski equation predicted [27]. Other caions including Li^+, Ca^{2+}, Mg^{2+}, Al^{3+} (1 M) with different hydrated radius lead to the response current changes under 100 mW/cm^2 light irradiation (Fig. S10). As we expected, the larger the ions, the more difficult it is to cross the nanochannels, resulting in a smaller current. In addition, deionized (DI) water was also tested, showing a small current of ~0.8 μA (Fig. S11), due to the protons in water.

For nanofluidic applications, two compartment cells are routinely used. Our device also functions with such configuration (Fig. S12), pumping ions from one reservoir to another, with the ionic current increasing with the light power density. Meanwhile, the potential was also recorded and reached ~14 mV under the 600 mW/cm^2 (Fig. S13). We also tested the potential for DI water, which is ~44 mV (Fig. S14). The increasing potential with decreasing electrolyte concentration is in agreement with other literatures [6]. Note that in this configuration, the electrodes are placed in the reservoirs instead of on the MXene film.

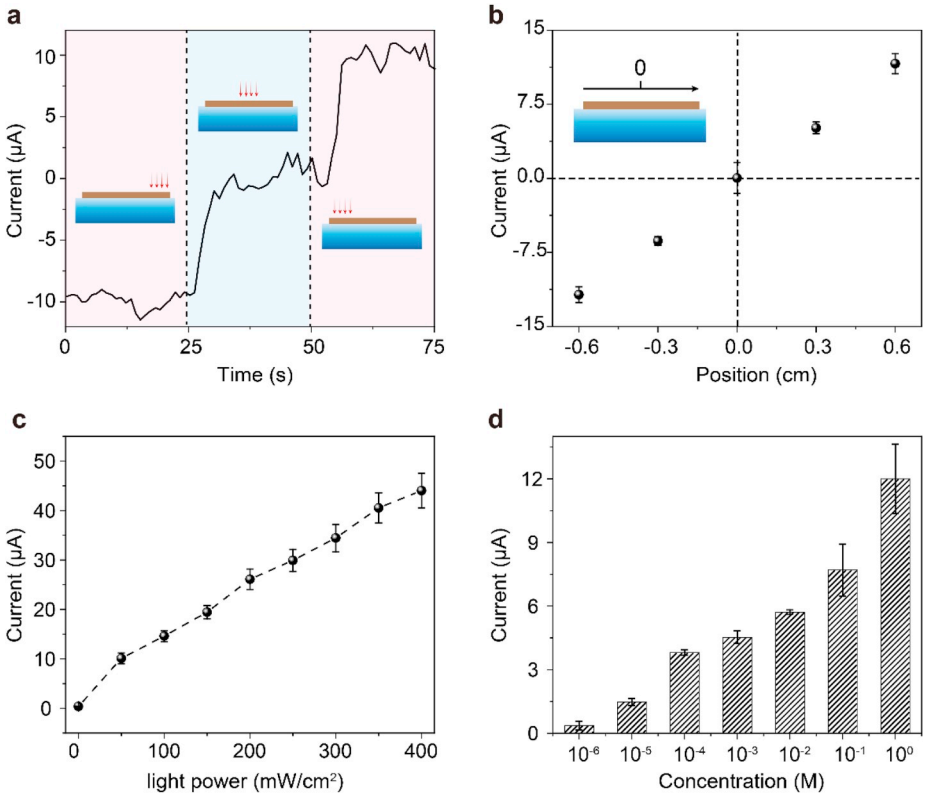

Fig. 3. Effect of light irradiation asymmetry, light power, and ionic concentration. The current generation is strongly dependent on the asymmetry of light irradiation, as demonstrated by a) its continuous response to light moving from the left end to the center to the right end of the film, and b) its average value for different irradiation positions. c) The current increases approximately linearly with the increase of light power. d) It also increases with the increase of ionic concentration.

To demonstrate the potential of harvesting solar power, we placed the device under natural sunshine (July 25, 2019, in Tianjin, China, sunny with intermittent cloud. Inset in Fig. 4) and recorded the generated current from morning to night (Fig. 4). In reality, sunlight irradiation is not asymmetric. To address this, half of the MXene film was bent under water (inset in Fig. 4). The current is strongly dependent on the sunshine. From 6:00 in the morning to noon, the ionic current increased from 4.7 μA to 10.5 μA. At 15:00 when the weather turned cloudy, a sudden drop in current was recorded, which then increased back as the weather turned sunny. It is noteworthy that a current of more than 5 μA was still generated after sunset (around 19:30), which is attributed to the ever-present natural water evaporation (Fig. 2e). In addition, we also tested the half sealed MXene film as shown in Fig. 2e. The response current was also closely related to the solar power variation (Fig. S15). Considering that seawater is the most abundant water source, 0.5 M NaCl solution was chosen to simulate sea water, and the current was shown in Fig. S16. This suggests a key advantage of nanofluidic photothermal electricity generation: it delivers electricity even when there is no sunshine, without the need of thermal storage facilities.

We note that the stability of MXene film is a concern in practical applications. Compared with MXene dispersion, the MXene membrane by vacuum filtration is much denser, which enables much stronger antioxidation ability [28]. While we carried on low power ultrasonic exfoliation to obtain more large flakes to improve antioxidation performance. To better illustrate, a piece of MXene membrane floated on 1 M NaCl solution under the natural sunlight irradiation, and we tracked its evolution by Raman test (Fig. S17). We observed no obvious oxidation for a duration of 21 days.

3. Conclusion

In this work, we demonstrated a nanofluidic photothermal generator

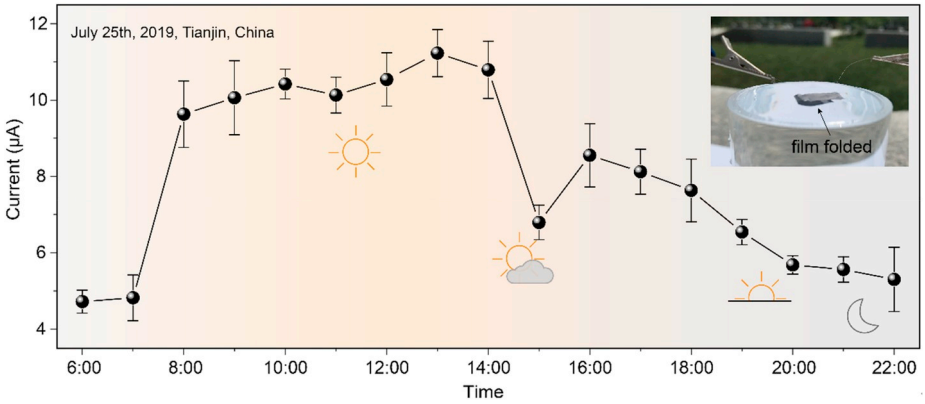

Fig. 4. Proof-of-concept application. Harvesting solar power. MXene film floating on 1 M NaCl solution was placed outdoor for electricity generation from 6:00 a.m. to 22:00 p.m. For asymmetric light irradiation, half of the film was folded under water. The current is dependent on the sunshine, but is still generated at night due to the ever-present water evaporation.

that is reminiscent of concentrating solar power. MXene film was utilized to convert asymmetric light irradiation to an evaporation gradient, pumping water through nanofluidic channels, inducing a streaming current. Remarkably, the nanofluidic photocurrent is orders of magnitude higher than other two-dimensional materials under similar light power density, as shown in Table S1 [29–32] If deployed for solar thermal power in the future, it may show remarkable advantages. Firstly, its configuration is extremely simple, which helps cut installation cost and makes it more suitable for dispatched energy generation. Secondly, thanks to the evaporation based mechanism, it also enables electricity production at night. Thirdly, its small size enables its use for small scale power delivery, and in miniaturized devices. Fourthly, it could also be combined with solar desalination technologies, harvesting power while desalinating water.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Characterization of MXene nanosheets, optical image of the generator set-up, power generation.

Supplementary data to this article can be found online at https://doi.org/10.1016/j.nanoen.2020.104481.

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