Single- and few-layers MoS₂ nanocomposite as piezo-catalyst in dark and self-powered active sensor

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ABSTRACT

Over the past decades, water pollution has been suggested as the leading factor to infectious diseases. There has been a worldwide concern to use photocatalysts to degrade organic pollutants in waste water. However, the requirement of light assistance in degradation process has limited the application of photocatalysts. In this paper, MoS₂/PDMS nanocomposite was fabricated in order to overcome this problem. The results showed that MoS₂/PDMS nanocomposite can provide a high degradation activity to purify the waste water without light assistance. The MoS₂/PDMS nanocomposite preserved an activity of 67% toward dye Rhodamine B degradation even in the fourth cycling test. We found that the high degradation activity of MoS₂/PDMS nanocomposite was based on the piezo-catalytic effect of single- and few-layers MoS₂ nanoflowers in the nanocomposite. We also demonstrated that MoS₂/PDMS nanocomposite was a useful material in the fabrication of nanogenerator to harvest waste water energy. Through the direct coating of MoS₂/PDMS nanocomposite on a metal grid, electric outputs of 23 V and 13 mA/m² can be generated when a water flow (20 mL/s) was passing the nanogenerator. In addition, when coating MoS₂/PDMS nanocomposite on a flat electrode and placing it inside a water pipe, the nanogenerator could not only act as the source of electric output, but also as a self-powered sensor to locate the water passage route and/or the contamination areas in the waste water.

1. Introduction

To break down the energy crisis and environmental concerns, photocatalytic hydrogen evolution from water splitting has a very prospective potential [1]. A semiconductor material, for instance titanium dioxide (TiO₂), is regarded as a promising material in environmental purification and hydrogen energy production [2]. One of the main concerns of using catalysts is its band gap that lies in the ultraviolet range. To solve this drawback, semiconductors with a moderate bandgap from doping transition metals [3–6] have been developed to reduce its band gap and the recombination rate of photogenerated electron–hole pairs. Thus, many studies report that TiO₂ nanomaterials with some co-catalyst can extend their absorbance spectrum from ultraviolet to visible-light thereby enhancing its photocatalyst performance. However, to maintain and stabilize the catalysts materials in ambient air is still a critical task, as semiconductor materials using dopant-free have been in the spotlight in recent years [7,8].

Another critical regulatory issue in healthcare is that water waste and soil pollution are frequently as well as directly caused because of the inefficiency in the disposal of waste. Therefore, it is important to consider how to deal with the waste disposal problem. Although photocatalyst materials [3–5,9,10] have been developed for more than 50 years in environmental purification and renewable energy conversion, most importantly, the superior catalyst is characterized to have a high degradation activity in the dark. Up to now, there are rare materials in which can precede the degradation activity to purify the water waste without light assistance.

Single-layer MoS₂ has been confirmed to be a direct band gap semiconductor ~1.29 eV [11]. It is an emerging material with wide-ranging potential for applications in electronics [12,13]. Although the bulk MoS₂ is not a promising photocatalysts material if it is only incorporated with the semiconductor materials to form an heterojunction nanostructures [14], however, in our recent work [15] we have discovered that the single- and few-layers MoS₂ nanoflowers (NFs) exhibit significantly enhances their degradation activity for decompos-
ing the organic dyes by introducing a mechanical force to the MoS2 NFs. The high degradation activity of the MoS2 NFs stems from their piezoelectric property of the single and few-layers as encountered by the mechanical strains, which, in turn induced the electron-hole pairs separation to generate the high reactive radicals for the removal dye solution. The piezoelectric potential induced the electron-hole pairs separation to proceed with the generation of the reactive species, and it is called the piezo-catalyst effect [16].

Nowadays, there are limited materials in which one can simultaneously proceed with the degradation activity to purify the water waste and energy harvesting through the mechanical energy from the flowing water. To extend the new catalyst’s in commercial applications, we implement the entire catalyst pipeline using polydimethylsiloxane (PDMS) mixed with the MoS2 NFs. We successfully fabricated the highly efficient catalysts. The as-synthesized single- and few-layers MoS2 NFs were encapsulated in the PDMS film (MoS2/PDMS film), which can exhibit high degradation activity for destroying the Rhodamine B dye (RB) in the dark. As the encapsulated MoS2/PDMS film was used as a negative layer, while copper acted as a positive layer, the triboelectric nanogenerator (TENG) can be therefore fabricated for energy harvesting through water. Due to the MoS2 NFs exhibiting a high catalytically active surface on the active edge sites, which induced the polar molecular to be adsorbed on the polarized surface sites and forming the reactive species, for instance, the free radical oxygen, hydrogen peroxide, and hydroxyl radical, to decompose the dye solutions. As a consequence, the MoS2/PDMS film is not only used as an efficient triboelectric layer to harvest the mechanical energy of waste water, but the device can also be utilized as an active sensor for the monitoring of flowing water and its contamination.

The concept of harvesting the mechanical energy of waste water is based on the hybrid of contact electrification between insulating polymer, water, and the electrostatic effect [17–20]. Different to the traditional triboelectric nanogenerator that needs both triboelectric layers that are solid materials [21–26] water itself, here is one of the contact materials to cause the triboelectric charges and generate electric outputs. We have demonstrated that the MoS2/PDMS either can be coated on the metal grid and/or placed inside the water pipe to harvest the mechanical energy of waste water. In addition, the electric output of the water-TENG is highly dependent on the separation of water and the MoS2/PDMS, as the contamination existing in the water sample would cause the polarity and the final electric output. These results about water-TENG are important because the energy from waste water is unlimited and could become a new source of renewable energy [27].

2. Experimental section

2.1. Preparation of MoS2 nanoflowers

MoS2 nanoflowers were synthesized by a hydrothermal process, which is similar to our previous work [15]. First, the Na2MoO4·2H2O and CH3NaS powder were dissolved in 1-Butyl-3-methylimidazolium chloride to prepare the precursor. Then, a diluted HCl solution was progressively titrated into the precursor. Finally, the as-prepared precursor was transferred to a Teflon-lined stainless steel autoclave and maintained at 220 °C for 24 h to produce MoS2 nanoflowers.

2.2. Fabrication of MoS2/PDMS TENGs

Two different water-TENGs based on MoS2/PDMS nanocomposite were fabricated to harvest the mechanical energy of waste water. The working principle of water-TENGs was designed as single-electrode mode. First, a stainless steel with dimensions of 5 cm×5 cm was cleaned with acetone, isopropanol, and deionized water, respectively. The size of each grid was around 2 cm² and the diameter of metal wire in the stainless steel grid was 200 μm. Before the coating of MoS2/PDMS nanocomposite, a conducting wire was connected to the stainless steel as a lead for subsequently electric measurement. A MoS2/PDMS mixture with weight percentage of 5% was then prepared and coated on the stainless steel through the dip coating process. The curing temperature for the water-TENG was set up at 120 °C for 1 h. The second water-TENG was constructed as a thin-layered device. A polyethylene terephthalate (PET) sheet with dimensions of 2 cm×8 cm was selected as the substrates. Copper film (thickness around 100 nm) was deposited on the PET substrate by a DC magnetron sputter. A conducting wire was connected to the copper film as a lead for subsequently electric measurement. Then the MoS2/PDMS mixture with weight percentage of 5% was coated on the copper film through the spin coating process. The curing temperature for the water-TENG was also set up at 120 °C for 1 h.

2.3. Characterization

The high-resolution transmission electron microscope (HRTEM, JEOL JEM-3000F), field emission scanning electron microscope (FESEM, Hitachi S-4800), and x-ray diffractometer (Burker, D8SISIS) were employed to characterize the materials’ properties of the MoS2 nanoflowers. The ultrasonic wave (250 W, 40 kHz) was used to evaluate the degradation activity of the MoS2/PDMS nanocomposite in dark. The Hitachi spectrophotometer (UV–vis) was used to measure the decomposition property of the catalysts. A piezoresponse force microscopy (PFM, Bruker, ICON) was employed to measure the piezoresponse activity of the MoS2 NFs. For the measurement of electric outputs of water-TENGs, a programmable electrometer (Keithley Model 6514) and a low-noise current preamplifier (Stanford Research System Model SR570) were used.

3. Results and discussion

The TEM image in Fig. 1a reveals that the MoS2 NFs consist of abundant nanopetals with highly active surface sites. The HRTEM image in Fig. 1b further demonstrates that the petals are ranged from single-layer to few layers (see the black arrowheads). The lattice fringe between layers is around 0.64 nm (see the inset image in Fig. 1b). The HRTEM image in Fig. 1c and its corresponding fast Fourier transform (FFT) image (see the inset Fig. 1c) reveal that the basal plane of the single-layer MoS2 is (001). The XRD pattern of Fig. 1d indicates that the as-synthesized products belong to a single phase of MoS2 (JCPDS No. 37-1492) with a space group of p63/mmc [28]. It should be noted that the peak belongs to plane (002) of the MoS2 NFs shift to a lower angle indicating an expansion in the c-axis of the MoS2 crystal has a larger d spacing in contrast to the reported value [12]. The (100) plane shift to a higher angle, which demonstrated an in-plane compression in the MoS2 NFs. In addition, when comparing with the MoS2 commercial sheets, the peak at (002) of the MoS2 NFs exhibit a much broader peak (see the inset image in Fig. 1d), implying that the MoS2 NFs possess abundant single- and few- layered structures [15]. The SEM image (Fig. S1) further shows the high purity of the as-synthesized MoS2 NFs.

The MoS2 NFs were uniformly deposited on the PDMS’s surface and then exposed to ambient air to fabricate the TENG film (see the inset Fig. 2a) to investigate their degradation activity under ultrasonic wave in the dark. Fig. 2b reveals that the MoS2 NFs film retains almost 67% of its initially degradation activity even in the fourth cycling test. The first cycling degradation activity can be reached through 99% dye decomposition. The reason for the decreased activity of decolorization may be attributed to the peel off from the MoS2 NFs during ultrasonic vibration. Although the degradation activity was progressively decreased, the activity still retained over 67% and became stable after the third cycling test. The high degradation activity of the MoS2 NFs is attributed to the piezo-catalyst effect [15], see details below.

The piezo-catalytic activity of the as-prepared MoS2/PDMS was
further confirmed by measuring the formation of active ‘OH upon the ultrasonic vibration, which is considered to be the most important oxidative species in catalytic reactions. To measure the formation of ‘OH, we used terephthalic acid (TA) as an indicator based on the turn-on fluorescence when reacting with ‘OH [29]. Fig. 2b displays the fluorescence spectra of the TA solution in the presence of the pure PDMS and MoS2/PDMS film. A gradual increase in the fluorescence intensity at 420 nm was observed upon increasing the ultrasonic vibration time (from 0 to 20 min). The fluorescence intensity is proportional to the amount of produced ‘OH. On the other hand, the fluorescence intensity did not increase in the absence of ultrasonic vibration or MoS2 NFs (Fig. S2).

To further demonstrate the piezo-catalyst activity of the MoS2 NFs, it is critical to investigate the decoloration rate of the RB solution that was not caused by its adsorption effect. The MoS2 NFs were encapsulated in the polydimethylsiloxane film with the different catalysts, such as the MoS2 NFs, commercial MoS2 sheets, TiO2-P25 nanoparticles (size ~20 nm) [10,30], and blank PDMS film, to assure their degradation activity under an ultrasonic wave in the dark. As shown in the schematic diagram in the inset image of Fig. 2c, all the testing catalysts were encapsulated in the PDMS film without exposure to the ambient air [46]. Fig. 2c further shows that there is no degradation activity for the pure PDMS film in a dye solution after 3.5 h under the continuously ultrasonic vibration. In contrast, the TiO2-P25 nanoparticles mixed with the PDMS film is still retained with almost no degradation activity under the same degradation condition. However, when observing the MoS2 NFs/PDMS film, which shows a dramatic degradation activity in comparison with the TiO2-P25/PDMS film and the blank PDMS film, the degradation activity of the MoS2/PDMS is twice that of others samples.

It should be noted that the testing conditions was proceeded in dark without external light source. Thus, we postulated that the MoS2 NFs possess abundant single- and odd few-layers, which acted as a key component to dominate the piezo-catalyst activity. To evaluate the piezo-electric potential of the MoS2 NFs, the piezoresponsive force microscopy was employed to demonstrate the electromechanical response of the as-synthesized MoS2 NFs. The MoS2 NFs were directly grown on the conductive glass. During the measurement, the electric field was simultaneously applied to acquire the piezoresponse of the MoS2 NFs. The AFM topography and its corresponding PFM phase images are as shown in Fig. 3a, which clearly reveals the presence of irregularly shaped domain walls. Fig. 3b further displays the corresponding piezoresponse amplitude image, which is evidence that the important characteristically piezo-electric response was indeed created from the MoS2 NFs under an external load, and records when the PFM tip scanned across the MoS2 NFs’ surface.

Although our PFM measurement has been demonstrated as an obviously piezo-electric potential that indeed form on the active-edge surface sites of the MoS2 NFs, how the encapsulated single- and few-layered MoS2 NFs in the PDMS film can significantly decompose the RB dye in the dark in contrast to other catalysts, when applying a mechanical strain on its surface? First, to understand the carriers’ concentration of the MoS2 NFs, the Hall measurement revealed that the electron mobility and electron concentration were ~13 cm2 V−1s−1 and 4×1015 cm3, respectively [15]. This indicated that the VS (single sulfur vacancy) and/or V2s (double sulfur vacancy) should be predominant in the single-layer MoS2 [31], thereby inducing localized donor states inside the bandgap [32]. Fig. 3c shows when the active edge sites of the single-layer MoS2 position on the PDMS film’s surface, which were sustained by a mechanical force. The Mo-S dipoles are then stressed, and form a polarization aligned from the S to the Mo site, then created an electric field that propagated in the zigzag and/or armchair direction to generate the electron-hole pairs separation. After that, the electrons and holes were then transferred in an opposite direction to...
participate in the reaction with the water molecules. Therefore, the water molecule of the positive ends will be induced to be absorbed on the surface with the negative charge ends of the Mo-S dipoles, while that of the negative ends will be tripped on the positive charge ends of the Mo-S dipoles. Finally, the absorbed polar molecule on the MoS2/PDMS will create the abundantly radical species, such as free radical oxygen, hydroxyl radical, and hydrogen peroxide for decomposing the dye solution [3].

To demonstrate that this concept can be used to harvest the mechanical energy of waste water, we first coated the MoS2/PDMS on a commercial stainless steel grid as a water-TENG and placed it under a kitchen faucet (Fig. 4a). The dimensions of the water-TENG chosen here were 5 cm×5 cm in order to cover all the water flow from the faucet. The fabrication of the water-TENG was conducted through the dip coating process. The weight percentage of the MoS2 in the MoS2/PDMS mixture was 5%. The diameter of metal wire in the stainless steel grid was 200 µm and the size of each grid was around 2 cm². The operation of water-TENG was adopted by a single-electrode mode, which has been verified as a convenient approach for the energy harvesting and self-powered sensing applications [33–37]. Self-powered sensing systems, with their convenient sensing strategy, could be the most desirable and promising candidates for sensor development because those devices can be activated without using batteries as the power sources [38–43]. The distance between the water outlet and the water-TENG was fixed at around 30 cm. Fig. 4b shows the output voltage of the water-TENG generated by the water flow from the faucet. We can observe that the output voltage of the water-TENG was highly dependent on the water flow rate. This was because the higher water flow rate would contribute to the situation of more water contact and being separate from the water-TENG at the same time. The output voltage of the water-TENG reached a saturated value of 23 V when the water flow rate was 20 mL/s. In addition, the water-TENG also functions as a self-powered sensor for the water flow rate detection. To highlight the application, we used commercial LEDs as the indicators to replace the heavy and expensive electrometer. It is clearly shown that when the water flow rate reaches 20 mL/s, the electric output generated from the water-TENG can drive 9 LEDs. However, as the water flow rate decreases to 2.5 mL/s, the generated electric output can only light-up 2 LEDs. Fig. 4c represents the output current density of the water-TENG obtained from the water flow. The output current density was calculated by dividing the output current with all the metal grid contact areas. It should be noted that the maximum output current density can reach 13 mA/m² and the signal varies due to the unstable water flow from the faucet. The electric output decreases to zero when the faucet is turned off, revealing that the electric output is generated from the water flow (data not shown here). Fig. 4d clearly shows that both the output voltage and current density are dependent on the water flow rate.

We then measured the electrical output of the water-TENG after connecting loads of different resistances while keeping the water flow rate at 20 mL/s. As shown in Fig. 4e, when the resistance is below...
of water cannot fully pass the water-TENG (v) because of the amount of flowing water passes through the MoS2/PDMS surface. The dimensions of each water-TENG were 2 cm x 8 cm. The water-TENG which is furthest away from the water outlet generates the maximum electric output. The output voltage for water-TENG (i) and water-TENG (v) are 5 V and 27 V, respectively. The output current density for water-TENG (i) and water-TENG (v) are 4 mA/m² and 8 mA/m², respectively. The output current density will also increase if the water flow rate is increased due to the faster electron transferring time between the conducting layer and the ground. Fig. 5d clearly shows that both the output voltage and current density are dependent on the passing distance of the flowing water. Two reasons may contribute to this result. The first is the triboelectric charges which are generated when the water passing through the MoS2/PDMS surface can accumulate, and therefore the water-TENG (v) can provide the maximum electric output [44,45]. The other reason is that more water will pass the water-TENG (v) because of the amount of water cannot fulfill the water tube. The AC output could be transformed to the unidirectional pulse output by attaching a full-wave rectifying bridge. The rectified output can then be utilized to charge a 33-μF capacitor (Fig. 5e). However, since each water-TENG can generate an electric output, the water-TENG can function like a self-powered sensor to tell where the water is passing through. This demonstration could be important because it represents not only in the future we can collect the waste water energy from the environment during daily life, but also we are now moving forward to discover and facilitate new renewable energy sources. We also demonstrated that the water-TENG can detect the contamination in the waste water. Fig. 5f shows that the generated output will decrease as the amount of oil content increases. This is because the strong interaction between oil and the PDMS surface would hinder the water to contact with the MoS2/PDMS and thereby contributing to the decreased output.

4. Conclusion

In summary, we have demonstrated that the MoS2/PDMS nanocomposite was not only a piezo-catalyst but also a triboelectric layer in TENG to harvest water mechanical energy. The MoS2 NFs exhibit abundant single- and odd few-layers, which act as a key component to enhance the piezo-catalytic effect. Under an ultrasonic vibration in the dark, the MoS2/PDMS nanocomposite dramatically decomposed the RB dye in contrast to the TiO2/PDMS composite. In addition, water-TENGs were fabricated by simply coating the MoS2/PDMS nanocomposite on different metal substrates. These water-TENGs provided an efficient way to harvest the water mechanical energy from different sources. All the results indicate that the MoS2/PDMS nanocomposite was capable to purify the waste water and collect its mechanical energy in the near future.

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Fig. 5. (a) Illustration of the thin Water-TENG attached on different positions inside a polymer tube. The distance between the water inlet and water-TENG (i), (ii), (iii), (iv), and (v) are 2, 9.5, 16, 22.5, and 38 cm, respectively. (b) Output voltage of thin water-TENG attached on different positions inside a polymer tube. (c) Rectified output current density of thin different water-TENG attached on different positions inside a polymer tube. (d) Dependence of output voltage and current density on thin water-TENG attached on different positions inside a polymer tube. (e) Charging curve of a 33-μF capacitor by thin water-TENG attached on different positions (iii), (iv), and (v) inside the polymer tube. (f) Electric output of thin water-TENG when the flow water containing different amount of oil.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.nanoen.2016.12.013.

References

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