Flexible and Environment-friendly Regenerated Cellulose/MoS₂ Nanosheet Nanogenerators with high Piezoelectricity and Output Performance

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Abstract

Flexible piezoelectric nanogenerators for energy harvesting are getting more and more attention nowadays by converting the mechanical energy to electric energy. Here, an environment-friendly piezoelectric nanogenerator based on the regenerated cellulose (RC)/MoS₂ nanosheet nanocomposite successfully exhibited a relative high output voltage of 2 V and current of 150 nA under slight press which were 5 and 7.5 times higher than those of the neat RC film, *i.e.* 0.4 V and 20 nA, respectively. In particular, the MoS₂ nanosheets were obtained through a simple, facile and low-cost pathway by mechanical exfoliation in triethanolamine. The nanocomposite film with MoS₂ nanosheet content of 4% exhibited a high piezoelectric constant (d_{33}) of 19 pC/N, which was 6.3 times higher than that of the neat RC film (*i.e.* 3 pC/N). Thus, the RC/MoS₂ piezoelectric nanogenerator has great potential applications in the fields of energy harvester, sensors and is of great significance to environment protection.

Highlights

1. MoS₂ nanosheets were prepared by facile exfoliation in triethanolamine.
2. The MoS₂ nanosheets greatly improved the piezoelectricity of cellulose.
3. The nanogenerator is flexible and environment-friendly with high output performance.

1. Introduction

With the consuming of fossil energy and deteriorating of environment, the quest for clean and renewable energy has become an urgent challenge (Goldemberg 2007; Wang et al. 2019). Energy harvesting technology is one of the potential methods in energy utilization. There are many sustainable energy sources that can be used in energy harvesting such as solar energy, wind energy (Fan et al. 2016). Piezoelectric materials have attracted more and more attention as a new pathway that can convert mechanical energy in ambient environment to electric energy and is promising to realize energy generation (Sappati and Bhadra 2018; Park et al. 2014; Zhao et al. 2020). In 2006, Wang et al. (2016) developed a piezoelectric nanogenerator made of ZnO nanowire arrays for the first time, which could harvest mechanical energy and convert to electric energy. There is a potential difference when stress is applied to piezoelectric materials, which is called positive piezoelectric effect. Besides, the converse piezoelectric effect is that the material deforms under electric stimulation (Wei et al. 2018). Energy harvesting technology inspired by piezoelectric effect can be used in nanogenerator (Ye et al. 2019), self-powered sensor and so on (Fang et al. 2019). The devices could convert mechanical energy from human daily life such as walking, bending at anytime and anywhere to achieve the purpose of energy utilization (Yang et al. 2016; Xu et al. 2010). Furthermore, when this kind of self-driven sensor used in vivo environment as medical device (Zhao et al. 2020), the problem of battery replacement can be avoided because it can extract biochemical energy like heartbeat (Wang and Wu 2012; Vivekananthan et al. 2018).

So far, some types of piezoelectric materials have been studied (Chen et al. 2020). Organic piezoelectric polymers such as polyvinylidene fluoride (PVDF) and their copolymer polyvinylidene fluoride-trifluoroethylene P(VDF-TrFE) (Li et al. 2020; Yang et al. 2020; Lovinger 1983), are flexible and light weight but of low piezoelectric coefficient. On the other hand, inorganic piezoelectric ceramics such as lead zirconate titanate piezoelectric ceramics (PZT) (Park et al. 2017), potassium sodium niobate (KNN) and barium titanate BaTiO₃ (Lv et al. 2020; Koda and Sodano 2014) exhibit superior piezoelectric properties but high brittleness, poor toughness and some high toxicity, thus their application is limited (Shi et al. 2019). For practical application, the polymer matrix usually composites with inorganic piezoelectric ceramic to prepare the flexible nanogenerator with optimized piezoelectricity (Wu et al. 2019).

Furthermore, most synthetic polymers, *e.g.* PVDF and P(VDF-TrFE), are not biodegradable and they would cause severe environmental problems after usage. Moreover, they are not renewable and biocompatible. Therefore, seeking for renewable, biodegradable, and biocompatible natural polymer for piezoelectric nanogenerator is urgent. Cellulose is the most abundant and widespread natural polymer in the nature (Kim et al. 2019; Wang et al. 2014; Song et al. 2021). It is a hydrophilic glucan biopolymer consists of a linear chain of two anhydroglucose rings joined via a β -1,4 glycosidic linkage (Pandey et al. 2010; Klemm et al. 1998). Compared with many synthetic polymers, cellulose has many excellent features: renewability, biocompatibility, biodegradability, high strength, and low thermal expansion (Tayeb 2019; Mishra et al. 2019). They have been explored for applications in electronics and functional devices (Soba et al. 2016; Chen et al. 2020; Toroń et al. 2018; Zhai et al. 2015; Yin et al. 2020). However, cellulose cannot be dissolved in common solvent or melt because of its strong intra and inter hydrogen bonding (Zhang et al. 2007). Zhang et al found that cellulose could be dissolved in NaOH/urea aqueous solution under low temperature (Cai and Zhang 2005). Cellulose films could be obtained through this non-toxic and low-cost solvent system after regeneration (Qi et al. 2009).

Recently, as a novel high-performance piezoelectric material, monolayer or few-layer molybdenum disulfide (MoS₂) has attracted great attention (Sohn et al. 2019; Wu et al. 2021). Sahatiya et al. fabricated a nanogenerator which employ both piezoelectricity and triboelectricity based on MoS₂, cellulose and PVDF (Sahatiya et al. 2018). MoS₂ has layered structure in which a molybdenum plane is sandwiched between two sulfide planes connected by Van der Waals force, while the molybdenum and sulfide atom are covalently bonded (Acharya et al. 2018). Zhou et al. found that MoS₂ with odd-number layers could generate high piezoelectric voltage and current under stress, which increased with the number of layers decreased. MoS₂ with odd number has strong piezoelectric effect because of the asymmetry of positive and negative charge resulting from the deformation under external forces. On the contrary, MoS₂ with even number did not exhibit piezoelectricity owing to the presence of a projected inversion symmetry (Zhou et al. 2016), the positive and negative charge cancel each other out. There are several methods to obtain MoS₂ nanosheet, such as chemical vapor deposition (CVD) and mechanical delamination (Krishnamoorthy et al. 2016), but these methods are of low yield and efficiency. However, liquid exfoliation is a simple way to prepare 2D materials (Niu et al. 2016). Recently, we found that monolayer

or few-layer MoS₂ nanosheets could be obtained by mechanically stirring in triethanolamine, which is effective and low cost (Chen et al. 2017).

Here, we constructed a flexible, lead-free and biocompatible piezoelectric nanogenerator by compositing of MoS₂ nanosheets and cellulose molecules for energy harvesting. MoS₂ nanosheets were one-step exfoliated by triethanolamine, and cellulose was dissolved in NaOH/urea/H₂O solution. MoS₂/cellulose nanocomposite films were obtained by blending exfoliated MoS₂ nanosheets and cellulose, followed by regeneration, washing, and natural drying. Then, they were used to fabricate the piezoelectric nanogenerator with Al foil as the electrode, Cu wire as the connecting wire, and polyimide (PI) as the encapsulation layer. The piezoelectricity, output voltage and current of the nanogenerator under press were studied in details.

2. Materials And Methods

2.1 Materials

Cellulose sample (cotton linters pulp, α -cellulose content of more than 95%) with a weight-average molecular weight of 10×10^4 g/mol was provided by Hubei Chemical Fiber Co., Ltd. (Xiangyang, China). Molybdenum disulfide (MoS₂, 98%) was bought from Sigma-Aldrich Corporation (Saint Louis, USA). Triethanolamine (C₆H₁₅NO₃, 98%), sodium hydroxide (NaOH, AR), urea (AR) and other chemical reagents were purchased by Shanghai Aladdin Industrial Corporation, China.

2.2 Exfoliation of MoS₂ nanosheets

0.5 g MoS₂ was added to 50 ml triethanolamine and stirred for 8 h at 1000 r/min, followed by centrifugation for 30 minutes at 4500 r/min. After washing the supernatant with deionized water and filtering several times to remove triethanolamine, the obtained product was dispersed in deionized water followed by freeze-drying to prepare the MoS₂ nanosheets.

2.3 Preparation of RC/MoS₂ films

The NaOH, urea and deionized water were weighed at mass ratio of 7: 12: 81 and well mixed to make a NaOH/urea/H₂O solution. The obtained MoS₂ nanosheets were homogeneously dispersed in the NaOH/urea/H₂O solution by sonication and cooled to -13 °C. Then a desired amount of cellulose was dissolved in the above dispersion to prepare the composite solution. After removing bubbles by centrifugation, the composite hydrogels were prepared by casting the composite solution on the glass plate and then immersing in dilute sulphuric acid (5%) for 5 minutes. The regenerated cellulose (RC)/MoS₂ nanosheet composite films with thickness of 20–30 μ m were finally obtained after washing and immersing the composite hydrogels in water to remove residual reagent, followed by air-drying. These obtained films were denoted as RC, RC/MoS₂1, RC/MoS₂2, RC/MoS₂4, and RC/MoS₂8,

respectively, with incorporation of 0 wt%, 1 wt%, 2 wt%, 4 wt%, and 8 wt% MoS₂ nanosheets in the composites.

2.4 Preparation of RC/MoS₂ nanogenerators

The above obtained films were polarized under an electric field of 15 MV/m in silicone oil bath for 40 min at room temperature. Then for construction of nanogenerators, these films were sandwiched between Al foil as electrode, copper wires were connected to the Al foils as connecting wires, and polyimide (PI) as encapsulation layer to protect nanogenerators from the influence of external charge.

2.5 Characterization

The morphology and microstructure of the sample was characterized by scanning electron microscope (SEM) (JSM-IT300, JEOL, Japan) after the sample was fractured in liquid nitrogen. Fourier-transform infrared (FTIR) spectra of the samples were examined by FTIR spectrometer (Nicolet6700, USA). The X-ray diffraction (XRD) (D8 Advance, AXS, German) analysis was recorded with Cu K α source radiation. The mechanical property was carried out by universal tester (RGM-4100, Geger, China), the samples were selected from the uniform part of the films and cut into 30 mm · 5 mm, and the stretching speed was set at 2 mm/min. Thermal stability test (TGA) was measured by thermal analyzer (STA499C, Netzsch, Germany) in the nitrogen atmosphere and the temperature with the range of 0 to 1000 °C at an increase rate of 10 °C/min. Dielectric constant and loss was tested through Agilent equipment (HIOKI3532-50, HIOKI, Japan) in the frequency from 100 to 1M Hz. The piezoelectric coefficient d_{33} was obtained via quasi-static d_{33} tester (ZJ-3A, Chinese academy of sciences) after polarization. The piezoelectric performance including output voltage and current of the nanogenerator was measured by electrochemical workstation under a slight press about 0.88 kPa (CHI660E, Shanghai, China).

3. Result And Discussion

3.1 Structure of RC/MoS₂ nanocomposites

Figure 1 shows the fabrication process of RC/MoS₂ film and construction of piezoelectric nanogenerator. The film was fabricated through blending, casting, regeneration, air-drying and the process is relatively simple and environmentally friendly. Besides, the obtained device has superior flexibility so that it can be used in many fields, *e.g.* detection of human physical signals.

Figure 2 shows SEM images of the cross-sections of the RC and RC-MoS₂4 films. The layered structure of the RC film which comprised of uniform and compact fibrils was observed in Fig. 2(a, b). Figure 2(c, d) reveal the morphology of RC-MoS₂4 film, where with the incorporation of MoS₂ nanosheets, more obvious and compact layered structure was clearly observed. Moreover, there is no obvious aggregation and defect in the RC-MoS₂ composite film, and it shows good compatibility between MoS₂ nanosheets and cellulose molecules, probably owing to that the intercalation of cellulose molecules in MoS₂

nanosheets and formation of hydrogen bonding between them provide hindrance to prevent MoS₂ nanosheet from stacking.

To further clarify the hydrogen bonding between cellulose molecules and MoS₂ nanosheets, and also their crystal structure, FTIR and XRD measurements were used to characterize the RC-MoS₂ films. Figure 3 is FTIR spectra of RC-MoS₂ films with different filler content which was recorded from 4000 to 400 cm⁻¹. The broad absorption band around 3448 cm⁻¹ is corresponding to stretching vibration of hydroxyl groups of cellulose. Compared with RC film, this broad band of RC-MoS₂ film shifted to lower wavenumbers which indicated that with the addition of MoS₂, original hydrogen bonding in cellulose molecules were broken and new stronger hydrogen bondings between cellulose molecules and MoS₂ nanosheets were formed (Raghunathan et al. 2017). Besides, the peaks at 1418 cm⁻¹ and 1017 cm⁻¹ represent the bending vibration of C-H and stretching vibration of C-O-C group.

Figure S1 shows the XRD patterns of the RC, MoS₂, and RC-MoS₂ composite films. The XRD pattern of the bulk MoS₂ displays a (002) plane at $2\theta = 14.4^\circ$ which is feature peak of MoS₂. The *d*-spacing of the (002) plane of bulk MoS₂ was calculated to be 0.61 nm using the Bragg equation. On the other hand, the RC film exhibits three 2θ diffraction peaks at 12°, 20°, and 23°, owing to the (1-10), (110) and (020) crystal planes of cellulose II, respectively (French 2014, 2020). The relative higher intensity of the 2θ diffraction peaks at 12° indicates the preferred orientation of the (1-10) plane parallel to the film surface, probably because of the regeneration of cellulose in the aqueous system and the film drying process (Isobe et al. 2011; Yang et al. 2015; Yin et al. 2020). For the RC-MoS₂ composite films, the feature peaks of XRD patterns are almost corresponding to the primary feature peaks of MoS₂ and RC. The *d*-spacing of the (002) plane of MoS₂ in the composites slightly increased to 0.62 nm from 0.61 nm of the neat MoS₂. While the increase is relative low compared with 0.4 nm of the cellulose molecule thickness, it's probably owing to that some cellulose molecules were intercalated between MoS₂ nanosheets to form the "brick-mortar" structure.

3.2 Thermal stability

Thermogravimetric (TG) and differential thermogravimetric (DTG) analyses were conducted from 0 to 1000 °C to study the thermal stability of RC-MoS₂ nanocomposite films. Figure 4(a) reveals the thermal decomposition process: from room temperature to 100 °C, there is the evaporation of moisture in the films; between 300 °C and 650 °C, the mass loss occurs because of the cleavage of cellulose molecular chain and carbonization. Moreover, the residual weight of the composites were higher than that of RC, owing to the high thermal stability of MoS₂. Figure 4(b) is differential curve of TG curve and indicates the rate of mass loss. The mass loss and decomposition rate of RC-MoS₂ film decreased after addition of MoS₂ nanosheet for the reason that MoS₂ has good thermal stability and formed strong hydrogen bond with cellulose. Besides, thermal decomposition temperature of the RC-MoS₂ composite is a bit higher

compared with RC. Homogenous dispersion of MoS₂ in RC enhances the thermal stability of RC which may inspires the high-temperature application.

3.3 Mechanical property

Figure 5 shows the mechanical properties of RC-MoS₂ films with different MoS₂ content. For RC-MoS₂1, the tensile strength (Fig. 5b), Young's Modulus (Fig. 5c) and elongation at break (Fig. 5d) were evidently improved and gradually decreased as the MoS₂ content continuously increased. The tensile strength of composites depends much on the interaction between filler and matrix. It increased from 57 MPa to 94 MPa with the increase of MoS₂ content from 0 to 4 wt%, because the strong hydrogen bond formed and stress transfer occurred between cellulose molecules and MoS₂ nanosheets. However, when the content of MoS₂ continuously increased, there would be more defects, so that the tensile strength decreased. Similarly, moderate addition of MoS₂ nanosheets were beneficial for the MoS₂ improvement of Young's Modulus and elongation at break as a kind of reinforcing material, but when the content was over 2 wt%, MoS₂ nanosheets may aggregate and the films became non-uniform and stress concentration happened, leading to poor mechanical properties.

3.4 Piezoelectric property

Piezoelectric constant (d_{33}) is an important index to characterize the piezoelectric properties; it is the conversion coefficient of transform between mechanical and electric energy. As shown in Fig. 6, the d_{33} of the neat RC film was 3 pC/N, which reveals that cellulose could be used as a kind of flexible piezoelectric matrix with good advantages of renewability, biodegradability, and biocompatibility. The d_{33} of RC-MoS₂ films first increased and then decreased with the increased MoS₂ content. When the content of MoS₂ was 4%, the d_{33} reached the maximum value of 19 pC/N. When the MoS₂ content was higher than 4%, d_{33} decreased probably owing to that the aggregation and stack of MoS₂ nanosheet occurred and led to actual lower proportion of MoS₂ nanosheet.

To further study the practical application of the RC-MoS₂ piezoelectric films, the nanogenerators were constructed using these piezoelectric films through sandwiched structure. The films were first polarized and then sandwiched between Al foil, which acted as electrode. PI was used as encapsulation layer because it can prevent charge in surrounding environment from interfering the test owing to its insulation property. Figure 7 (a),(b) shows energy harvesting performance of the RC-MoS₂ nanogenerators with different filler content under a slight press about 0.88 kPa. The variation trend of output open-circuit voltage and short-circuit current was consistent with d_{33} . The maximum open-circuit voltage was 2 V and short-circuit current was 150 nA, which were 5 and 7.5 times higher than those of the neat RC film, *i.e.* 0.4 V and 20 nA, respectively. Therefore, the incorporation of MoS₂ nanosheets greatly improved the piezoelectric and output properties of the RC film owing to the outstanding piezoelectricity of monolayer or odd-layer MoS₂ nanosheets. Fig. S2 shows the "switch polarity" test. When switch the device in the

forward or reversed mode, the amplitude of output performance is reversed. It indicates that the performance of RC-MoS₂ is generated by piezoelectricity. These flexible RC-MoS₂ nanogenerators are easily fabricated, successfully convert mechanical energy to electric energy, and can be used in complex environment after encapsulation. They have potential applications in the fields of sensors, electronics, and electric skins owing to the good ability of energy harvesting. Besides, these devices have advantages of biocompatibility and biodegradability, which may inspire in-vivo applications.

4. Conclusion

In this work, cellulose was dissolved and blended with MoS₂ nanosheets in NaOH/urea aqueous solution to prepare the RC-MoS₂ piezoelectric films and nanogenerators. The structures of the RC-MoS₂ composite films were studied by SEM, FTIR and XRD, and the results indicated the formation of nanolayered structure and strong hydrogen bonding between cellulose molecules and MoS₂ nanosheets. Furthermore, the piezoelectric property of the films and their potential applications in energy harvesting were studied in details. The RC-MoS₂4 film exhibited a high d_{33} of 19 pC/N, output voltage of 2 V, and current of 150 nA under a slight press, which were 6.3, 5, and 7.5 times higher than those of the RC film, respectively. The incorporation of MoS₂ nanosheets thus greatly improved the piezoelectricity and energy harvesting of the RC film, which could inspire further research. Moreover, the incorporation of MoS₂ nanosheets also improved the mechanical properties and thermal stability of the RC film. As a whole, the flexible, renewable, biodegradable, and biocompatible RC-MoS₂ piezoelectric films with high piezoelectricity and output performance are of great significance to environment protection and have potential applications in high-performance energy harvester, wearable sensor, electric skin, *etc.*

Declarations

Compliance with ethical standards

Conflict of interest

The authors declare that they have no conflict of interest.

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Figures

Figure 1

Schematic of fabrication process for the RC/MoS₂ nanogenerator

Figure 2

SEM images of cross-sections of the RC (a, b) and RC-MoS₂₄ (c, d) films.

Figure 3

FTIR spectra of RC and RC-MoS₂ films.

Figure 4

TG (a) and DTG (b) curves of RC and RC-MoS₂ films.

Figure 5

Stress-Strain (a), Tensile strength (b), Young's Modulus (c) and elongation at break (d) of the RC and RC-MoS₂ composite films with different MoS₂ content.

Figure 6

Effects of MoS₂ contents on the piezoelectric constants (d_{33}) of RC-MoS₂ films.

Figure 7

The open-circuit voltage (a) and short-circuit current (b) Piezoelectric voltage of the RC-MoS₂ 4 based PENG with forward and reversed connection modes of the RC and RC-MoS₂ composite films.

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