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Superior MoS_2-decorated CNT composite materials for photoelectric detectors

Wang Jinxiao[a], Yang Jianfeng[a,*], Yang Jun[c,**], Qiao Guanjun[b], Wang Hang[c], Hu WangRui[c]

[a] State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an, 710049, PR China
[b] College of Materials Science and Engineering, Jiangsu University, Zhenjiang, 212013, PR China
[c] School of Metallurgical Engineering, Xi'an University of Architecture and Technology, Xi'an, 710055, PR China

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ABSTRACT

Carbon nanotubes (CNTs), outstanding flexible and photoelectric materials, have inspired tremendous innovations in the fields of stretchable and wearable electronics. Exquisite optoelectronic materials are decorated on carbon nanotube walls is an universal method under modification process for CNT. This modification promotes the light-matter interactions and efficient charge-transfer pathways. In this respect, it is still challenging to prepare excellent CNT composites and fabricate state-of-the-art carbon-based flexible electronic devices effectly. Herein, we designed a MoS2-decorated CNT photoelectric composite materials by a facile self-assembly method, which realized exact compatibility and ingenious connection of CNT and MoS2. The flexible photoelectric electronic devices were fabricated by micro-nanofabrication technologies. The photocurrent of CNT-MoS2 exhibited 4 times higher than pure CNT materials, which showed superior photoresponse and recovery ability. The photoinduced charge transfer theory proved that the MoS2 is exceedingly good optical gain materials and benefiting from the interfacial charge-transfer transition. Therefore, the MoS2 can serve as a complement in applications that require excellent photovoltaic semiconductors, which has potential for obstaining the novel proporties nanomaterial system. The enhancement of photosensing performance showing the broad prospect of the burgeoning high performance wearable sensors.

1. Introduction

Wearable sensors are of significant interest in many fields such as skin electronics [1–4], intelligent prosthesis controllers [5] and the construction of man-machine interactive systems [6–8]. For the sake of realizing these targets, the requirement for relevant sensors have an accurately conversion between external information and electrical signals. In addition, the sensing materials possess outstanding flexibility and exceptional processability in order to meet the portable, easily-integrated wearable electronics. However, the fabrication of high-resolution and perfectly sensitive sensors face the challenge of extending the photo-detection so as to detect the sophisticated signals rapidly and precisely.

CNTs have potential application prospects in flexible photoelectric sensors due to their excellent mechanical and electrical properties [9–11]. CNTs composed of strong sp^2 hybrid C–C bonds, demonstrate the mechanical and electrical properties between graphites and diamonds [12]. The bending of sp^2 bond caused the appearance of smaller pipe diameter and broader energy band, which means the properties can be tailor by changing the structure of CNTs. The previous studies revealed CNTs can express metallicity and semiconducting result from the different diameter and helicity [13]. Hence, it is feasible to make CNTs possess band gap of semiconductor properties by changing the diameter and helicity. This can allow light wave response to be adjusted in a wide range.

In order to improve the photoelectric properties, some optoelectronic semiconducting materials are decorated on carbon nanotube walls is an universal method [12]. All kinds of organic materials with high photo-sensitivity in visible light region such as dyes, conjugated polymers, conductive polymers and aromatic compounds [14–17]. Previous studies showed the composite structures are formed to the conduct network in the interconnection between CNTs and some materials [18–21]. The external stimuli such as light, heat, pressure, gas lead to the more change of electrical resistivity or capacity change by the conduct network formed between CNTs and some materials, so it enhances the sensing performance. Nanoparticles can modified the

* Corresponding author.
** Corresponding author.
E-mail addresses: yang155@mail.xjtu.edu.cn (Y. Jianfeng), yj-yangjun@xauat.edu.cn (Y. Jun).

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CNTs by Van der Waals' force, hydrogen bond and π-π stacking interaction [22–24]. The process of modification mainly include the acidification of CNTs, the addition of some surface active agent, the assembly of modifier through the surface active agent. Wong [25] successfully incorporated CNTs into nanoparticles (CdSe, TiO_2) by taking advantage of 1-Ethyl-3-(3-dimethylaminopropyl) carbodimide. Yu [26] realized the Cu_2O composite via polyhydroxy activation treatment. Dali Shao [27] synthesized ZnO-MWCNT hybrid via atomic layer deposition of a uniform ZnO thin film on the outside surface of the MWCNT. Such narrow bandgap organic semiconductors must have a large conjugated system, and require tedious preparation and complex processing. In addition, most of these compounds only exist in the state of solution, it is difficult to form a stable molecular structure.

Among these modifiers, MoS_2 [28–30], a semiconductor in the family of transition metal dichalcogenide (TMD) materials, is of particular interest in owing to excellent photochemical stability. It can be considered as a candidate material for optoelectronic composite due to excellent synergistic effect and improvement of charge transfer ability [28]. These nanostructures induce the frequency of localized surface plasmon resonance when interacted with other semiconductor. The light absorption can be transformed by means of the redistribution, localization, and enhancement of the electromagnetic field. However, there still exist obstacles to the cleverly combination of MoS_2 and CNT under the condition of maintaining their unique properties. The perfect decoration becomes the key point for exploring high-performance nanocomposite optoelectronic devices. In addition, the photochemical catalysis may play a role in the sensing performance [31–33], thus designing all kinds of the composite structrue is considered to be an effective method to enhance the sensing performance.

Here, we prepared a MoS_2-decorated CNTs (MoS_2-CNT) photoelectric composite materials and designed corresponding flexible photoelectric electronic devices. Firstly, the chitosan was coated on the CNTs surface by interacting with the carboxyl groups. The Mo^{2+} ions were coordinated with functional groups on chitosan and interacted with S^{2-} ions. And then the materials were deposited on flexible PDMS substrates, and the Au electrodes were built by the micro-nanofabrication technologies. Finally, the wires were linked to the sensors by the electric soldering irons and solder wires. The photoelectric properties of MoS_2-CNT were explored by the construction of photoelectric sensing test system. The MoS_2-CNT showed outstanding photoelectric properties by the localized surface plasmon resonance and exhibit great potential for high-performance nanocomposite optoelectronic devices.

2. Experimental

2.1. Preparation

The 0.5 g CNT was added into the mixture of 6 mL concentrated sulfuric acid and 2 mL concentrated nitric acid and then was ultrasonically dispersed. The precipitate was produced by the processing of miscible liquid settled, filtrated and rinsed. The functionalized CNT (f-CNT) was received by dried the precipitate at 60 °C holding for 24 h.

For MoS_2 modification, the 0.5 g f-CNT mixed with 1.5 g chitosan was added into dilute acetic acid solution (100 ml 0.1 mol/L) to get the chitosan-coating CNT (chitosan-CNT). The sodium sulfide and ammonium molybdate were added into the solution and stirred at 80 °C 8 h. After that, the precipitate was dried at 60 °C holding for 24 h to get the MoS_2-decorated CNT composite materials (CNT-MoS_2).

2.2. Characterization

The morphology and crystal lattice of the samples were characterized by Transmission Electron Microscope (JEOL JEM-2100Plus). The crystal structure was identified by using XRD (X-ray diffraction, Bruker D8 ADVANCE, The Netherlands, Cu-Kα_1 radiation of λ = 0.15406 nm, 40 kV, 40 mA), Raman spectra (532 nm argon laser, HR Evolution 20 mW, Britain) and X-ray photo-electron spectroscopy (Thermo Fisher ESCALAB Xi+).

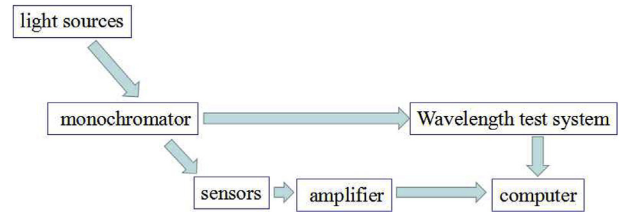

Fig. 1. The diagram of photoelectric sensing test system.

2.3. Construction of sensor and photoelectric sensing test system

The photoelectric sensing test system consists of light source, monochromator, sensors, amplifier, wavelength testing system, computer as shown in Fig. 1. The sensor was excited via the illumination of specific wave band light filtered by the monochromator. The signal change was amplified and shown in computer.

3. Results and discussion

3.1. The characterization of CNT-MoS_2

Fig. 2 is the XRD characterization of the CNT-MoS_2 composite materials. The peak of MoS_2 could be observed clearly and consistent with standard hexagonal MoS_2 card (JCPDS No.37-1492) [34,35]. According the Scherrer formula, the size of MoS_2 particles can be rough estimated (about 17 nm).

Fig. 3 displays the comparing of the TEM image of chitosan-CNT and CNT-MoS_2. It is clear observed that the diameter of chitosan-CNT is approximately 50–60 nm from Fig. 3a and the smaller MoS_2 nanoparticles are decorated on the chitosan-CNT surface according to the Fig. 3b. It is verified in HRTEM, where the lattice spacing of 1.82 Å corresponds to the MoS_2 (105) plane [36]. The size of MoS_2 nanoparticles is almost in conformity with XRD results.

The calculation theory shows that the MoS_2 have five vibration modes. The E_{2g} and A_{1g} vibration modes are obvious in the raman spectrum, which usually are used to distinguishing the MoS_2 component as seen in Fig. 4a. The characteristic peaks at about 384.8, 402.4, which are assigned to E_{2g}, A_{1g} modes [37], respectively. The EDS elemental analysis was carried out with and spectra of CNT-MoS_2 for the sake of investigating the content elements, as shown in Fig. 4b. It can be seen clearly that the C, Mo, S element is identified in the EDS the spectrum, we can calculate the MoS_2 concentration to be about 12.6 mol%.

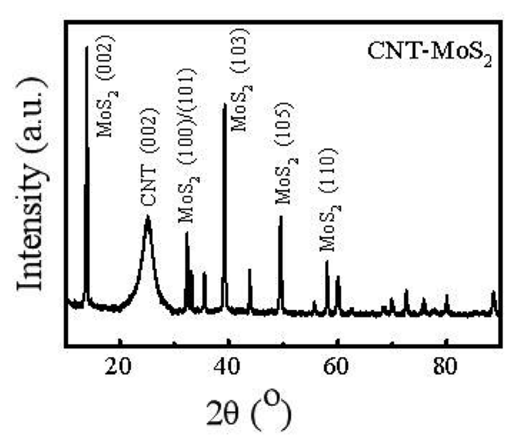

Fig. 2. XRD images of CNT-MoS_2.