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Preparation of acylamino copper Phthalocyanine modified multiwalled carbon nanotubes thin films with oxygen plasma treatment

Li-hua Yu [a], Rui Wang [a,b,*], Lei Xu [a]

[a] School of Textiles, Tianjin Polytechnic University, Tianjin 300387, China
[b] Key Laboratory of Advanced Textile Composite Materials, Ministry of Education of China, Tianjin 300387, China

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ABSTRACT

Hybrid thin films based on multi-walled carbon nanotubes (MWCNTs) and acylamino copper phthalocyanine (AM-CuPc) were prepared with oxygen plasma treatment technology. The effect of doping ratio on the photoelectric property of the films was investigated. The structure and morphology were characterized by Fourier transformed infrared spectrometer (FTIR) and field emission scanning electron microscopy (FESEM). The functional composites exhibited excellent dispersing property and the covalent bonds were formed between MWCNT and AM-CuPc. The UV–vis absorption spectra showed the absorbility was improved. In addition, the band gap was affected by the doping ratio and it was minimum of 1.63 eV when the MWCNT-doping content was 40%. It will supply a new way to synthetize solar energy materials with different band gap.

1. Introduction

As a kind of novel semiconductor material, CNTs receive considerable attention for their various applications as photovoltaic material [1], electrochemical sensor [2] and dielectric material [3]. Since the energy issue gets worse, there are more studies on photovoltaic material based on CNTs [4,5]. CNTs can be used as electrode active material in dye sensitized solar cells (DSSC) due to their good mechanical properties and excellent electrical conductivity [6]. Besides, the unique hollow structure of CNTs is conducive to adsorb dye sensitizer [7], leaving them efficient carriers. However the micro solubility and hard dispersion in any organic solvent are certain restrictions on their application [8]. Hence the CNTs need to be functionalized. Compared with the traditional mixed acid method, low temperature plasma technology is more convenient and environmental without change the original structure of CNTs. Moreover, different atmosphere can be chosen according to the functional group we need [9].

Phthalocyanine can provide electron as a kind of p-type semiconductor material. It has good film-forming performance and can be used as dye sensitizer in DSSC [10]. Phthalocyanine molecule can be adsorbed on the surface of CNTs by physical or chemical modification. Considerable efforts have been devoted to fabricating dendritic phthalocyanine-SWNTs nanoconjugates of He et al. [11]. But there is very little research on the doping ratio of CuPc and CNTs. In this work, we use plasma stripping machine to deal with the MWCNTs by low temperature plasma discharge, with oxygen as gas medium. Then the hybrid films are prepared with the modified MWCNTs and AM-CuPc under different doping ratios by spin coating method.

2. Experimental

MWCNTs (outer diameter: 3–20 nm; Purity: >95) were purchased from the A Johnson Matthey Company in the US. They were treated with low temperature oxygen plasma by the following procedure described. 5 mg MWCNTs were put into the quartz tube of the plasma stripping machine at 20 W. Then remove the gas inside the pipe and access to medium gas (O_2). In our previous studies, AM-CuPc has been synthesized with success. Phthalic anhydride (2.73 g), urea (22.5 g) and copper chloride (2.13 g) were used as the starting materials. Subsequently, composites were synthesized with different MWCNT-doping ratios of 100%, 80%, 60%, 40%, 20%. The DCC/DEC (1,3dicyclohexylcarbodiimide) was added and the blend was sonicated for 1 h. Then the composites were filtered in formic acid, washed in deionized water. Finally, the hybrid films were obtained by spin coating method on the SnO_2 glass which we have prepared before [12].

XPS (K-Sepna) was utilized to study the chemical composition

* Corresponding author at: Key Laboratory of Advanced Textile Composite Materials, Ministry of Education of China, Tianjin 300387, China.
E-mail address: wangrui@tjpu.edu.cn (R. Wang).

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of MWCNTs with low-temperature oxygen plasma treatment. FTIR (TEN-SOR37) was utilized to study the characteristic absorption peaks. SEM (HITACHI S-4800) was employed to investigate the morphology. Absorption spectra were performed with UV–vis spectroscopy (UV-7504C) using quartz cuvettes. The band gap was measured with electrochemical work station (ZENNIUM). All the tests were conducted in room temperature.

3. Results and discussion

3.1. FTIR spectra

The reaction process is shown in Fig. 1. During the oxygen plasma treatment, carboxyl group and hydroxyl group are grafted onto the MWCNTs. The number of carboxyl group depends on the treatment condition, such as treat time, power and pressure, etc. Experiments prove that the surface of MWCNTs have been grafted with the maximum carboxyl groups when the process is in 15 min, under 20 W of power. The XPS spectra (Fig. 2a) show that the elements oxygen and carbon appear on the surface of MWCNTs. In the inserted XPS C1s spectra, the peaks of sp^2 and sp^3 carbon atoms of original carbon nanotube appear on 284.58 and 285.88 eV [13]. The characteristic peak of C=O appears on 290.18 eV. These can prove the generation of carboxyl groups. Then with the help of DCC/DEC, the covalent bond is formed between MWCNTs and AM-CuPc. The FT-IR spectra confirm this conclusion. As observed in Fig. 2b, the characterized absorption peak of CuPc are observed at 719.81, 1050.55, 1150.83 cm^{-1}. The peaks at 1684.06 cm^{-1} and 3652.57 cm^{-1} in the curve suggest the presence of amido bonds [14].

3.2. SEM

Fig. 3 shows the SEM images of MWCNT/AM-CuPc hybrid films. The result indicates that oxygen plasma treatment can waken the agglomeration between the MWCNTs successfully. Van der Waals interactions might be weakened and the the dispersibility is improved. These can benefit MWCNTs as the application of nanometer materials. Fig. 3(a) is the image of pure MWCNTs and the MWCNTs are twisted with uniform diameter (7–15 nm). It can be discovered that oxygen plasma treatment doesn't break the matrix structure of MWCNTs. In Fig. 3(b), AM-CuPc disperse uniformly in the surrounding of MWCNTs. They are probably connected with chemically adsorbed and also some physically adsorbed on the surface of MWCNTs. However, with more AM-CuPc in the composites materials, the phenomenon of agglomeration has increased trend. There are no obvious clumps in Fig. 3(c). But in Fig. 3(d) the AM-CuPc don't disperse well and clumps start to appear. In Fig. 3(e), more AM-CuPc clump up together that made it uneven in surface and thickness. The reason may be that the binding force is too weak to absorb dye molecules.

3.3. UV–vis absorption spectra

The absorption spectra of Fig. 4 are obtained by coating the MWCNTs/AM-CuPc hybrid film onto a quartz substrate. The composites (curve: b–e) show stronger absorbility in UV and visible region, by contrast to the single MWCNTs (curve: a). The curve (a) is smooth and has no strong absorption peak. It indicates that with the addition of AM-CuPc, the light absorption property becomes well. A better absorption can contribute to improve the photovoltaic performance. Curve (b–e) exhibit two strong peaks, one in the visible (denoted as Q band) and one in the UV (denoted as the B band). But their peaks shift towards the blue end of the spectrum by 3–9 nm. We speculate that this phenomenon might stem from the formation of covalent bonds, as similar to the report related in the literature [14].

3.4. Measurement on electrochemical workstation

For photovoltaic material, low band gap is conducive to molecular laser excitation. Table. 1 shows the energy level structure and band gap of the MWCNTs/AM-CuPc films. Measurements were carried out in electrochemical work station (10 mV S^{-1}, −2.5 V∼2.5 V). Auxiliary electrodes and reference electrode were platinum strips and SCE (saturated calomel electrode), respectively. There's a relationship between energy level structure, E_{ox} and E_{red}:

$$E_{HOMO} = -4.47 - eE_{ox} \quad (1)$$

$$E_{LUMO} = 4.47 - eE_{red} \quad (2)$$

The band gap get through electrochemical methods can be expressed as:

$$E_g = E_{LUMO} - E_{HOMO} \quad (3)$$

Table. 1 displays that the increase of AM-CuPc in the composite narrows the band gap. When the MWCNT-doping content is 40%, the band gap is the minimum (1.63 eV). This phenomenon may be explained by the Moss–Burstein band filling effect [15]. The E_g will change when other materials are doped in the semiconductor materials. As an n-type semiconductor, the Fermi level of MWCNTs is inside the conduction band. The composite perform smaller E_g value with the increase of MWCNT-doping content.

4. Conclusions

In summary, we synthesized MWCNTs/AM-CuPc hybrid films according to different proportion by oxygen plasma treatment technology. The composites had a low aggregation tendency and good absorption both in the UV and visible region. The doping ratio had effect on the band gap of hybrid films. When the MWCNT-doping content was 40%, the band gap was minimum

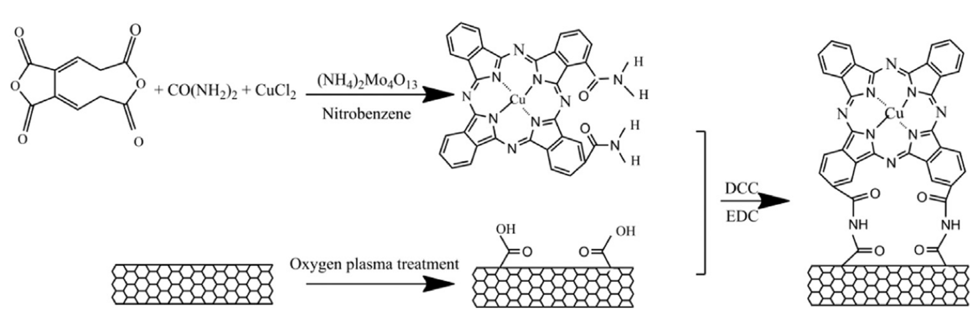

Fig. 1. Illustration of preparation process of MWCNTs/AM-CuPc composites.