Optoelectrical Characteristics of Conjugated Polymer and Functionalized Multi-walled Carbon Tube Composite

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Abstract

Poly (2-methoxy-5-octoxy-1, 4-phenylenevinylene) (MO-PPV) and functionalized multi-walled carbon tube (MO-PPV/MWNTs) composites with different MWNTs concentration were synthesized by *in situ* polymerization. The composites were characterized by AFM, PL spectra and UV-vis absorption spectra. The AFM phase image shows a good dispersion of MWNTs in the polymer matrix. PL and UV-vis spectra exhibited a blue shift of the main band.

Introduction

Conjugated polymers [1], such as poly (2-methoxy-5-octoxy-1, 4-phenylenevinylene) (MO-PPV), are a novel class of materials for application optoelectronic devices because of good processibility and flexibility, compared to the inorganic counterparts. However most polymers possess a low conductivity and so require high "turn-on" field to generate sufficient carries to produce excitons, which decay radiatively. This high field generally induces large thermal effects, consequently causing device breakdown.

Carbon nanotubes (CNTs) have excellent electronic, thermal and optical properties. However the lack of solubility in solvents results in a marked obstacle toward harnessing their application.

Composites of polymer and CNTs can effectively improve the electrical and optical characteristics of materials. Curran et al. fabricated PmPV/CNTs composites by physical "doping", and showed that a low concentration CNTs will dramatically improved its electrical conductivity, comparing to the pristine [2].Yilmaz et al. [3] synthesized a multi-walled carbon nanotubes (MWNTs) and polyaniline (PANI) composites by *in situ* chemical polymerization method, the effective site-selective interactions between the ring of PANI and the MWNTs facilitate charge-transfer processes between the two components.

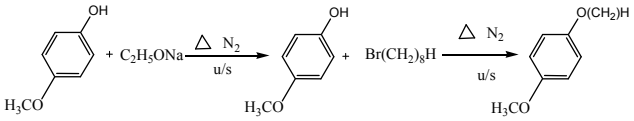
In this study, we synthesized MO-PPV/MWNTs composites with different MWNTs concentration by in situ polymerization. In this composite the two components are covalently linked, so the phase separation was prevented and the character of MO-PPV was improved by addition of MWNTs.

Experiment

4-methoxyphenol was purchased from Alfa Aesar, MWNTs produced by chemical vapor deposition (CVD) with an average diameter 10nm, a length of 5-15*u*m, a surface area of 40-300m^2/g , a purity of 97% , were purchased from Shenzhen Nanotech Port Co. Other reagents were commercially available. THF was distilled from sodium prior to use.

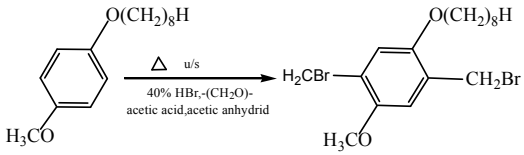
The nanotubes were first oxidation as the following procedure:0.2g raw nanotubes were suspended in 40mL mixture of concentrated nitric and sulphuric acids in a ratio of 1:3 for about 24 h at 40°C. After cooling to ambient temperature, 1000mL deionized water was added to the reaction, settled down for 48 h, then poured the upper layer water, repeated this procedure until the PH at 7. As demonstrated by other researchers [4, 5], some functional groups such as carboxyl acid were introduced into the CNTs surface after oxidation.

The synthetic procedure was an improved Gilch route, showed in scheme 1, 2, 3.



Scheme 1. Synthetic route of methoxy-4-octoxy-benzene

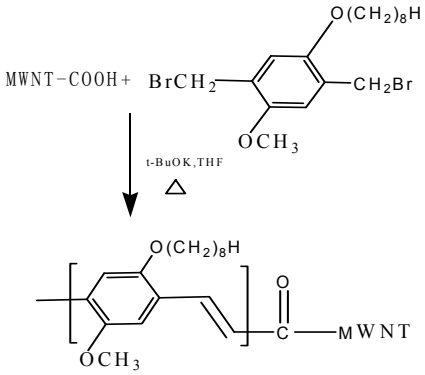
Synthesis of methoxy-4-octoxy-benzene, to a round-bottom flask were added ethanol (70mL) and sodium (5g), after sodium disappeared, to this solution was added 4-methoxyphenol(10g), and a N2 atmosphere was established. The reaction was then heated to 70°C for 7 hours. After allowing the reaction to cool to ambient temperature, the reaction was purified by recrystallization from ethanol for three times.



Scheme 2. Synthetic route of α , α -Dibromo-2-methoxy-5-octoxy-xylene

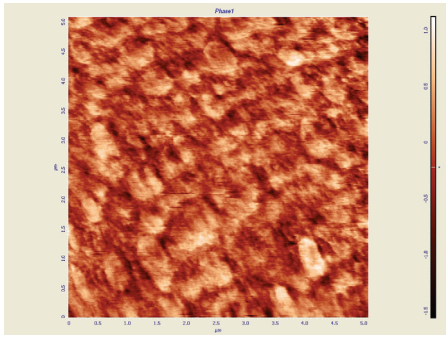
Synthesis of α, α-Dibromo-2-methoxy-5-octoxy-xylene,to a round-bottom flask were added 38% HBr (8mL), acetic anhydride(10mL) and paraformaldehyde (1.8g).A N_2 atmosphere was established followed by heating the reaction

to 70°C for 3 h. After allowing the reaction to cool to ambient temperature, purified by recrystallization from ethanol, repeated 3 times.

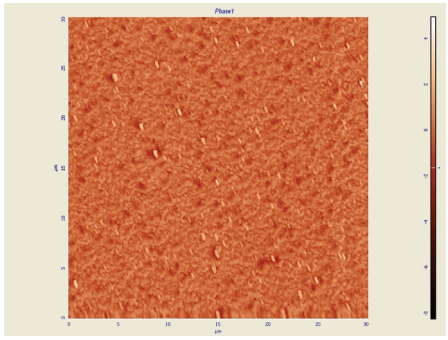


Scheme 3. *In situ* polymerization of MO-PPV/MWNTs composites

Synthesis of MWNTs/MO-PPV composites, to a round-bottom flask, well flushed with N_2, were added monomer (0.32g), oxidized MWNTs (0.5, 1 wt. %) and THF(36mL) under ultrasound. *tert*-butoxide (0.42g) was added to the reaction. After complete addition of the base, the reaction was stirred for additional 8 h. The reaction was poured into rapidly stirred methanol, and the resulting polymer was wash with solvent many times and collected by filtration .



(a)



(b)

Figure 1. AFM phase image of (a) MO-PPV/MWNTs composites (with 1 wt. % MWNTs) and (b) MO-PPV and MWNTs blends (with 1 wt.% MWNTs)

Atom force microscopy (AFM) and Spectrophotometer were used to characterize the composite. AFM image was obtained on a solverp47, PL and absorption spectra were collected by Hitachi F24500 and UNICO UV22102PCS respectively.

Results and discussion

Figure 2a shows AFM phase image of composite film. All thin film was deposited from the same solution at the same concentration (5mg/mL) and spin speed (1000rmp). The phase image showed that the MWNTs were well dispersed in the composites. This may be explained by the formation of polymerization core around the MWNTs, because the monomer was absorbed into the surface of MWNTs. As the polymerization proceeds, the increasing MO-PPV molecules break down the bundles into individual CNTs, so the MWNTs can be dispersed into the MO-PPV matrix uniformly and individually [6].

In order to make a comparison, we also blend the MWNTs with MO-PPV, and obtained thin film with the same way as the composites film. From figure 2b, the CNTs were arranged in bundles in the image.

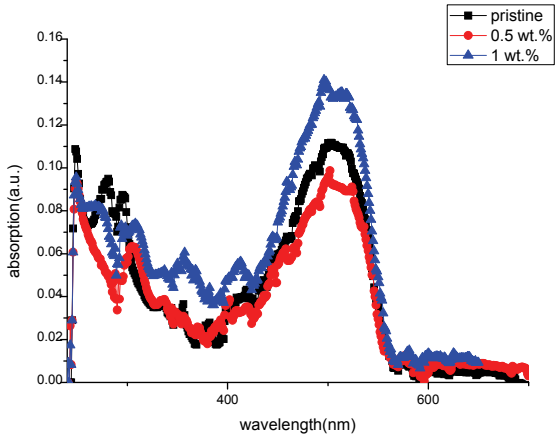


Figure 2. Absorption spectra of MOPPV and MO-PPV/MWNTs composites

Figure 3 was the normalized UV-vis absorption spectra of pure MWNTs, pure MO-PPV and MO-PPV/MWNTs composites in the tetrahydrofuran with concentrations of functionalized MWNTs from 0.5 and 1 wt. % at ambient temperature. It is showed that the broad absorption band of MO-PPV solution containing one main peak, according to the calculation of L. Yang [7], this main band contains three peaks, which should be logically assigned to the transition of the vibronic structures (0-0, 0-1, 0-2). Moreover, absorption spectra of the composites showed slight changes compared to pure MO-PPV. The main band is continuously blue-shifted from 503 nm in the polymer to 498 nm in the composite of 1 wt.% nanotubes. This blue-shift showed that the effective conjugation length of MO-PPVwas shortened with the increased content of nanotubes. According to the theoretical study of Zhao and Lu[8], the coupling of π electrons between the nanotubes and aromatic molecules could create scattering centers in the electronic transport process. Therefore, the π conjugated length was also shortened by these scattering centers.

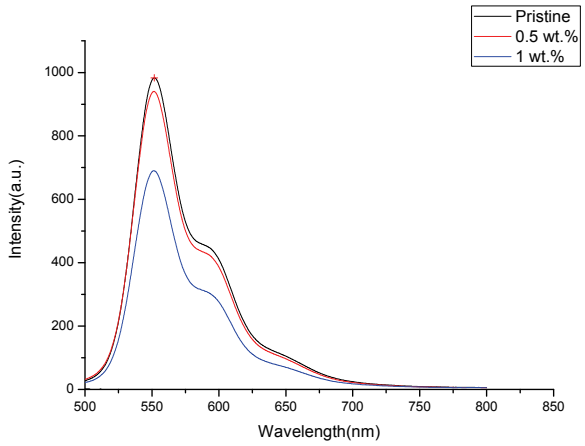


Figure 3. PL spectra of MO-PPV and MO-PPV/MWNTs composites thin film excited at 470nm

Figure 4 showed the PL spectra of the thin film of MO-PPV and MO-PPV/MWNTs composites. It is observed from the figure that luminescence is gradual decreased and a slight blue shift of luminescence peak of the composite. The emission band shifted from 552nm in the polymer to 548nm in the composite of 1 wt. % nanotubes.

The reduction in luminescence was caused by quenching. It has been proved that CNTs are efficient electron acceptor in composites, which dissociated the photo generated excitons. If the excitons were efficiently dissociated, direct excitons recombination was suppressed and thus the photoluminescence emission was quenched.

Comparing to the UV－vis absorption spectra, the slight blue-shift of the PL peak further confirmed that the nanotubes shortened the effective π conjugation length of MO-PPV chains in the composites.

Conclusions

In conclusion, we have synthesized MO-PPV/MWNTs composites by in situ polymerization. Comparing to uncovalent MO-PPV/MWNTs blends, the composites has a good carbon nanotubes dispersity. The PL and UV-vis spectra showed that the effective conjugated length of MO-PPV was shortened by the MWNTs.

References

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