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Covalent Functionalization of Carbon Nanotube by Tetrasubtituted Amino Manganese Phthalocyanine

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Abstract: The multiwall carbon nanotube (MWCNT) bonded to 2, 9, 16, 23-tetraamino manganese phthalocyanine (TAMnPc) was obtained by covalent functionalization, and its chemical structure was characterized by TEM. The photoconductivity of single-layered photoreceptors, where MWCNT bonded by TAMnPc (MWCNT-b-TAMnPc) served as the charge generation material (CGM), was also studied.

Keywords: Multiwall carbon nanotube, tetrasubstituted amino manganese phthalocyanine, synthesize, covalent functionalization, photoconductivity.

The organic chemical modification of carbon nanotube (CNT) has received much recent attention since 1998[1-2]. Recently some progress has been made on chemical functionalization of the chemically etched carbon nanotube. Additionally, both covalent and noncovalent sidewall functionalization have been explored[3-5]. But most of them are concerned with the chemically functionalization by small organic molecules like aromatic amines. Some interesting property might be explored *via* the chemically functionalization of CNT by active component like phthalocyanine (Pc). In this paper, we first synthesized and characterized the covalent functionalization of carbon nanotube by TAMnPc, aiming at improving their compatible performance with polymer matrix and assembly of CNT with Pc in one single molecule. Another objective is to obtain the TAMnPc composites with high photogeneration efficiency by chemically bonded MWCNT.

The reactions for chemical modification of MWCNT bonded by TAMnPc were carried out in the following way:

Scheme 1

$$\text{MWCNT} \xrightarrow[\text{sonicate}]{H_2SO_4/HNO_3} \text{MWCNT-COOH} \xrightarrow[\text{pyridine}]{SOCl_2} \text{MWCNT-COCl} \xrightarrow[\text{pyridine, DMF}]{\text{TAMnPc}} \text{MWCNT-b -TAMnPc}$$

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MWCNT was sonicated in a mixture of concentrated sulfuric and nitric acid (3:1 by volume) for 16 h at 40℃. The obtained carboxyl-terminated MWCNT (0.5 g) was then refluxed in excess $SOCl_2$ (50 mL) at 70℃ for 24 h. The excess $SOCl_2$ was removed by distillation and the remaining solid was dried in the vacuum. The solid (0.1 g) reacted with TAMnPc (1.5 g) in 100 mL dimethyl formamide (DMF) mixed with several drops of pyridine at 100℃ for 10 days. The excess TAMnPc was removed completely by washing with anhydrous redistilled dimethyl sulphoxide (DMSO), giving a black solid after filtration. By weighing MWCNT before and after chemical modification, the amount of TAMnPc bonded to MWCNT was approximately calculated to be 10 percent by weight.

MWCNT-b-TAMnPc shows enhanced solubility in many common solvents and good miscibility with general substrates as well. **Figure 1** shows the TEM images of MWCNT-b-TAMnPc and MWCNT films casted from suspension in 1,4-dioxane. From **Figure 1a**, we find that each MWCNT before modification is mainly a long and folded pipe. After bonding TAMnPc to MWCNT, MWCNT-b-TAMnPc exhibited a stretched or unfolded feature with TAMnPc units (black dots) mainly congregating in the tip or opening MWCNT (**Figure 1b-d**) in MWCNT-b-TAMnPc film, indicating increased solubility in solvents and good miscibility with substrates.

The xerographic properties of the MWCNT-b-TAMnPc, TAMnPc or MWCNT/ TAMnPc (9:1, by wt.) blended composite in single-layered photoreceptors device under the exposure of various wavelengths are summarized in **Figure 2**.

Figure 1 TEM images of MWCNT (a) and MWCNT-b-TAMnPc (b-d)

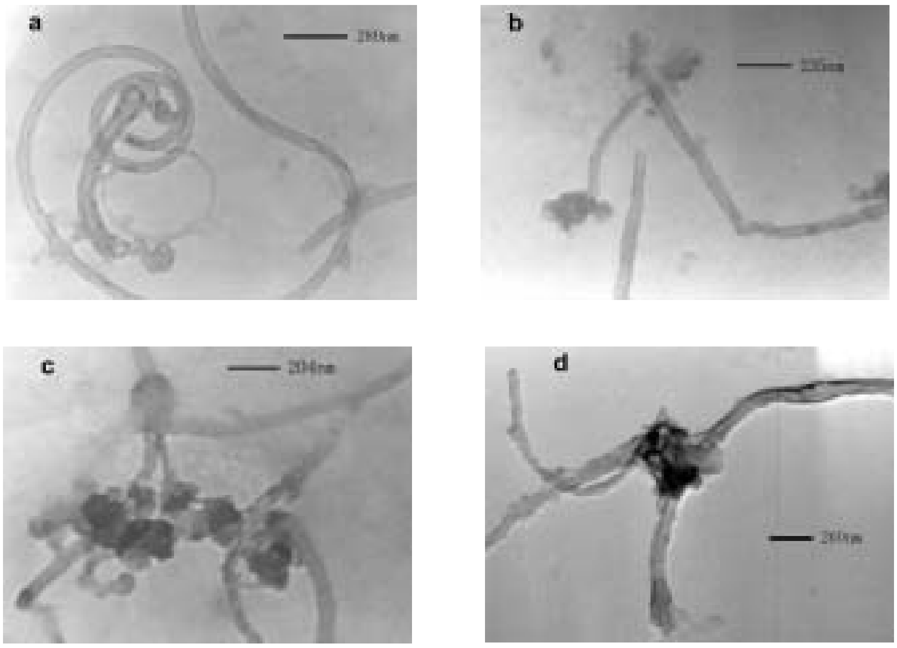
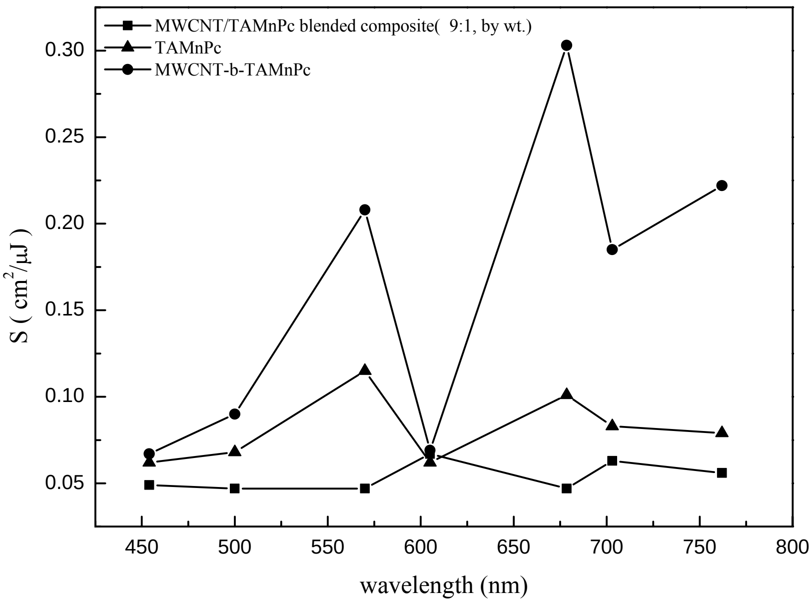


Figure 2 Photosensitivity of the photoreceptors based on MWCNT-b-TAMnPc, TAMnPc, and MWCNT/TAMnPc blended composites (9:1, by weight) at various wavelengths*.



*Where charge transport material (CTM)=*N*,*N*–diethyl-4-aminobenzaldehyde-1-phenyl-1-(α-naphthyl) hydrazone (DENPH), charge generation material (CGM)=MWCNT-b-TAMnPc, or TAMnPc, or MWCNT/TAMnPc blended composites (9:1, by weight), CGM:CTM:Pc=1:70:76, the samples were treated with 1,4-dioxane, and exposed to a light of intensity of 30 Lx.

We can see that TAMnPc shows good photoconductivity with photosensitivity (S) of 0.1 $cm^2/\mu J$ upon exposure to the wavelength of 679 nm. Under the same experimental conditions, MWCNT-b-TAMnPc has high photosensitivity of 0.3 $cm^2/\mu J$, 3 and 6 times higher, than that of TAMnPc and MWCNT/TAMnPc blended compounds with the similar component ratio. When the photoreceptors are exposed to other monochromatic wavelengths of 450, 500, 570, 605, 703, and 762 nm, the similar results are obtained with the exception of 605 nm, under which the photoreceptors show almost the same photosensitivity, of which the reason is unknown yet. It is seen clearly that when MWCNT-b-TAMnPc is used in single-layered photoreceptor device, the composite photosensitivity is dramatically improved than that of pure TAMnPc, especially over MWCNT/TAMnPc blended composite.

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