

Hyperbranched Poly(amidoamine)-modified Multi-walled Carbon Nanotubes via Grafting-from Method

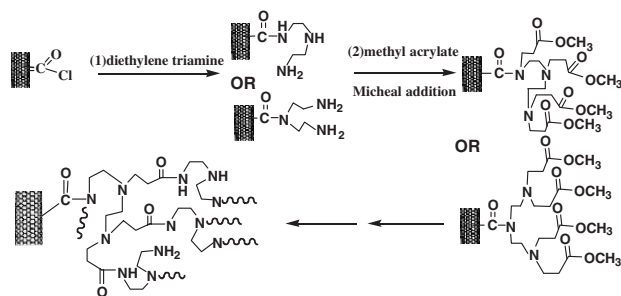
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Hyperbranched poly(amidoamine) (h-PAMAM)-grafted multi-walled carbon nanotubes (MWNTs) were successfully synthesized by grafting-from method. The modified MWNTs, which gave stable dispersion in organic solvents, were reacted with the fluorescein isothiocyanate (FITC) and then showed strong photoluminescent property.

Carbon nanotubes, single-walled (SWNTs) or multi-walled (MWNTs), have earned great reputation for their unique physical, chemical, thermal, and mechanical properties,¹ which open broad scope of further applications,² such as chemical sensors, biological probes, electrochemical devices, and so on. But carbon nanotubes' potential progresses are greatly impeded by their poor solubility in both organic and inorganic solvents because of strong van der Waals attraction among nanotubes. Thus various methods³ have been adopted to make nanotubes soluble. However, only a few articles⁴ described hyperbranched polymer or dendrimer-modified carbon nanotubes: Star^{4a} clipped rigid hyperbranched poly(*m*-phenylenevinylene)-co-[(2,5-dioctoxy-*p*-phenylene) vinylene] around SWNT, Sun^{4b} amidated or etherified dendrimer with SWNT, and Sano^{4c} used poly(amidoamine) dendrimer to prepare SWNT stars and so on. While all of the methods mentioned above are 'grafting-on' that means attaching pre-prepared polymers on nanotubes directly, here we describe the first preparation by 'grafting-from' method:⁵ initiating hyperbranched poly(amidoamine) (h-PAMAM) from the surface of carbon nanotubes. The h-PAMAM has high solubility in polar solvents which may improve the solubility of MWNTs and a large number of amino groups on its periphery which can be used for further reactions.



Scheme 1. Reaction scheme for the modified MWNTs via grafting-from method.

The growth of h-PAMAM from nanotubes is described in Scheme 1 and details of experiments were as follows: The acid chloride-terminated MWNTs⁶ were reacted with extra diethylene triamine to change into amino-terminated MWNTs. Then the mixtures of methyl acrylate and diethylene triamine (molar

ratio 1:1) in methanol solution were added into the reaction. After 12 h in 40 °C, the reaction was moved to vacuum with the temperature increasing from 40 to 120 °C stepwise in 6 h. The products were washed by methanol thrice to remove unreacted methyl acrylate, diethylene triamine, and ungrafted h-PAMAM, then dialyzed to get h-PAMAM grafted MWNTs (MWNT-f-PAMAM). As comparison, we also used grafting-on method (reacting pre-prepared h-PAMAM⁷ with acid chloride-terminated MWNT directly) to prepare h-PAMAM modified MWNTs (MWNT-o-PAMAM).

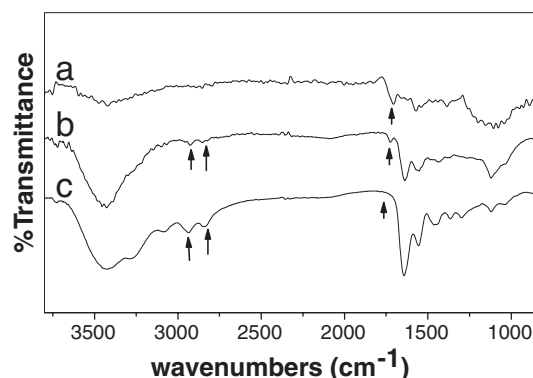


Figure 1. FTIR transmittance spectra of a) carboxy-terminated MWNT, b) MWNT-o-PAMAM and c) MWNT-f-PAMAM.

The proof of higher efficiency of grafting-from method came from FTIR spectrum (recorded on Nicolet Magna-550 spectrometer) of carboxy-terminated MWNT (a), MWNT-o-PAMAM (b) and MWNT-f-PAMAM (c), respectively (shown in Figure 1). In both curve b and curve c new peaks appeared at 1644 cm^{-1} ascribing to C=O of -CONH- in h-PAMAM and on the surface of MWNT and new peaks at 2940 cm^{-1} and 2840 cm^{-1} ascribing to C-H stretch modes, which are the evidences⁸ of successful grafting h-PAMAM on/from MWNT. The peaks at 1730 cm^{-1} ascribing to C=O of -COOH which totally disappeared in curve c while just diminished in curve b (compared with the curve a), indicated that the complete reaction of C=O in the carboxy-terminated MWNT in grafting-from method while incomplete reaction and remaining of C=O in grafting-on method.

Thermogravimetric analysis (recorded with Pyris 1 TGA of PERKIN ELMER at a heating rate of 10 °C/min from 80 to 800 °C under nitrogen atmosphere) results also supported the assumption that grafting-from method is superior to grafting-on method: weight-loss of MWNT-f-PAMAM was 76% whereas that of MWNT-o-PAMAM was only 17%. The reason why the grafting-on method is not efficient as the grafting-from method is maybe due to effect of steric hindrance of hyperbranched pol-

y(amidoamine) in the high molecular weight⁹ and the small amount of carboxy group¹⁰ on the defects of carbon nanotubes. For this reason we made diethylene triamine react with the carboxy group of MWNTs firstly in order to avoid steric hindrance effect. The further reaction between amino group and methyl acrylate to form hyperbranched polymer is easy to carry out.

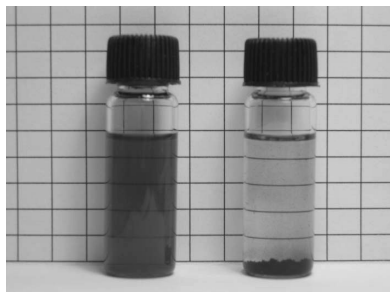


Figure 2. Ethanol solutions of MWNT-f-PAMAM (left) and carboxy-terminated MWNT (right).

MWNT-f-PAMAM stands homogeneously (see Figure 2) and would not precipitate even after 15 days in many polar solvents like methanol, ethanol, water and so on, whereas the unmodified MWNTs become turbid and deposited in the bottom just after two hours. The soluble MWNT-f-PAMAM is surely due to the high solubility of h-PAMAM in polar solvents and breaking of MWNTs bundles for the existence of h-PAMAM. Figure 3, a typical transmission electron microscope (TEM) of MWNT-f-PAMAM, also indicated a very well dispersion of nanotubes.

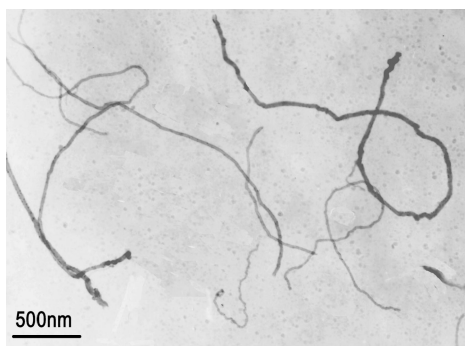


Figure 3. TEM image of MWNT-f-PAMAM.

Because of the lots of active amino groups of h-PAMAM, MWNT-f-PAMAM can be easily functionalized further, such as the preparation of fluorescent carbon nanotubes in this communication. Different from the published methods¹¹ to prepare fluorescent carbon nanotubes, our synthesis was as follows: 3 mg FITC was added into the methanol solution of MWNT-f-PAMAM, and then reacted for 2 days in room temperature. The amino group of h-PAMAM reacts with the isothiocyanate group of FITC to form fluorescent MWNT-f-PAMAM (MWNT-F), which also show good dispersion in methanol solution. MWNT-F shows strong fluorescence and its peak profile was same as that of FITC (Figure 4). It is known that when fluorescent reagents, such as porphyrin^{11a} or poly(aryleneethynylene)s,¹² were connected directly to nanotubes, the fluorescence will be quenched strongly. Such phenomenon arises from the π - π interaction between fluorescein and nanotubes which will

result in efficient energy transfer. The less fluorescence quenching in our results would be due to h-PAMAM which serve as spacer to reduce the energy transfer from FITC to nanotubes. Furthermore, through adjust the fluorescein amount bonding to hyperbranched polymer, we can adjust the fluorescent intensity of MWNT-F.

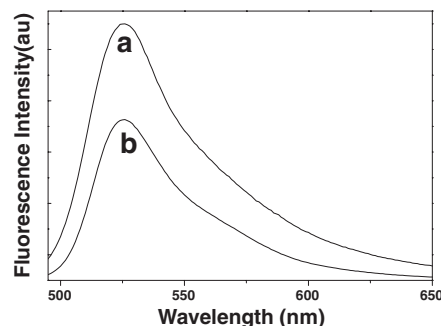


Figure 4. Fluorescent spectra of a) FITC and b) MWNT-F (washed by methanol to remove unreacted FITC). Fluorescent spectra recorded on FLS920 of Edinburgh Instruments. The samples in methanol solution were excited at 490 nm and all the lines in fluorescent spectra were normalized.

In conclusion, we have successfully synthesized hyperbranched poly (amidoamine)-grafted multi-walled carbon nanotubes via grafted-from method. The modified MWNTs well disperse in polar solvents and are available for further reactions, such as preparation fluorescent carbon nanotubes in this communication. The hyperbranched polymer grafted and fluorescent carbon nanotubes will open the doors for fundamental and practical applications.

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