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Structure dependent interaction between organic dyes and carbon nanotubes

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Abstract

Systematic studies on noncovalent functionalization of multiwalled carbon nanotubes (MWNTs) were assisted by a series of aromatic dye molecules with different structural characteristics. The effects of molecular structure on the affinities of different dyes to the MWNTs were evaluated. Two main factors have been found to play the key roles for the dye–MWNTs interactions, which are molecular geometry and charge. It was found that molecules with planar structures and high charge load are favored for the adsorption. This work not only demonstrates a simple and effective method to functionalize the sidewalls of carbon nanotubes but also give insight to the adsorption mechanism between the carbon nanotubes and aromatic molecules.

Keywords: Carbon nanotube; Sidewall functionalization; Organic dye; Noncovalent interactions

1. Introduction

Since their inception [1], carbon nanotubes (CNTs) have attracted great scientific attention, because of their unique structural, mechanical, and electronic properties, as well as potential applications in reinforced materials, nanoelectronic devices and field emitters, etc. [2]. Surface chemistry of carbon nanotubes is critical to their physical properties and applications. For instance, sidewall functionalization is one of the most important ways to make soluble nanotubes, and is also important for many applications such as nanotubes assembly [3,4] and chemical sensoring [5–7]. Many methods have been developed to perform sidewall functionalization to carbon nanotubes [8], such as chemical modification, chemical doping and physical treatment. Among them, modifying the nanotube surface using aromatic moieties through noncovalent interaction is a very attractive one [9]. Noncovalent functionalization to the CNT not only is a much simpler method compared with covalent functionalization but also has the advantage of preserving nanotube's sp^2 structure, thus the electronic properties [10–12].

Though noncovalent sidewall functionalization of CNTs using aromatics molecules has shown many exciting potentials, there has been very few systematic studies on their interaction mechanism. Herein, we studied the noncovalent attachment of a series of aromatic organic dyes onto CNTs (Scheme 1). The structures of the nine organic dyes studied in this work are shown in Scheme 1. Comparisons between these molecules make it possible to evaluate the effects of various factors on the adsorption.

These molecules can be classified into three different categories based on their morphologies. Firstly, the AO, AN, AR, RB and XO are (or could become) pseudo planar molecules. Secondly, the DIF and BTB are non-planner molecules. The third category consists of OG and PAN, which allow investigating how the azo group interacts with carbon nanotubes.

Besides molecular shape, these dyes can also be classified into three groups according to their loaded charges in protonic solvents. Firstly, AO possesses one positive charge. Secondly, AR, OG and XO have various negative charges. Thirdly, the AN, DIF, BTB and PAN are neutral molecules. It is therefore possible to investigate the role of electrostatic force in the interaction of dyes with CNTs [13].

2. Experiment

Organic dyes were dissolved in different solvents according to their solubility. For instance, AO, AR, RB, OG and XO were dissolved in water, while AO, AR, DIF, BTB, PAN

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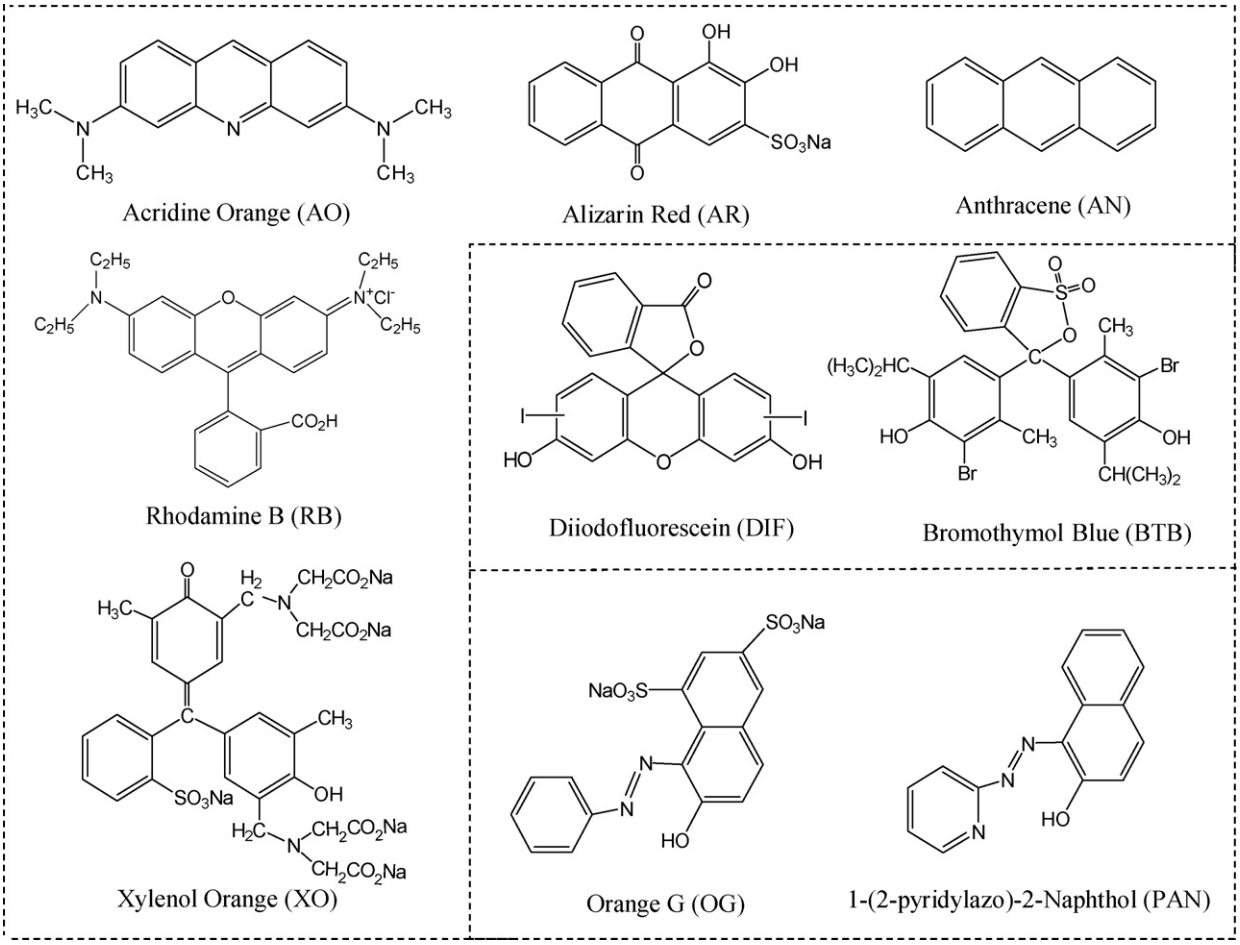

Scheme 1. Structures and names of the used dye molecules: acridine orange (AO); alizarin red (AR); anthracene (AN); rhodamine B (RB); diiodofluorescein (DIF); bromothymol blue (BTB); xylenol orange (XO); orange G (OG) and 1-(2-pyridylazo)-2-naphthol (PAN).

and OG in ethanol and AN in THF. MWNTs obtained from Shenzhen Nanotech Port Ltd. have typical diameter between 20 and 30 nm were used in this study. The CNTs were purified in 37% HCl prior of use. Purified MWNTs was added to dyes solutions and sonicated at r.t. for at least 12 h to reach a maximum adsorption. The modified carbon nanotubes were separated from the solution either by filtration or by using a 0.22 μm diameter cellalose acetate–cellulose nitrate (CA–CN) membrane. The dye–MWNTs adducts were thoroughly rinsed with solvents before being characterized. For simplification, in the following discussion, organic dyes adsorptive adducts on MWNTs are abbreviated as dye–MWNTs.

UV–vis absorption spectra were recorded using a Lambda-35 spectrophotometer (Perkin-Elmer, US). Samples for transmission electron micrographs (TEM) were cast onto standard carbon-coated copper grids and measured using a Hitachi 600 TEM operated at 100 kV.

3. Results and discussion

3.1. Characterization of the dye functionalized MWNTs

Fig. 1 shows the typical TEM images of MWNTs before and after the modification in dye solution. The TEM images show that most the unmodified nanotubes are entangled into bundles or particle like aggregations. Functionalization using dyes significantly reduced the amount of entangled and bundled MWNTs. Most of the dye-functionalized nanotubes are in debundled states under TEM. Little change was observed on the length of tubes.

The most visible effect of the adsorption of dyes molecules onto MWNTs surface is the improved solubility. It is well known that unmodified MWNTs cannot form stable suspension in common solvents even after several hours sonication. In contrast, after funtionalized by the dye molecules, most adducts can be quickly dispersed and form stable suspensions in aqueous or organic medium.

The different solubilites of dye–MWNTs adducts are summaried in Table 1. AO–MWNTs, AR–MWNTs, XO–MWNTs, OG–MWNTs can form homogeneous stable black suspension in water and AO–MWNTs, AR–MWNTs, DIF–MWNTs, OG–MWNTs are well dispersed in ethanol. The above adducts could remain stable and homogenous in solutions for several months. While, adducts of MWNTs with AN, RB, BTB and PAN are less stable in organic solvents.

The ability of various dyes to improve the solubility of MWNTs is somehow consistent with the trend of their solubility in solvents. For example, the solubility of RB, BTB and PAN are relative low in aqueous and organic solvents,