



## Review article

# New developments in non-covalent surface modification, dispersion and electrophoretic deposition of carbon nanotubes



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## ABSTRACT

This review describes new strategies for the non-covalent functionalization and dispersion of CNT using small molecules, such as commercial bile acid salts (BAS) and organic dyes. Efficient CNT dispersion was achieved due to the small size, charge and unique adsorption properties of BAS and dyes, which facilitated the bundle “unzipping” mechanism. The discovery of interesting electrochemical and film-forming properties of BAS and organic dyes allowed electrophoretic deposition (EPD) of CNT films by cathodic or anodic methods. Of particular importance is the efficiency of BAS dispersants in the sorting of CNT by diameter, chirality and length. These studies allowed for the efficient separation of SWCNT by electronic type and size, which addressed the urgent needs for many advanced applications. New dispersants allowed the fabrication of functional polymer coated CNT and development of advanced techniques for the fabrication of composites. Chelating dyes were used as co-dispersants for CNT and inorganic nanoparticles. The use of BAS and organic dyes for CNT dispersion has driven the development of advanced composites, films, aerogels for electrochemical, electronic, energy generation and storage, biomedical, sensor and other applications. Colloidal and interface chemistry of new dispersing agents is emerging as a new area of technological and scientific interest.

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## 1. Introduction

Carbon nanotubes (CNT) exhibit remarkable properties, such as high electrical conductivity, excellent mechanical properties and high thermal conductivity, which have been utilized in various applications [1,2]. The dispersion of single walled CNT (SWCNT) or multiwalled CNT (MWCNT) is a vital aspect for many advanced applications, including composites for energy storage, electronic and optoelectronic devices, sensors, transistors, integrated circuits, near-infrared detectors and other products. However, CNT exhibit a highly hydrophobic surface which promotes CNT aggregating into bundles. As-synthesized CNT usually vary in their diameter and chiral indices, which indicate how the graphene sheets are rolled up into tubular form. The CNT heterogeneity results in variation of electronic, mechanical and other properties, which limits CNT applications [3]. The as-synthesized SWCNT usually contain metallic and semiconducting SWCNT. It is known that the bandgap of semiconducting SWCNT scales inversely with SWCNT diameter [3]. Therefore, efficient dispersants are necessary for CNT sorting [3] in advanced separation techniques. However, in many cases SWCNT showed poor separation or limited stability in aqueous density gradients, created in the centrifugation separations [3]. Moreover, it is important to distinguish between true dispersion of individual CNT and dispersion of bundles [4].

The covalent modification of CNT has been reported to damage CNT and results in degradation of functional properties [5]. The noncovalent modification offers advantages for applications, based on electronic and mechanical properties of CNT. Different strategies have been developed for the non-covalent modification, based on the use of polymers and head-tail surfactants. However, it is difficult to avoid polymer wrapping of CNT bundles and separate individual CNT. Moreover, the polymer wrapping results in the formation of insulating layers on the CNT surface. In the non-covalent functionalization of CNT in solutions of head-tail surfactants, the hydrophobic tail groups of the head-tail surfactants interact with hydrophobic sidewalls of CNT, whereas the hydrophilic head groups encounter the aqueous environment [6]. The analysis of the literature indicates that relatively high concentrations of head-tail surfactants are necessary for efficient CNT dispersion [7–10]. The formation of the micelles at high surfactant concentrations promoted depletion-induced aggregation of CNT. The selection of efficient charged dispersants is critical for the development of advanced CNT film deposition techniques, such as electrophoretic deposition (EPD) [11].

Despite the impressive progress achieved in CNT dispersion and colloidal processing, good dispersion of CNT in suspensions and composites continues to be a real challenge. This review is focused on recent innovations in CNT dispersion technology. It covers the application of commercial salts of bile acids (BAS) and organic dyes for dispersion of CNT. BAS and organic dyes are of particular interest for CNT dispersion, because such small molecules can facilitate CNT dispersion via the “unzipping” mechanism [12,13]. This mechanism involves the formation of gaps or spaces at the CNT bundle ends in the ultrasonicated suspension [12]. The small molecule adsorption and diffusion then propagate the open space along the bundle length, facilitating the separation of individual CNT [12]. BAS and organic dyes showed excellent dispersion of CNT, which have been used for many applications, such as energy storage, optoelectronic and photovoltaic devices, sensors, catalysis, conductive films, functional CNT reinforced polymer composites, various biomedical applications, aerogels, flexible electronic devices, photodetectors and other applications. The use of BAS facilitated efficient sorting and separation of CNT. The analysis of dispersion efficiency of various BAS and organic dyes provides an insight into the influence of their chemical structure on CNT dispersion. Of particular interest

are film-forming and electrochemical properties of BAS and organic dyes, which allowed EPD of CNT and composite films.

## 2. Dispersion of CNT using BAS

This section describes CNT dispersion and EPD using BAS dispersants (Table 1). It is known that BAS and various BAS derivatives [14] are powerful anionic biosurfactants, which solubilize proteins, fatty acids, lipids, vitamins, monoglycerides and cholesterol. The solubility of cholesterol increased by six orders of magnitude in the presence of bile salts [15]. Due to high solubility in water, BAS have generated significant interest for CNT dispersion in aqueous suspensions. The possibility to achieve good CNT dispersion in relatively concentrated CNT suspensions offers many benefits for practical applications. Many fundamental investigations were focused on the SWCNT dispersion. A relatively recent development was the use of BAS for the dispersion of MWCNT. The application of BAS for CNT dispersion showed that BAS outperform various commercial surfactants [4]. BAS exhibit interesting gel-forming properties [16], which have attracted significant interest for applications in biosensors, chiral catalysts, non-linear optics and thin film devices. The electrochemical gel formation mechanisms, described in this section, pave the way for the EPD of advanced films, containing CNT and other functional materials.

### 2.1. Chemical structures of BAS

Fig. 1 shows chemical structures of different BAS, such as sodium salts of cholic acid (CAS) and deoxycholic acid (DCAS), containing  $\text{COO}^-$  groups and sodium salts of taurocholic acid (TCAS) and taurodeoxycholic acid (TDCAS), containing  $\text{SO}_3^-$  groups.

BAS have a rigid amphiphilic structure, which is fundamentally different from the structure of typical head-tail surfactants, composed of long hydrophobic tails and polar head groups. The steroid nucleus of BAS (Fig. 1) has three six-member and a five-member hydrocarbon rings [15]. As a general feature, BAS have convex hydrophobic and concave hydrophilic sides, which include methyl and OH groups, respectively. The structures of BAS also have a short hydrocarbon tail with anionic  $\text{COO}^-$  or  $\text{SO}_3^-$  groups. It will be shown below that the pH-dependent charge of BAS, containing  $\text{COO}^-$  is beneficial for gel formation and EPD of CNT films. The  $\text{SO}_3^-$  groups of BAS facilitated CNT dispersion at different pH and fabrication of advanced composites. The rigid amphiphilic structure of BAS allows the formation of stable micelles around SWCNT, which is beneficial for efficient dispersion [4]. The chiral properties of BAS are promising for chiral separation of SWCNT [4].

### 2.2. Adsorption of BAS on CNT

The adsorption of BAS on CNT is critical for dispersion. It is largely driven by the hydrophobic interactions of hydrophobic convex faces of steroid BAS backbones with CNT. BAS showed strong adsorption on SWCNT and MWCNT [17]. It was suggested [13] that steroidal surfactants can wrap around the SWCNT like a ring with the hydrophobic faces directed inward and the hydrophilic faces pointing outward. In this case, the enhanced BAS-SWCNT interactions and enhanced BAS coverage can be expected. In contrast, conventional surfactants with a flexible head-tail linear structure organize themselves perpendicularly to the SWCNT surface, providing lower covering level [13]. TEM observation of CAS adsorption on MWCNT showed that the hydrophobic interactions of MWCNT and hydrophobic CAS surface resulted in the formation of an asymmetric complex [18]. CAS showed lower self-aggregation tendency, compared to head-tail surfactants, such as sodium dodecyl sulfate (SDS) and allowed tighter coverage of the SWCNT

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