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Invited Review

# Carbon nanotube-based fluorescence sensors

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ABSTRACT

The one-dimensional π-conjugated structure endows carbon nanotube (CNT) with large specific surface area and excellent photophysical properties, thus providing a unique platform for the development of chemo- and biosensors based on optical signal output. Although CNT acts as an optical signal transducer, it does not own any intrinsic ability for the selective binding and recognition of analytes. Thus, hybridization of CNTs with functional components that specifically recognize various chemical and biomolecular analytes is often necessary in the preparation of CNT-based sensors. In this review, we summarize preparation and photophysical properties of CNT-based composites, and then highlight on fluorescence sensors based on CNT-composites. These composite sensors integrate the signal transduction property of CNT and the recognition properties of the hybridized functional components. The functional components selectively bind with the target analytes, whereas, CNTs transform the binding events into output signals detectable using spectrofluorometer. Particularly, we highlight on recent progress in the chemical and bimolecular sensors based on near-infrared fluorescence of semiconducting single-walled CNT (SWCNT) and the excellent fluorescence quenching ability of CNTs over conventional organic quenchers.



**Contents**



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## 1. Introduction

Carbon nanotubes (CNTs) are a kind of allotrope of carbon materials featured with a seamless tubular structure formed by curling-up graphene sheets, which are classified into single-walled CNTs (SWCNTs) and multi-walled CNTs (MWCNTs) according to their layers of graphene sheets [1–3]. This unique one-dimensional structure endows CNTs with high mechanical strength, large specific surface area, excellent electrical and thermal conductivity, good electrochemical stability, and rich electronic and photophysical properties [4–7]. Thus, CNTs have been explored for the applications as active components in composite materials with polymers or metals, antibiofouling and anticorrosion coatings, transparent conducting films, or in the microelectronic devices including field effect transistor (FET), thin-film transistors (TFTs) and nonvolatile memories, energy storage devices including lithium ion batteries, supercapacitors and fuel cells, water purification, and biotechnology [4–7]. Especially, their unique electrochemical, electronic and optical properties provide a unique platform for the development of chemo- and biosensors based on electrochemical [8–10], electrical [11,12] or optical signal outputs [13–16]. The activity of CNT-based sensors has been spurred since a publication by Santhanam and co-workers in 1996, in which they presented the first example of the electrocatalytic properties of CNT-modified electrode toward the oxidation of dopamine featured with an improved electron transfer rate [17]. The advancements in CNT synthesis, purification, and chemical modification enable the development of various sensing strategies for the detection of chemical and biological analytes one after another [8–16]. For instances, based on the SWCNT-based FET layout demonstrated in 1998 [18], Dai et al. firstly built SWCNT FET-based chemical sensor for the detection of $NO_2$ or $NH_3$, exhibiting a fast response and a substantially higher sensitivity than those of existing solid-state sensors at room temperature [19]. Soon later, it was reported that optical sensing can be achieved by using water-soluble SWCNT through surface modification, in which optical absorption of carboxylate functionalized SWCNTs reversibly responds to the pH change [20]. Within the past two decades, chemo- and biosensors based on CNTs and their composites have becoming a rapidly growing area due to their simplicity, sensitivity, and selectivity toward diverse analytes including DNA, proteins, small bioanalytes, and metal ions [8–16].

Up to date, most of the CNT-based sensors focus on electrochemical signal outputs over fluorescence measurements, possibly due to that the electrocatalytic properties of CNTs [17] were explored more early and extensively than their photophysical properties [21,22]. Electrochemical detection offers often-cited advantages of CNTs including wide potential window, relatively inert electrochemistry, electrocatalytic activity toward a variety of redox reactions, and sometimes amenability to operation in turbid samples [8–10]. However, the fluorescent strategy has inherent merits including the possibility for detecting a broader range of analytes including those without redox activity, the potential for constructing nanosensors operated within confined environments such as living cells, realizing in vivo imaging [15,16]. Thus, the development of fluorescent sensors based on CNTs has been becoming an attractive topic. CNT-based fluorescent sensors typically rely on either the near-infrared (NIR) photoluminescence (PL) of semiconducting SWCNTs [16] or the strikingly quenching ability of CNTs over conventional organic quenchers [13]. Although CNTs can act as a signal transduction substrate, they have no intrinsic recognition ability for selective binding and sensing. Thus, CNTs are usually needed to hybrid with a component having specific recognition unit to prepare composite probe to address this issue. Several reviews have covered preliminary results of this research area [13–16], but the tremendous activity in this field allows us to further provide a comprehensive overview to elucidate the basics, challenges, and opportunities of these novel florescent, composite sensing materials.

## 2. Synthesis of soluble CNT composites

One of the major challenges for the design of optical sensors with CNT composites is to obtain individual CNTs that can be dispersed well in suitable solvents, and further to integrate with functional recognition component to prepare soluble CNT composite probes. The synthesis and structure characterization of CNTs and their composite materials with satisfied dispersibility have been well summarized in some authoritative review articles [23–32], and will not be thoroughly discussed here. In this section, we will provide a brief survey of purification and modifications of CNTs with functional components in aqueous media, because these approaches are most relevant to the construction of CNT-based composite fluorescent probes summarized here. Arc discharge, laser ablation, and chemical vapor deposition (CVD) are the most popular methods to produce CNTs. Among them, CVD method is preferred because it can be easily scaled up, producing SWCNTs with relatively high quality. Especially, SWCNTs produced by decomposition of CO on bimetallic Co–Mo catalysts (CoMoCAT) [33,34] and high-pressure decomposition of iron pentacarbonyl in a heated flow of carbon monoxide (HiPco) [35] are most widely used to prepare fluorescent probes because they contain a large population of small diameter species with more impressive photophysical properties [36–39].