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Review: Recent developments of carbon nanotubes hybrid assemblies for sensing

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Abstract: In this review, we discuss state-of-the-art sensing methods for the detection of chemical and biological molecules, using a well-known and much studied material, carbon nanotubes, as the hybrid materials for fabrication assemblies. CNTs possesses a wide range of unique characteristics, including intriguing physical properties, higher aspect ratios, larger surface area, better chemical and thermal stability, and electronic and optical properties. The objective of this review is to present an overview of the synthetic strategies and their applications in both amperometric sensors and SPME fiber coatings. These methods are fast, sensitive, cheap and suitable for in-situ monitoring. We comprehensively review the mechanisms, the principles and the performances of chemical sensors and biosensors available in the literature.

Keywords: Carbon Nanotubes, Sensing, Amperometric Sensor, Solid-Phase Microextraction

1. Introduction

Carbon-based hybrids have been widely used for amperometric sensing and solid-phase microextracion (SPME). Since 1987 in history, carbon-based materials have received a lot of attention, for their unique features in a wide range of application [1].Carbon-nanotubes (CNTs) are one of the extensively studied carbon-based nanomaterials and have contributed to the development of studies in the fields of physics, chemistry and materials science.

CNTs were first found by Iijima in 1991. The structure of CNT could be described as cylindrical graphitic sheet rolled up into a seamless cylinder with diameter of the order of 1 nm. Because of their unique characteristics, CNTs exhibit excellent mechanical and electrical properties, along with their high thermal stability. CNTs have two morphologies: single-wall carbon nanotubes (SWCNTs) or with additional graphite tubes of MWCNTs. The length and diameter of MWCNTs are different from those of SWCNTs, and their properties of optical activity, mechanical strength and electrical conductivity also varies from SWCNTs.

CNTs have been increasingly fabricated as hybrids for transducer materials, especially as nanoscale electrodes for amperometric sensor fabrication [2, 3]. CNTs have incredibly enhanced the performance of electrochemical sensors regarding to the electrochemical reactivity, electron-transfer efficiency, lowering anodic over potential, sensitivity and detection time window. For example, MWCNTs and gold nanoparticles hybrid film coated on a glassy-carbon electrode has been shown to detect bisphenol-A in the several hundreds of nanomolar range [4]. SWCNTs covalently conjugated with β-cyclodextrin were found to improve the performance of amperometric sensor in nanomolar range[5].

CNTs have also been successfully applied to solid-phase microextraction (SPME), a solvent-free technique for integrated sampling, extraction and sample introduction. MWCNTs have been characterized as excellent sorbent for removing dioxins for environmental protection. The characteristic structures of CNTs allow them to interact with organic molecules via non-covalent interactions, such as hydrogen bonding, π-π stacking, electrostatic forces, van der Waals forces and hydrophobic interactions[6]. MWCNT-coated fibers for SPME were first reported to extract polybrominateddiphenyl ethers from food samples before gas chromatography (GC) with electron capture detection. Novel MWCNT-bonded silica fibers for SPME were also reported recently.

The objective of this review is to present an overview of the synthetic strategies and their applications in both amperometric sensors and SPME fiber coatings. By presenting different types of hybrid assembly, we aim to compare various aspects from different studies. Furthermore, we aim to bring discussions on the future directions where CNTs assembled materials will improved for better capability and versatility.

2. Electrochemical Sensing

The hybrid assemblies of polymer and CNTs have been successfully applied in electrochemical sensing. Wang et al. [7] reported an extremely low detection limit of 5.0 nM dopamine by electrodeposition of poly(3-methylthiophene) followed by drop coating of SWCNTs onto glassy carbon electrode (GCE). Compared with traditional polymer/GCE, and Naflon/SWCNT/GCE, the Naflon/SWCNT/polymer/GCE exhibits combined advantaged of poly(3-methylthiophene, CNTs and Naflon, with dramatic electrocatalytic effect on the oxidation of dopamine (Figure 1).

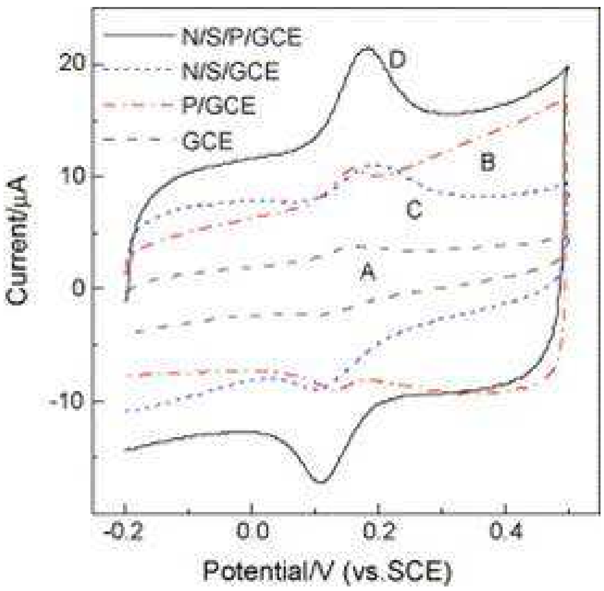

Figure 1. *CVs of 10.0 μM DA at the bare GCE (A), P/GCE (B), N/S/GCE (C), and N/S/P/GCE (D) in 0.1 M pH 7.0 PBS with a scan rate of 100 mV/s [7].*

Liu et al. [8] reported the method of layer-by-layer (LBL) assembling of conducting polymer, polyaniline (PANI), in the presence of poly(aminobenzenesulfonic acid)-modified single-walled carbon nanotubes (PABS−SWCNTs). The doping of PABS−SWCNTs to PANI inside the multilayer film effectively shifts its electroactivity to a neutral pH environment, which might be further applied for biological applications. The catalytic response of PANI/PABS−SWCNTs multilayer films are very stable and show a high electrocatalytic ability toward the oxidation of reduced β-nicotinamide adenine dinucleotide (NADH) at a much lower potential (about +50 mV vs Ag/AgCl), which makes it an ideal substrate for NADH detection and offers great promise for developing dehydrogenase-based biosensors depending on NADH as a cofactor. Keeping the potential at +0.2V, 0.5 mM NADH was flow-injected sequentially. It could be seen clearly (Figure2) that both the catalytic current and the response time are all very stable and reproducible, showing the suitability of PANI/PABS−SWCNTs multilayer films for repeated detection of NADH.

Generally, the methods of preparation for CNTs embedded fabrication include electrodeposition, electropolymerization, layer-by-layer assembly, drop coating, and potential dynamic electropolymerization. Among all of these, electrodeposition of such CNTs based hybrid assembly could be very important from the aspect of practical applications, due to their easy functionality into a thin layer on the electrode surface. However, chemistry methods own the advantages of scaling up capacity and real mass-production. A range of methods now have incorporated these two categories into electrochemical procedures. Such assembled electrode surfaces have significant advantages of high stability and excellent adherence with coated CNTs. These methods include post functionalization of electrodeposited polymers, secondary doping by surface modified nanostructures and electropolymerization on immobilized inorganics[9].

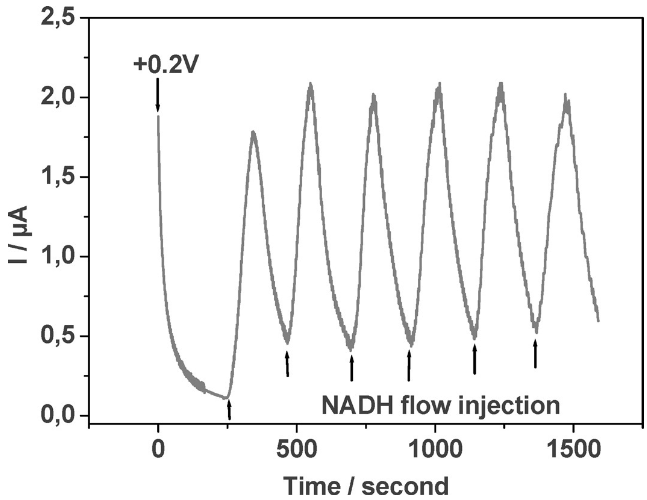

Figure 2. *The LBL assembled substrate can be used repeatedly for consecutive detection cycles of 0.5 mM NADH (1 mL/time) while the PANI/PABS−SWNTs multilayer film (12 bilayers) is kept in its oxidized state (+0.2 V) [8]. {Reprinted from [8]with permission from Langmiur}.*

3. Solid-Phase Microextraction

The quantity of analyte extracted using solid-phase microextraction (SPME) is based on the analyte distribution between the liquid or gaseous sample and the sorbent phase on a metallic or fused silica substrate. The type of coating for SPME fiber plays a very critical role in the procedures of extraction and desorption. Besides, the sensitivity/selectivity is also proportional towards the distribution constant between the analytes and the stationary phase.

Different from traditional materials for SPME coatings, carbon nanotubes offer a significant greater surface area-to-volume ratio that provides much profound extraction capacity and efficiency. Beyond that, the hydrogen bonding, π-π stacking, electrostatic forces, van der Waals forces and hydrophobic interactions could also make the carbon nanotubes good candidates for the component of adsorbents.

Recent research applying CNTs as SPME coatings involve several methods for CNT hybrid assembly. Several important techniques among them are sol-gel, surface chemically bonding and electrochemical deposition, as we discussed previously.

The sol–gel process is a very promising method for synthesizing inorganic polymer and organic- inorganic hybrid material, which was first discovered in the mid-1800s with Ebelman and Graham. For sol-gel technique, due to its introduction of strong chemically bonds between stationary phase and fiber surface, it has shown to be able to overcome the drawbacks of conventional SPME fibers, accordingly; the low operation temperature, instability against organic solvents and the shortage of fiber's lifetime. Furthermore, sol-gel technique could be performed under extraordinary mild conditions but produce much better accuracy and stability. In the history of sol-gel technique, different hybrids could be assembled on the SPME fiber to enhance the sensitivity and selectivity.

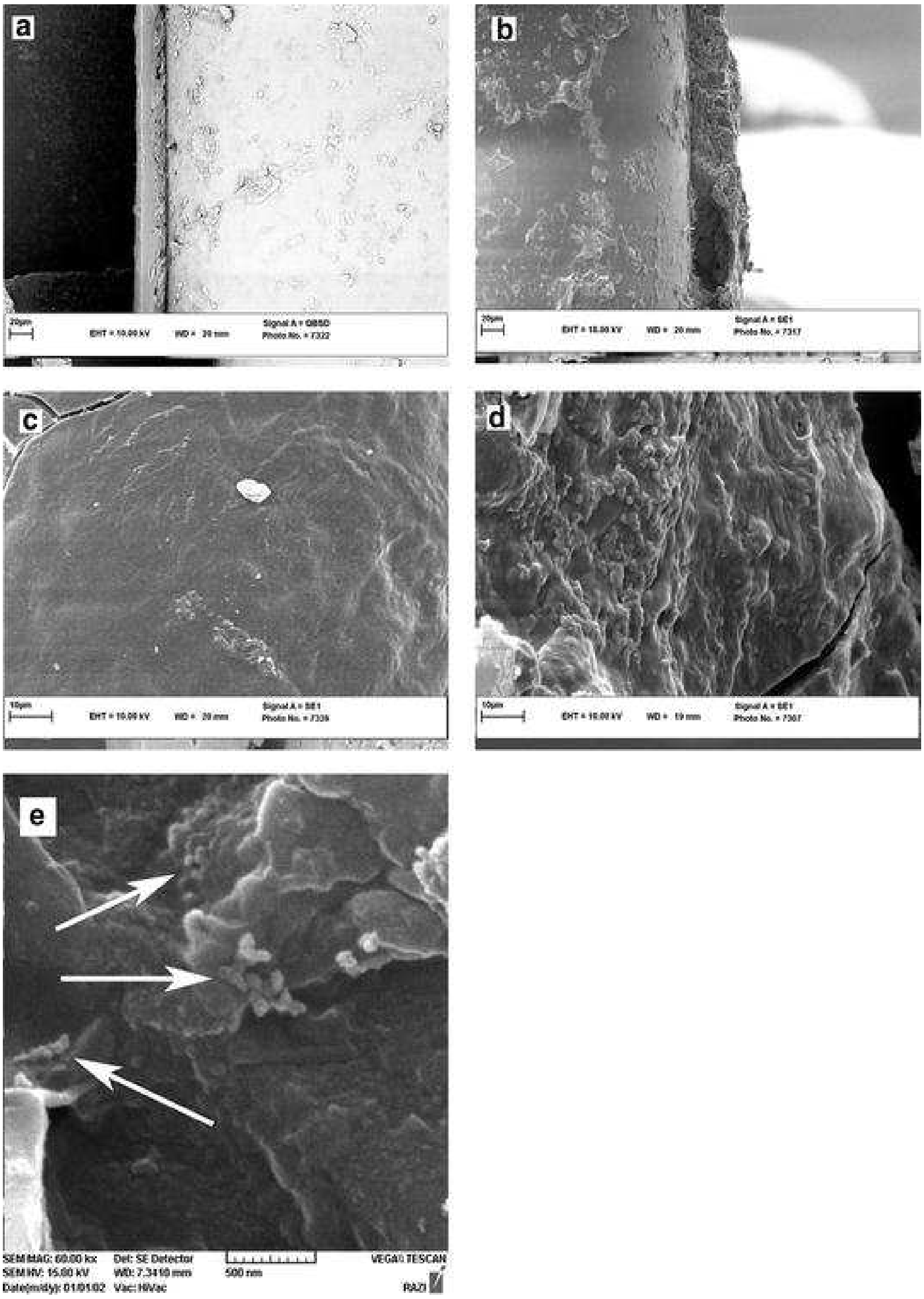

Figure 3. *a SEM image of cross section of PEG fiber (×1,000), b SEM image of cross section of PEG/CNTs fiber (1,000×), c surface image of PEG fiber (×5,000) and d surface image of PEG/CNTs fiber (5,000×) [10]. {Reprinted from [10]with permission from Springer}.*

Figure 3 denotes the sol-gel technology [10] for the preparation of solid-phase microextraction fibers for extracting methyl tert-butyl ether (MTBE) from environmental water samples. The combination of OH-functionalized MWCNTs and PEG as the main sol ingredients provided new high performance for SPME fiber. PEG led to provide a polar and porous structure (Figure 3) and MWCNTs enhanced the surface area and therefore adsorption properties of the coating to absorb non-polar analytes. The linear range for MTBE with PEG and PEG/CNT fibers were found to be 10-3,000 and 1-1,000 ng/mL and the detection limits were 1.0 and 0.3 ng/mL, respectively.

Zhang et al [11] reported the functionalization of single-wall carbon nanotubes with hydroxyl-terminated silicon oil, by the reactions of carbonyl chloride groups on the surface of SWCNTs and –OH groups of silicon oil (TSO-OH) (Figure 4). A better thermal stability (> 340 °C) and longer duration (> 200 times) were reported due to the incorporation of SWCNTs, which introduced the π-π stacking with polybrominateddiphenyl ethers and increased the surface-area-to-volume ratio when in contact with analytes. The porous structure (Figure 5) of the three dimensional silica network and the strong chemical bonding improved the extraction efficiency of SPME greatly. The detection limit of this method was reported to be 0.08-0.8 ng/L, with a precision rate of approximately 2.3-7.5% at the 50 ng/L level.

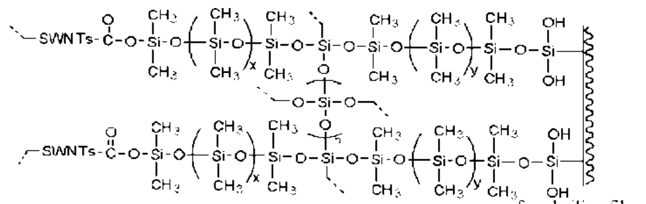

Figure 4. *The structure of the sol−gel SWCNTs-TSO-OH coating [11]. {Reprinted from [11] with permission from ACS Publications}.*

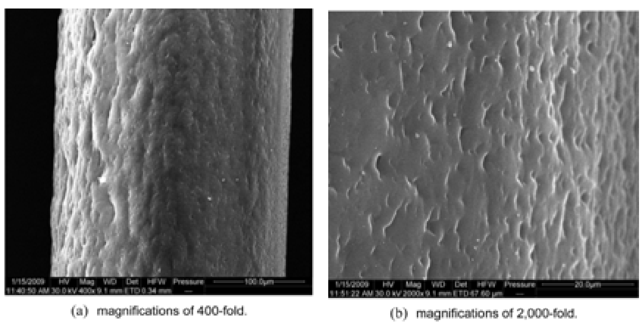

Figure 5. *Scanning electron micrographs of SWCNTs-TSO-OH coated fiber at different magnifications: (a) 400-fold and (b) 2 000-fold [11]. {Reprinted from [11] with permission from ACS Publications}.*

It was reported [12] that a modified version of electrophoretic deposition method in use for extraction of phenols from aqueous samples. In this method, the SPME fibers were replaced by a platinum plate coated with SWCNTs by the electrophoretic deposition. As shown in the illustrative of Figure 6, when a positive potential is applied to the plate, it resulted in the electrosoprtion of trace ions.

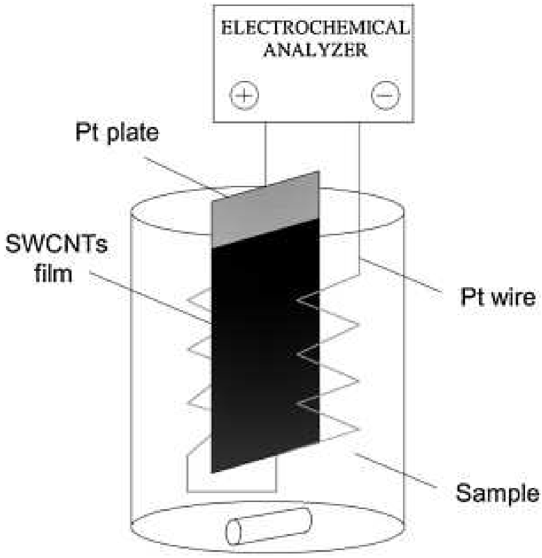

Figure 6. *Scheme of the extraction process (EE-SPME) by using a platinum plate coated with single-walled carbon nanotubes[12].*

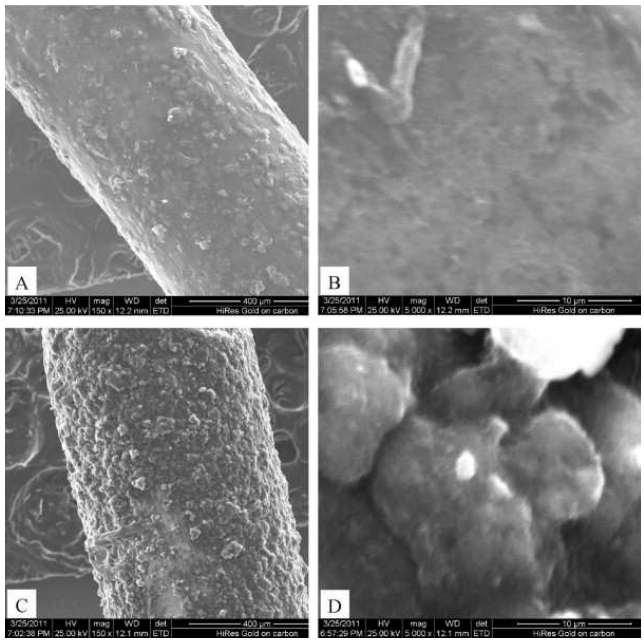

Figure 7. *SEM photographs of the MIPPy/MWCNTs/Pt (A and B) and NIPPy/MWCNTs/Pt fibers (C and D). (A and C) 150×; (B and D) 5000×[13].*

Liu et al [13]reported an electrochemical method of coating molecularly imprinted polyprrole/multi-wall carbon nanotubes composites on solid-phase microextraction fibers, in selective extraction of fluoroquinolones in aqueous samples. A direct current (DC) potential was applied to the imprinted polypyrole/MWCNTs/Pt fiber electrodes during the extraction and fluoroquinolone antibiotics ions' motion would be electrophoretically transferred to the coating surfaces. The MWCNTs coatings enhance the shape-complimentary cavities by hydrogel-bonding and ion-exchange interactions. Under optimized applied potential, extraction duration, aqueous pH, ionic strength and desorption solvent, the electrochemically enhanced SPME indicated very excellent selectivity and high extraction efficient to fluoroquinolone antibiotics. Figure 7 dipicts the porous morphological structure of the polypyrole/MWCNTs/Pt fiber electrodes.

Conventional fused-silica fibers have the advantages over metal fibers in solid phase microextraction because the surface modification of metal substrates is difficult for metal-based fibers. Instead, Liu et al. [14] demonstrated a novel protocol to solve this problem by the method of magnetron sputtering a solid Si interlayer on stainless steel fiber (Figure 8). With the aid of the Si interlayer, whose surface were easily modified with multiple active groups, the multi-wall carbon nanotubes materials were shown to successfully coat stably. The prepared composite materials were observed with excellent mechanical properties and long service life.

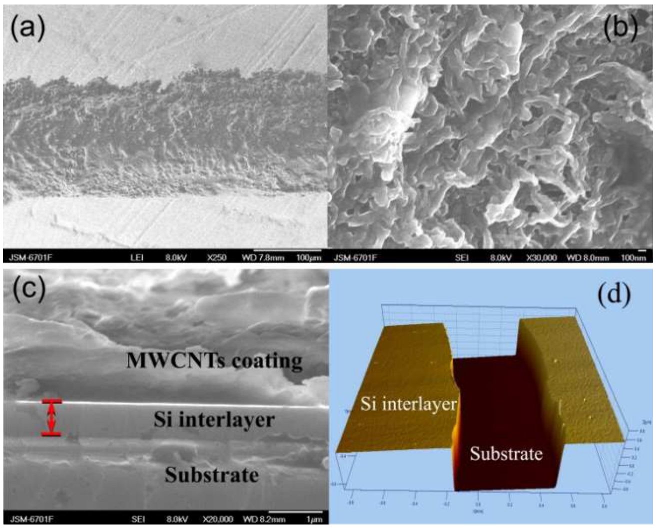

Figure 8. *(a) SEM micrograph of the MWCNTs/Si/Stainless Steel fiber at a magnification of 500×, (b) at a magnification of 20,000×, (c) cross-section micrograph; (d) 3D surface morphology of the stainless steel substrate after the deposition of Si interlayer[14].*

4. Conclusion

Based on the discussion above, it is evident that nanomaterials, such as carbon nanotubes, are promising materials for fabricating electrochemical sensors and solid-phase microextraction. Due the intrinsic properties of carbon nanotubes materials, CNTs have favored in the analysis of variety of analytes with extremely high sensitivity. Their associated fabricating methods enable fast, sensitive, cheap and suitable monitoring for electrochemical sensing and coating elements for solid-phase microextraction. The development of current CNTs coating techniques have brought many characteristic advantages. This paper summarizes the sensing application research with carbon nanotubes hybrid assemblies in recent decades. It focuses on electrochemical sensing and solid-phase microextraction referring to published outstanding reports. At the beginning of this paper, varied methods of CNT sample preparation and implementation are introduced in respect of not only the performance, but also the fabrication method. And in the latter part of this paper, SPME based CNT assemblies are extensively examined based on the preparation method and sensing mechanism. All critical figures in the referred papers are cited significantly.

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