Small molecules as cross-linkers: fabrication of carbon nanotubes/thionine self-assembled multilayers on amino functionalized surfaces†

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Electroactive and photoactive thionine molecules have been selected as cross-linkers to construct self-assembled multilayers containing carbon nanotubes (CNTs) *via* the alternate layer deposition technique. The resulting multilayer system can electrocatalyze the oxidation of NADH and offer potential applications in other fields such as biosenors and photovoltaic devices.

Carbon nanotubes (CNTs), a unique class of one-dimensional functional structures, are considered as promising building blocks for nanoscience and nanotechnology because of their high surface area, good mechanical strength and rich electronic properties.[1] To exploit the potential applications in future nanodevices, it is necessary to develop versatile approaches to assemble or integrate CNTs onto solid surfaces.[1b–f] In the past two decades, the layer-by-layer (LBL) self-assembly technique has become one of the most powerful methods for fabrication of multicomponent thin film on a nanometer scale,[2] due to its simplicity, controllability and versatility in combination with high quality and uniform coating. Recently, it has been successfully applied to fabricate CNTs multilayer films on various solid surfaces.[3–7] However, in these reported works, the cross-linkers employed to combine CNTs into multilayer structures are almost macromolecules such as poly(diallyldimethylammonium chloride) (PDDA), polyethylenimine (PEI), poly(4-vinylpyridine) (PVP), and poly(acrylic acid) (PAA). To the best of our knowledge, only small molecules have not yet been exploited to date as cross-linkers to fabricate self-assembled multialyers containing CNTs.

In this contribution, we describe the fabrication of CNTs/thionine self-assembled multilayers on amino functionalized surfaces by using thionine as cross-linkers. The choice of thionine is based on the following considerations. Thionine, a small planar molecule, contains one heterocyclic nitrogen atom and two amine groups symmetrically distributed on each side (Fig. S1, ESI†). It has recently been reported that ammonia, alkylamines, amine-terminated colloidal silica particles, and polymers PVP, PEI possess high binding affinity for CNTs *via* amine–nanotube interaction.[7] Such interaction might also take place between amino

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† Electronic supplementary information (ESI) available: Multilayer preparation procedure, chemical structure of thonine molecule, Raman spectroscopy of the CNTs/thionine multilayer, and cyclic voltammograms. See DOI: 10.1039/b508130k
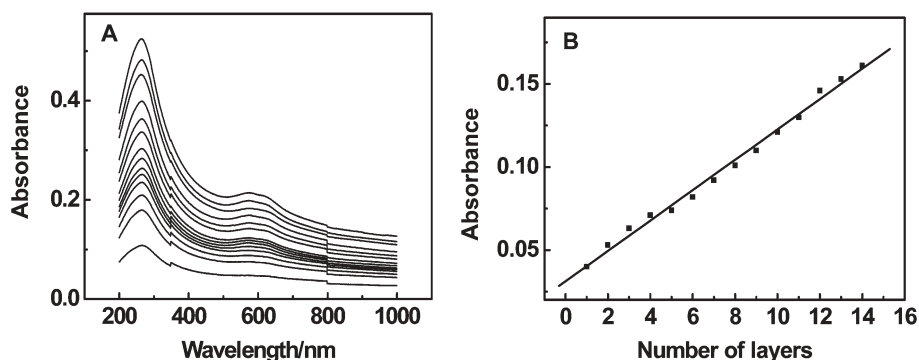
groups of thionine and CNTs. Also, there is π–π stacking force between CNTs and thionine molecules.[8] These interactions might account for thionine cross-linking CNTs. On the other hand, electroactive and photoactive thionine has been widely utilized as functional units in both photogalvanic cells[9] and electrochemical biosensors.[10] Incorporating such functional units into surface-confined systems might be significant for sensoric applications. In brief, thionine employed here act not only as cross-linkers to assemble multilayers containing CNTs, but also as functional components to enrich the properties of the composite films.

Build-up of CNTs/thionine multilayer is achieved by repeated immersion of (3-aminopropyl)trimethoxysilane (APTMS) pre-modified quartz slide or transparent indium tin oxide (ITO) glass in purified multiwalled CNTs dispersion and thionine solution. The experimental details were described in the ESI†. Fig. 1 shows UV-visible absorption spectra of the self-assembled multilayers upon stepwise deposition of CNTs and thionine (each curve corresponds to the respective CNTs layer that includes a top co-associated thionine layer). An absorption band at 267 nm indicates the presence of CNTs[4] while broad and weak absorption peaks in the range between 500 and 700 nm prove the presence of thionine.[9] With the number of CNTs/thionine bilayers increasing, the absorption band intensity at 267 nm increases gradually (Fig. 1A), demonstrating that thionine has successfully cross-linked CNTs into multilayer nanostructures. As seen from Fig. 1B, the linear increase in absorbance indicates that equal amounts of CNTs are assembled in each deposition bilayer, confirming that the film grows uniformly.

The assembly and morphology of the CNTs/thionine multilayers on APTMS pre-modified ITO surface were characterized by scanning electron microscopy (SEM) (Fig. 2). From these SEM images, obvious increase in surface coverage of nanotubes was observed upon stepwise assembly of thionine and CNTs, indicating thionine as cross-linkers successfully bridge the nanotubes into the desired multilayers. Most of the surface-confined CNTs are in the form of small bundles and single tubes with 20–40 nm in diameter and 0.5–1.5 μm in length. It was found that this film comprised lots of randomly oriented, uniformly distributed CNTs. This is different from the results of the modified electrode prepared by other methods such as cast coating, mixing CNTs with carbon paste that CNTs exist in the form of agglomerates or indiscernible nanotubes bundles.[11] Therefore, one may expect to obtain a uniform and three-dimensional CNTs multilayer film by simply choosing different deposition cycles in the LBL assembly process.

Raman spectroscopy was also employed to confirm thionine successfully cross-linking CNTs into the multilayers (Fig. S2, ESI†). Characteristic Raman peaks at 1588 cm^{-1} (G band), and

Fig. 1 (A) UV-visible absorption spectra of thionine cross-linked CNTs multilayer on ITO substrate (thionine as the outmost layer) with different number of layers: 1–14 (curves from bottom to top), respectively. (B) The absorbance at 267 nm as a function of the number of bilayers.
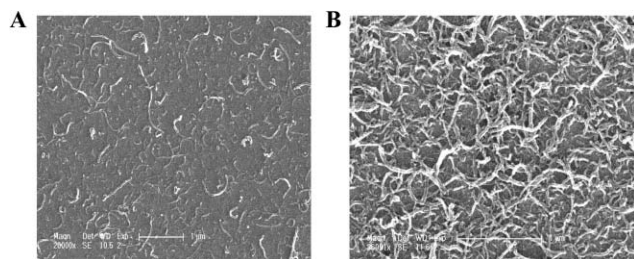

Fig. 2 Typical SEM images of (A) (CNTs)$_1$, (B) (CNTs/thionine)$_8$ on the APTMS pre-modified ITO surfaces. The scale bar is 1 μm.

1356 cm^{-1} (D band) are observed in both spectra of CNTs assembled into the multilayers and the purified CNTs powder sample.[12] It can be seen that thionine immobilized into the multilayers have Raman signatures nearly identical to the thionine powder sample.[13]

Further support for the formation of CNTs/thionine multilayer can be provided by electrochemistry characterization. Fig. 3A shows typical cyclic voltammograms (CVs) obtained at the multilayers modified ITO electrode. This redox wave at formal potential (E_f) *ca.* 0.29 V is ascribed to oxidation/reduction of thionine.[14,15] The uniform growth of the multilayer is confirmed by the good linear relationship between the peak currents and bilayer numbers (the inset of Fig. 3A), which is well consistent with the UV-visible spectroscopy. Based on the above-mentioned result that an equal amount of thionine was deposited in each deposition step, the average surface coverage for the thionine molecules per layer in the multilayers is estimated to be 3.3 × 10^{11} mol cm^{-2} or 2.0 × 10^{13} thionine per cm^2. Upon the stepwise formation of the multilayers, the increasing electrochemical response of thionine also implies that the multilayer exhibits three-dimensional electrical conductivity (Fig. 3A). Additionally, it is noted that the CNTs/thionine multilayers show very good redox reversibility with peak–to-peak separations being around 30 mV. The results show that thionine molecules may electrically communicate to each other due to the well-known interpenetration phenomenon within the layers that allows an electron hopping process between adjacent redox groups.[2d,2e]

Fig. 3B shows CVs of the ITO electrode with four bilayers at various scan rates in 0.5 M H$_2$SO$_4$ solution. The modified electrode shows the characteristic of chemically reversible surface redox electrochemistry. A plot of the cathodic peak current as a
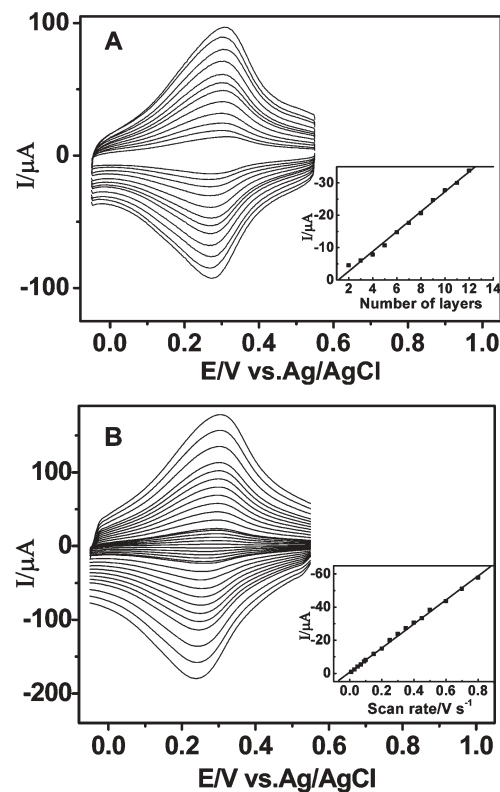

Fig. 3 (A) CVs of the CNTs/thionine multilayer (thionine as the outmost layer) with different number of layers: n = 2–13 (from inside to outside) in 0.5 M H$_2$SO$_4$, respectively. Scan rate: 100 mV s^{-1}. The inset shows the relationship of reduction peak current *vs.* number of bilayers. (B) CVs of four bilayers CNTs/thionine film with different scan rates: 10, 30, 50, 70, 90, 110, 130, 150, 200, 250, 300, 350, 400, 450, 500, 600, 700, 800 mV s^{-1}, respectively. The inset shows the relationship of reduction peak current *vs.* scan rates. Electrode area: 0.196 cm^2.

function of scan rate is linear up to 800 mV s^{-1} (the inset of Fig. 3B). Also, the formal potentials are independent of scan rates and the cathodic and anodic peak currents ratio is unity at all scan rates. All of these demonstrate that the redox processes of surface-confined thionine are fast from the underlying substrate to successive CNTs/thionine bilayers. In addition, the multilayers modified electrode was found to be extremely stable during the whole electrochemical measurement even when continuous cycling
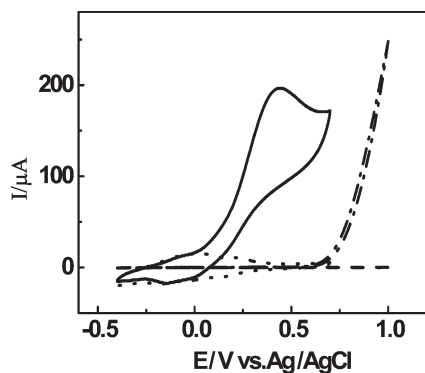
Fig. 4 CVs of (CNTs/thionine)$_{13}$ multilayer in absence (dotted line) and presence (solid line) of 0.5 mM NADH. The dashed line shows CV of bare ITO electrode in absence of 0.5 mM NADH. The dash-dotted line shows CV of bare ITO electrode in presence of 0.5 mM NADH. Supporting electrolyte: pH 7.0 phosphate buffer; scan rate: 20 mV s^{-1}.

between −0.4 and 0.6 V for 1 h. This facile electron accessibility and good stability of the as-prepared multilayers offered the possibility for electrochemical catalysis.

It has been shown that CNTs[16] and thionine[15] possess electro-catalytic activity toward the oxidation of reduced β-nicotinamide adenine dinucleotide (NADH), respectively. Recent studies demonstrated that CNTs could promote the electron transfer at the electrochemical interface and may serve as excellent trans-ducers for biosensors,[1b,1c] which make the composite systems containing CNTs more attractive.[17] Here, the electrocatalytic activity of the CNTs/thionine composite multilayer toward NADH oxidation was investigated. Both CNTs and thionine catalyze NADH oxidation (Fig. S3, ESI†). Shown in Fig. 4 are typical CVs of the multilayer modified ITO electrode and bare ITO electrode in phosphate buffer (pH 7.0) with and without NADH. In presence of NADH, a remarkable catalytic oxidation current at the modified electrode occurs at *ca.* 0.0 V, which shifts 600 mV more negative than that of the bare ITO electrode (*ca.* 0.6 V). The well-behaved electrocatalysis behaviour of the CNTs/thionine assemblies demonstrates that the surface-confined nano-structured multilayers are accessible to analyte molecules and electrically connected with the underlying electrode. Further experiments also show that the catalytic peak current increases with the number of CNTs/thionine bilayers increasing. Detailed studies on the observed electrocatalytic effects and the utilization of this NADH transducer for sensing applications are underway.

In conclusion, only using thionine molecules as cross-linkers, the CNTs/thionine self-assembled multilayers are successfully fabricated on amino functionalized surfaces by "bottom-up" self-assembly strategy. Such thionine cross-linked CNTs self-assembled multilayers exhibit facile electron accessibility. Besides, due to the presence of reactive amino groups on the thionine, the resulting multilayer can be used to anchor enzymes or other biomolecules, which offer the possibility of developing bioelectrochemical devices. Furthermore, dyes molecules that are bound to CNTs by π-stacking or electrostatic interaction have been shown to extend their photoresponse.[18] Therefore, incorporating thionine into such surface-confined multilayers containing CNTs might also be significant for photo-electrochemical applications.

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