

Thionine-interlinked multi-walled carbon nanotube/gold nanoparticle composites

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Received 13 February 2007; accepted 17 May 2007

Available online 2 June 2007

Abstract

Multi-walled carbon nanotube (MWCNT)/thionine/gold nanoparticle composites were prepared by binding gold nanoparticles to the surfaces of thionine-coated carbon nanotubes. TEM images show gold nanoparticles distributed uniformly on nanotube walls and ends. UV–Vis, Raman, FT-IR, and zeta potential measurements were used to examine the properties of the resulting products. The composites demonstrate significant electrocatalytic activity for oxygen reduction. Although only gold nanoparticles were investigated here, the method could be easily extended to attach other metallic nanoparticles to the sidewalls of carbon nanotubes.

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1. Introduction

Carbon nanotubes (CNTs) can be considered ideal templates for formation of one-dimensional nanoparticle assemblies due to their unique structural, mechanical, electronic and thermal properties. However, pristine CNTs often exhibit poor solubility and tend to aggregate in aqueous environments [1], lack fluorescence in the visible range [2], or may be toxic [3]. A promising approach to overcoming these limitations is surface functionalization with groups that confer desirable properties [4,5]. CNT/nanoparticle hybrid materials, in which nanoparticles are attached to CNT surfaces, have been reported to exhibit catalytic activity, enhanced electrical conductivity, and hydrogen-sensing capability [6], suggesting broad potential application in optoelectronics [7], molecular sensors [8] and heterogeneous

catalysis. In particular, nanometal-CNT composites, e.g., single-walled-carbon-nanotube (SWCNT)-supported platinum [9] and multi-walled-carbon-nanotube (MWCNT)-supported Pd, Rh, and Rh/Pd [10], have been prepared by a variety of methods, including physical vapor deposition [11], thermal decomposition [12], electroless deposition [13], and polymer-assisted hybridization [14].

Certain properties of gold nanoparticles (e.g., quantized charging/discharging [15,16], conductivity [17], and catalytic [18] and photocatalytic [19] activity) suggest that gold-nanoparticle-functionalized MWCNTs may prove applicable in future fabrication of nanodevices, enabling further miniaturization of integrated circuits [20]. In this work, Au nanoparticles were non-covalently attached to MWCNTs in the presence of thionine (see Fig. 1). In solution, thionine in protonated form (Thi^+) is shown to adsorb to MWCNT walls via π – π stacking interaction. Upon subsequent addition of negatively charged gold nanoparticles, electrostatic interaction with thionine serves to “glue” the

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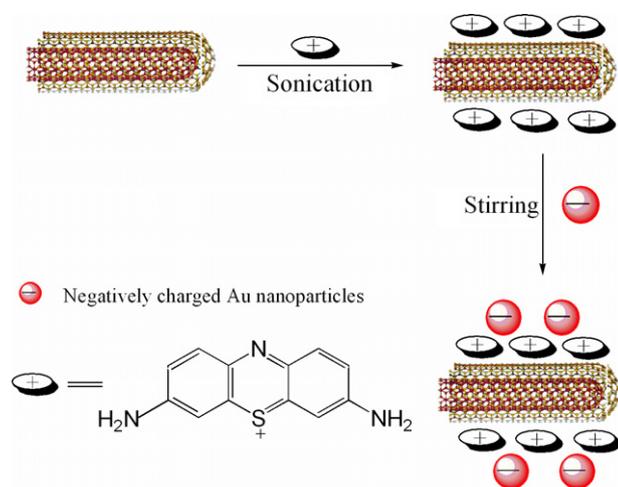


Fig. 1. Proposed mechanism of thionine-mediated adsorption of gold nanoparticles on MWCNTs.

gold onto the MWCNTs. The resulting MWCNT/thionine/gold nanocomposites demonstrate significant electrocatalytic potential for oxygen reduction.

2. Experimental

2.1. Reagents

Thionin acetate (85%) and $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (99.999%) were purchased from Aldrich. Trisodium citrate (99.5%) and sodium borohydride (NaBH_4 , 96%) were available from Beijing Chemical Reagents Company. MWCNTs prepared by chemical vapor deposition (CVD) were purchased from Shenzhen Nanotech Port Ltd. Co. (China). All solvents were of analytical grade. Ultrapure water from a Milli-Q plus system (Millipore Co., >18 M Ω cm) was used in all aqueous solutions and rinsing procedures.

2.2. Instruments and measurements

TEM images were obtained using a Hitachi H-8100 microscope at 200 kV. Chemical composition analysis was performed using a scanning electron microscope (XL30 ESEM FEG; 20 kV) equipped with a Phoenix energy dispersive X-ray (EDX) analyzer. Zeta potentials (effective surface charge) were measured by dynamic light scattering (Zetasizer 3000, Malvern Instruments, France). Normal Raman (NR) spectra were recorded using a Renishaw 2000 system with an Argon ion laser (514.5 nm) and CCD detector. FT-IR spectra were collected using a Bruker Tensor 27 Spectrometer in KBr pellet form. UV–Vis spectra were acquired with a Cary 500 UV–Visible–NIR spectrometer (Varian). Cyclic voltammetry (CV) scans were recorded using a CHI660 electrochemical workstation (Chenhua, Shanghai) with a conventional three-electrode electrochemical cell using a glass carbon (GC) electrode (3-mm diameter), KCl-saturated silver-silver chloride (Ag/AgCl) and a platinum wire as the working, reference and counter electrodes, respectively. All potentials reported here refer to the Ag/AgCl (sat. KCl) reference electrode.

2.3. Synthesis of MWCNT/thionine sample

Carbon nanotubes require surface activation before nanoclusters can be attached. The pristine MWCNTs were purified and activated as follows, based on the method of Li and Grennberg [21]. The as-received MWCNTs were treated with a 1:3 v/v mixture of HNO_3 (65%) and H_2SO_4 (98%) at 50 °C for 5 h with continuous ultrasonication (20 W). The resulting solid was collected by filtration and washed by resuspension in water and ethanol successively, until the wash pH approached 6. The

dark product was dried at 60 °C in a vacuum oven overnight. Subsequently, MWCNTs (0.001 g) were dispersed in 1 ml water with sonication, then mixed with 1 ml of thionine solution (2 mg/ml) and sonicated at room temperature for at least 12 h. The purple color of thionine solution disappeared and a black solution resulted, indicating thionine was dissolved completely into MWCNTs [22]. The MWCNT/thionine solutions were stored until time of use.

2.4. Preparation of gold nanoparticles

Gold nanoparticles were prepared following Gao et al. [23]. Briefly, 18.40 ml of distilled water, 0.50 ml of 0.001 M $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ aqueous solution, and 0.50 ml of 0.01 M trisodium citrate aqueous solution were mixed. Then, 0.60 ml of 0.1 M NaBH_4 aqueous solution was added (total volume 20.00 ml) with vigorous stirring. The resulting solution turned pink, indicating formation of gold nanoparticles. Gold-nanoparticle solutions were used within two hours of preparation.

2.5. Synthesis of MWCNT/thionine/Au composites

In a typical preparation, 0.2 ml of MWCNT/thionine was added dropwise into 20 ml of as-prepared gold colloid under vigorous agitation. Immediately, the pink color faded; then changed slowly into gray, indicating formation of MWCNT/thionine/Au composites. After stirring for an additional 8 h, a black precipitate was isolated by centrifugation. The black precipitate was washed with distilled water several times and dried under vacuum at 60 °C overnight.

3. Results and discussion

Fig. 1 illustrates the hypothesized mechanism of thionine-mediated adsorption of gold nanoparticles on MWCNTs. Here, positively charged thionine molecules enable negatively charged gold nanoparticles to bind to the anionic MWCNT surfaces. In the remainder of this section, we discuss analytical results supporting this rationale.

Catalytic activity of gold is known to depend strongly on the size and type of support [24]. Extremely small metal particles (diameter <10 nm) are of tremendous interest due to their unusual catalytic and optical properties [25]. Consequently, the obtained gold nanoparticles, with average diameter ~ 7 nm, were anticipated to provide catalytic activity when attached to MWCNTs. Further, the gold nanoparticles bear considerable negative charge from citrate incorporated during preparation [26], which should afford ready adsorption on the MWCNT– Thi^+ surface. TEM images of the expected MWCNT/thionine/Au composite (Fig. 2A) confirmed that gold nanoparticles were typically bound on MWCNT walls and ends with fairly even distribution, although a few aggregates were observed. And free nanoparticles could not be observed in the background of TEM images, indicating their strong interactions with MWCNTs. Fig. 2B shows a typical TEM image of as-prepared gold nanoparticles, with average diameter ~ 7 nm. Comparison with Fig. 2A indicates that the size distribution of gold nanoparticles did not change significantly upon binding to MWCNT/thionine. EDX analysis of MWCNT/thionine/Au composites (Fig. 2C) reveals an Au peak originating from gold nanoparticles and N and S peaks attributable to adsorbed thionine. In a control case absent thionine, however, the density of

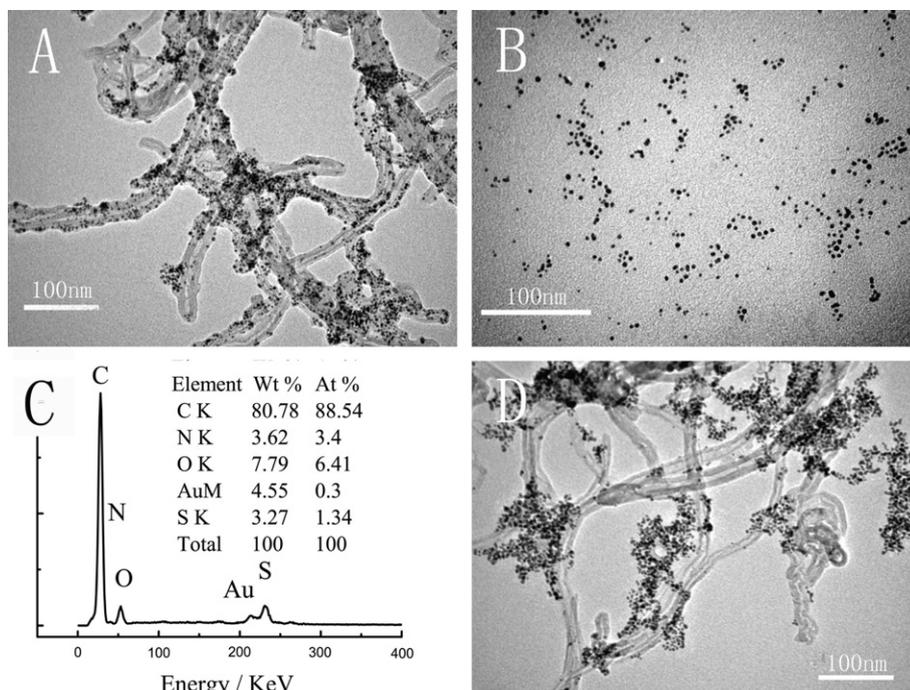


Fig. 2. TEM images of (A) MWCNT/thionine/Au, (B) as-prepared Au nanoparticles, and (D) MWCNT/Au composite without adsorbed thionine interlinkers; (C) EDX spectrum of MWCNT/thionine/Au.

adsorbed gold nanoparticles along MWCNTs was lower than on thionine-coated MWCNTs, as shown in Fig. 2D. And most gold nanoparticles distributed on the background of TEM images. The control result qualitatively supports the proposed mechanism of Thi^+ -mediated electrostatic adsorption of gold nanoparticles. These results suggest that negatively-charged gold nanoparticles can also be used to examine defects or charged sites on CNT walls [27].

Prior to addition of gold nanoparticles, MWCNT/thionine samples were characterized by UV–Vis, NR and FT-IR. Fig. 3 shows typical UV–Vis absorption spectra of (a) MWCNT/thionine solution and (b) aqueous thionine solution. In spectrum (b), the 599 nm main peak is characteristic of monomeric thionine, while the 560 nm shoulder can be attributed to the H-type dimer aggregate [28]. Spec-

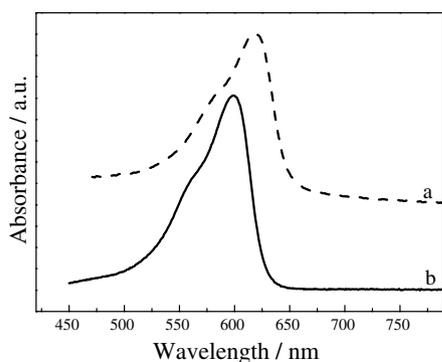


Fig. 3. UV–Vis absorption spectra of: (a) MWCNT/thionine solution and (b) aqueous thionine solution.

trum (a) suggests that the dimerization equilibrium is not significantly disrupted when thionine is adsorbed on MWCNTs. The observed red shift is evidence of strong interaction between MWCNTs and thionine molecules [22], which are small enough to penetrate into the interior of the carbon nanotubes and bind there, as well as on the outer walls. In addition, the NR spectra (Fig. 4) are substantially similar, indicating no significant change in thionine native structure upon interaction with MWCNTs. While it has been reported previously that carboxylate groups on activated CNT surfaces can react with thionine primary amine groups [29], FT-IR spectra of MWCNT/thionine samples (Fig. 5b) do not exhibit amide C–N stretching vibrations in the range of $1000\text{--}1500\text{ cm}^{-1}$. These observations indicate that covalent bonds have not formed between MWCNTs and thionine [30], thus implying that strong interactions arise from $\pi\text{--}\pi$ stacking between these conjugated frames.

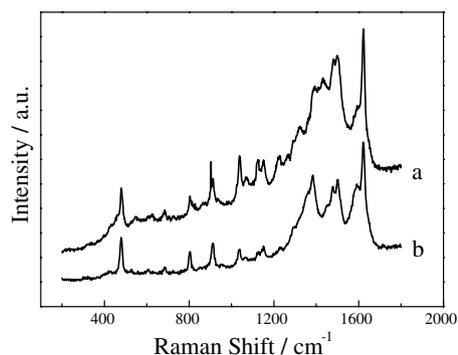


Fig. 4. NR spectra of: (a) thionine and (b) MWCNT/thionine solution.

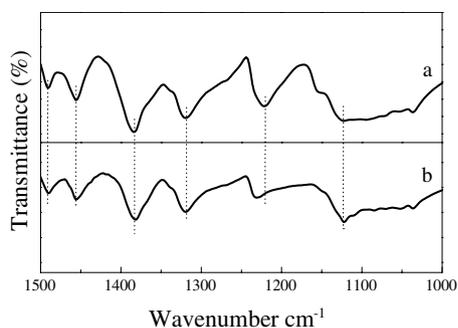


Fig. 5. FT-IR spectra of: (a) thionine and (b) MWCNT/thionine solution.

Zeta potential measurement of surface charge is widely used to monitor buildup of layered structures [31]. Fig. 6 shows experimental values of zeta potential measured from aqueous solution of the various materials prepared in this work. Gold nanoparticles (with citrate incorporated during preparation) showed a zeta potential of near -20 mV. The ζ value measured for MWCNTs was -15 ± 2 mV, ascribed to surface carboxylic acid groups produced during chemical oxidation. Upon adsorption of thionine, however, the ζ value of MWCNT/thionine increased to ca. $+5$ mV. Finally, with gold nanoparticles adsorbed, the ζ potential of MWCNT/thionine/Au decreased to -35 mV. In summary, these various characterization results support the rationale shown in Fig. 1.

To assess electrocatalytic potential, nanocomposites were applied to a glass carbon electrode which was then used for to perform cyclic voltammetry measurements in a dioxygen reducing system. In the presence of O_2 , a significant catalytic reduction current peak occurs at -0.34 V (Fig. 7, dashed line), which shifts positively by 300 mV when compared to that at the bare GC electrode (-0.65 V) [32]. However, for nitrogen-saturated and air-saturated reaction systems, current peaks are not readily discernable. As a comparison, a small reduction peak current occurs at a negative potential on the MWCNT-modified GC electrode. These results indicate that MWCNT/thionine/Au composites possess high electrocatalytic activity for O_2 reduction.

In a control case absent MWCNTs and thionine, where the same amount of Au nanoparticles was applied to the GC electrode, the observed oxygen-reduction current was approximately 1.25% of that measured with MWCNT/

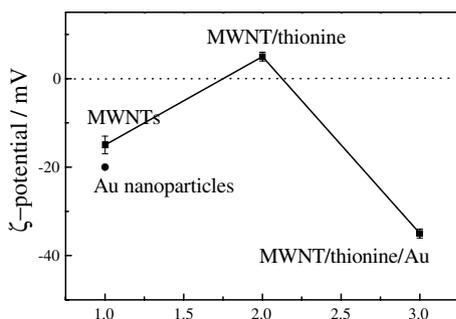


Fig. 6. Changes in zeta potentials along with the kinds of materials.

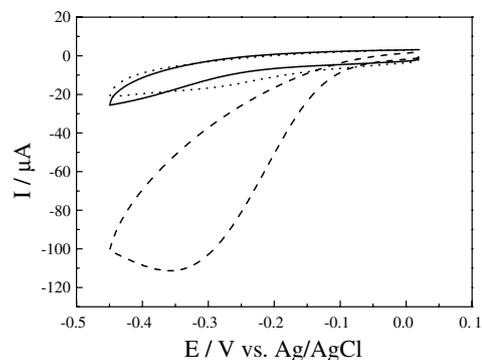


Fig. 7. Cyclic voltammograms of O_2 reduction at the GC electrode coated with the MWCNT/thionine/Au composite. Supporting electrolyte: in N_2 saturated (solid), air-saturated (dotted), and O_2 saturated (dash) 0.5 M H_2SO_4 solution. Scan rate: 0.05 V s^{-1} .

thionine/gold-nanoparticle composites, although the reduction occurred at almost the same potential. Moreover, without MWCNT/thionine, gold nanoparticles aggregated completely after only a few hours, losing all electrocatalytic activity for oxygen reduction. In comparison, after two weeks incubation, the size distribution and electrocatalytic activity of gold nanoparticles did not change significantly when bound to MWCNTs. These results definitely showed a synergistic effect between MWCNTs and gold nanoparticles, and MWCNTs are good substrates to maintain the size distribution and good electrocatalytic activity of gold nanoparticles.

4. Conclusions

In conclusion, we have synthesized MWCNT/thionine/Au composites using thionine molecules as interlinkers. π - π stacking interactions between MWCNTs and thionine, and electrostatic interactions between thionine and Au nanoparticles, resulted in the formation of MWCNT/thionine/Au composites. Most gold nanoparticles distributed uniformly on the walls and ends of nanotubes. The composites showed significantly enhanced stability and electrocatalytic activity for oxygen reduction, relative to a control case containing only gold nanoparticles. Attachment of metal nanoparticles onto CNTs could also serve potentially to detect the presence of certain functional groups on the surfaces, and further to prove a successful derivatization. In addition, the attached metallic nanoparticles may be useful in identifying the locations of defects, grafting, or chemical reaction sites on the tube wall. Although only gold nanoparticles were used in this study, similar method could be easily extended to attach other metallic nanoparticles to sidewalls of carbon nanotubes.

Acknowledgements

The authors are most grateful to the National Science Foundation of China (No. 20475053 and No. 20673109), Department of Science and Technology of Jilin Province

(No. 20050102) and Ministry of Science and Technology of China (No. 2006BAKB05).

References

- [1] Liu J, Rinzler AG, Dai H, Hafner JH, Bradley RK, Boul PJ, et al. Fullerene pipes. *Science* 1998;280:1253–6.
- [2] Didenko VV, Moore VC, Baskin DS, Smalley RE. Visualization of individual single-walled carbon nanotubes by fluorescent polymer wrapping. *NanoLett* 2005;5(8):1563–7.
- [3] Bottini M, Bruckner S, Nika K, Bottini N, Bellucci S, Magrini A, et al. Multi-walled carbon nanotubes induce T lymphocyte apoptosis. *Toxicol Lett* 2006;160(2):121–6.
- [4] Chen J, Hamon MA, Hu H, Chen Y, Rao AM, Eklund PC, et al. Solution properties of single-walled carbon nanotubes. *Science* 1998; 282:95–8.
- [5] Chen RJ, Zhang YG, Wang DW, Dai HJ. Noncovalent sidewall functionalization of single-walled carbon nanotubes for protein immobilization. *J Am Chem Soc* 2001;123(16):3838–9.
- [6] Kim DS, Lee T, Geckeler KE. Hole-doped single-walled carbon nanotubes: ornamenting with gold nanoparticles in water. *Angew Chem Int Edit* 2006;45(1):104–7.
- [7] Kovtyukhova NI, Kelley BK, Mallouk TE. Coaxially gated in-wire thin-film transistors made by template assembly. *J Am Chem Soc* 2004;126:12738–9.
- [8] Huang JG, Kunitake T, Onoue S. A facile route to a highly stabilized hierarchical hybrid of titania nanotube and gold nanoparticle. *Chem Commun* 2004:1008–9.
- [9] Hrapovic S, Liu Y, Male KB, Luong JHT. Electrochemical biosensing platforms using platinum nanoparticles and carbon nanotubes. *Anal Chem* 2004;76(4):1083–8.
- [10] Yoon B, Wai CM. Microemulsion-templated synthesis of carbon nanotube-supported Pd and Rh nanoparticles for catalytic applications. *J Am Chem Soc* 2005;127(49):17174–5.
- [11] Zhang Y, Dai H. Formation of metal nanowires on suspended single-walled carbon nanotubes. *Appl Phys Lett* 2000;77(19):3015–7.
- [12] Xue B, Chen P, Hong Q, Lin J, Tan KL. Growth of Pd, Pt, Ag and Au nanoparticles on carbon nanotubes. *J Mater Chem* 2001;11(9): 2378–81.
- [13] Li J, Moskovits M, Haslett TL. Nanoscale electroless metal deposition in aligned carbon nanotubes. *Chem Mater* 1998;10(7):1963–7.
- [14] Jiang K, Eitan A, Schadler LS, Ajayan PM, Siegel RW. Selective attachment of gold nanoparticles to nitrogen-doped carbon nanotubes. *NanoLett* 2003;3(3):275–7.
- [15] Chen S, Ingram RS, Hostetler MJ, Pietron JJ, Murray RW, Schaff TG, et al. Gold nanoelectrodes of varied size: transition to molecule-like charging. *Science* 1998;280:2098–101.
- [16] Chen S, Murray RW. Electrochemical quantized capacitance charging of surface ensembles of gold nanoparticles. *J Phys Chem B* 1999; 103(45):9996–10000.
- [17] Li J, Yamada Y, Murakoshi K, Nakato Y. Sustainable metal nanocontacts showing quantized conductance prepared at a gap of thin metal wires in solution. *Chem Commun* 2001:2170–1.
- [18] Haruta M. Size- and support-dependency in the catalysis of gold. *Catal Today* 1997;36(1):153–6.
- [19] Subramanian V, Wolf EE, Kamat PV. Green emission to probe photoinduced charging events in ZnO–Au nanoparticles. Charge distribution and Fermi-level equilibration. *J Phys Chem B* 2003; 107(30):7479–85.
- [20] Wang T, Hu X, Dong S. Noncovalent functionalization of multi-walled carbon nanotubes: application in hybrid nanostructures. *J Phys Chem B* 2006;110(13):6631–6.
- [21] Li J, Grennberg H. Microwave-assisted covalent sidewall functionalization of multiwalled carbon nanotubes. *Chem Eur J* 2006;12(14): 287–91.
- [22] Li QW, Zhang J, Yan H, He MS, Liu ZF. Thionine-mediated chemistry of carbon nanotubes. *Carbon* 2004;42(2):287–91.
- [23] Gao J, Bender CM, Murphy CJ. Dependence of the gold nanorod aspect ratio on the nature of the directing surfactant in aqueous solution. *Langmuir* 2003;19(21):9065–70.
- [24] Santhosh P, Gopalana A, Lee KP. Gold nanoparticles dispersed polyaniline grafted multiwall carbon nanotubes as newer electrocatalysts: preparation and performances for methanol oxidation. *J Catal* 2006;238(1):177–85.
- [25] Sudeep PK, Kamat PV. Photosensitized growth of silver nanoparticles under visible light irradiation: a mechanistic investigation. *Chem Mater* 2005;17(22):5404–10.
- [26] Weitz DA, Lin MY, Sandroff CJ. Colloidal aggregation revisited: new insights based on fractal structure and surface-enhanced Raman scattering. *Surf Sci* 1985;158(1–3):147–64.
- [27] Kim B, Sigmund WM. Functionalized multiwall carbon nanotube/gold nanoparticle composites. *Langmuir* 2004;20(19):8239–42.
- [28] Ding Y, Zhang X, Liu X, Guo R. Adsorption characteristics of thionine on gold nanoparticles. *Langmuir* 2006;22(5):2292–8.
- [29] Huang M, Jiang H, Qu X, Xu Z, Wang Y, Dong S. Small molecules as cross-linkers: fabrication of carbon nanotubes/thionine self-assembled multilayers on amino functionalized surfaces. *Chem Commun* 2005:5560–2.
- [30] Kovtyukhova NI, Mallouk TE. Ultrathin anisotropic films assembled from individual single-walled carbon nanotubes and amine polymers. *J Phys Chem B* 2005;109(7):2540–5.
- [31] Johnston APR, Zelikin AN, Lee L, Caruso F. Approaches to quantifying and visualizing polyelectrolyte multilayer film formation on particles. *Anal Chem* 2006;78(16):5913–9.
- [32] Shen Y, Liu J, Jiang J, Liu B, Dong S. Fabrication of a metalloporphyrin-polyoxometalate hybrid film by a layer-by-layer method and its catalysis for hydrogen evolution and dioxygen reduction. *J Phys Chem B* 2003;107(36):9744–8.