

Fabrication and Biosensing with CNT/Aligned Mesostructured Silica Core–Shell Nanowires

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ABSTRACT We report the synthesis of carbon nanotubes (CNTs) /mesostructured silica core–shell nanowires via an interfacial surfactant templating approach. The nanowires possess perpendicularly aligned and uniform accessible mesopores, high surface area and large pore volume. When dimethyl sulfoxide reductase (DMSOR) enzyme is immobilized on the core–shell nanowires, the complex can enhance the electrical communication between the active sites of the enzyme and the electrode surface in the presence of a mediator. The unique properties of the CNTs and the uniform accessible mesopores of the nanowires have made this material promising in the applications as carbon nanotubes field-effect transistors, electrochemical detection, and biosensors.

KEYWORDS: carbon nanotubes • core–shell mesostructure • electrochemistry

1. INTRODUCTION

At the molecular level, enzyme-electrode-based electrochemical sensors offer elegant routes for interfacing, biological recognition, and electronic signal transduction. In addition, electrochemical devices are uniquely qualified for meeting the size, cost, low volume, and power requirements of decentralized testing. This presents great potential for a wide range of biomedical or environmental applications (1). For application in biosensors, the enzymes should be immobilized crucially on the electrode surface to avoid complications linked to the solution systems (2, 3). A challenge in amperometric enzyme electrodes is the establishment of satisfactory electrical communication between the active sites of the enzyme and the electrode surface (4). Therefore, suitable electrode materials and immobilization methods of enzymes onto the electrode surface are important for the promotion of their electrochemical reactions and the preservation of bioactivities.

Various materials, including carbon nanotubes (CNTs) (5), inorganic porous materials (6–9), small organic compounds (10), and semiconductor metal oxides (11), have been used as matrices for enzyme immobilization. The investigation on carbon nanotubes with remarkable electron conductivity and high chemical stability has gained considerable attention in enhancing electron transfer between enzymes and elec-

trode surfaces (5, 12, 13). However, unresolved issues around the poor solubility and processability of CNTs present major barrier for studying their properties and potential applications. Specifically, in terms of practical applications, the surface functionalization of CNTs remains to be a significant challenge. At present, versatile strategies have been developed to functionalize CNTs with organic (14), inorganic (15), and biological species (16). Among them, the CNTs with porous silica shell (CNT@SiO₂ nanowires) is the most widely studied, this is due to a variety of factors including insulating properties, good dispersibility in aqueous solution, high adsorption capacity, biocompatibility, and facilitory functionalization without the disruption of the CNTs structure (17).

Two general strategies have been utilized for the silica functionalization of CNTs. The first involves covalent functionalization of silica onto carbon nanotube sidewalls using a range of either silyl or silane derivatives (18, 19). Despite covalent functionalization being a robust and a well-controlled process, it has the potential to seriously compromise or otherwise destroy the desirable electronic and optical properties of the carbon nanotubes to a large extent. An alternative strategy is to coat CNTs with silica using a noncovalent methodology, in which the protective layer of silica only weakly perturbs the electronic structure of CNTs. Silica-coated CNTs were achieved by using a chemical vapor deposition method, and the produced nanowires have heterostructures with a carbon nanotubes core and a uniform silica insulating shell (20). CNTs were also coated with a fluorine-doped silica layer through a liquid-phase deposition process using a SiO₂–H₂SiF₆ solution and a surfactant-stabilized CNTs solution (21). In addition to the above-mentioned techniques, the sol–gel method in particular has been extensively used for the preparation of CNT@SiO₂

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nanowires because of its well-known convenient processing methodologies (22). Our previous report (23) presented a fabrication technique for CNT@SiO₂ nanowires with a CNTs core and mesoporous silica shell, utilizing an interfacial surfactant template together with sol–gel process. However, all reported CNT@SiO₂ nanowires to date possess randomly aligned mesoporous channels. Highly valued CNT@SiO₂ nanowires with uniform mesoporous silica shell, perpendicularly aligned/orientated and accessible mesopores, and high dispersibility have not been reported in the literature. The investigation of such CNT@SiO₂ nanowires is the main aim of our research.

Herein, we report a novel synthesis technique for the preparation of CNT@SiO₂ nanowires via the interfacial surfactant (octadecyltrimethylammonium bromide, ODTMA) templating approach. The core–shell nanowires possess high surface area, large pore volume, and perpendicularly orientated and uniform accessible mesopores. More interestingly, under conditions where dimethyl sulfoxide reductase (DMSOR) is immobilized on core–shell nanowires, the CNT@SiO₂ nanowires can enhance the electrical communication between the active sites of the enzyme and the electrode surface in the presence of a mediator. This leads to many favorable properties for electrochemical detection and biosensing systems.

2. EXPERIMENTAL METHODS

2.1. Chemicals. Tetraethoxysilane (TEOS, 99%), octadecyltrimethylammonium bromide (ODTMA, 97%), and sodium hydroxide (98%) were purchased from Aldrich. CNTs were obtained from Chengdu Organic Chemicals Co. Ltd., China. All chemicals were used as received without any purification. DMSO reductase was purified from *R. capsulatus* strain H123 according to the method reported in the literature (24). The mediator (trans-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine)cobalt(III) (denoted as [Co(transdiammac)]³⁺) was synthesized according to the published procedure (25). The reaction solution consisted of 50 mM purged tris–buffle solution (pH 8.0) with 30 μM [Co(transdiammac)]³⁺ mediator.

2.2. Fabrication of CNT@SiO₂ Nanowires. Water-soluble carbon nanotubes: CNTs were refluxed and sonicated in 3:1 H₂SO₄:HNO₃ mixture at 140 °C for 8 h. The mixture was then cooled to room temperature and washed with distilled water until the pH value of the filtrate reached 7. The 0.01 g of CNTs was then dispersed into 96 mL of aqueous solution containing 0.20 g of ODTMA. The suspension was treated by sonication for 4 h. TEM images (Figure 1A) show that the diameter of CNTs is 40–50 nm and the length from hundreds nanometers to micrometers.

CNT@SiO₂ nanowires: In a typical experiment, 0.5 mL of NaOH solution (2.0 M) was added into 96 mL of aqueous solution containing 0.01 g of CNTs and 0.20 g of ODTMA. Then the solution was maintained at 70 °C for 20 min before 0.8 g of TEOS was added under stirring. The reaction stopped after 2 h stirring and the gel-like composite was filtered. The materials were washed with a mixed solvent containing 100 mL of ethanol and 2–4 mL of 32% (w/w) HCl at 60 °C to remove ODTMA templates completely and then dried at 50 °C.

2.3. Characterization. X-ray diffraction pattern (XRD) measurements were performed on a Rigaku D/max-2550 V diffractometer by using Co Kα radiation at 30 kV and 15 mA. Nitrogen sorption isotherms of samples were obtained by a Micromeritics ASAP2020 analyzer at –196 °C. Before the measurements were taken, the samples were degassed at 150 °C for 6–8 h in

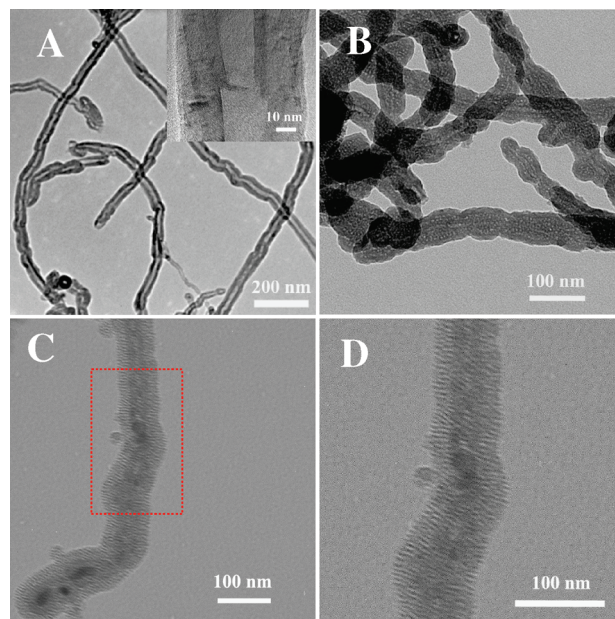


FIGURE 1. (A) TEM and HRTEM images of water-soluble carbon nanotubes and (B–D) CNT@SiO₂ nanowires.

vacuum. The pore size distribution was calculated with the Barrett–Joyner–Halenda (BJH) method using the adsorption branch. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were obtained by a FEI Tecnai F20 electron microscope.

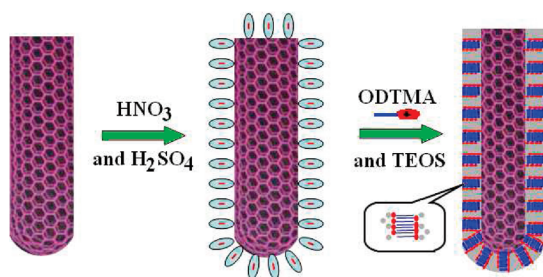
2.4. Preparation of Electrode and Electrochemical Measurements. The pyrolytic graphite electrode (3 mm in diameter) surface was simply cut into 1 μm using a micro thin slicer, followed by sonicating within the mixture of ethanol and distilled water for 5 min to obtain clean surface. CNTs were dispersed in the aqueous solution of octadecyltrimethylammonium bromide (ODTMA, 1% by weight) under the ultrasonication to form a 1 mg/mL black CNTs suspension. Four μL of this suspension was cast onto the surface of the pyrolytic graphite electrode with a microsyringe and then dried at ambient temperature. Two microliters of DMSOR (352 μM) was then dropped onto the CNTs-modified pyrolytic graphite electrode surface and dried in a fridge at 4 °C. To avoid the enzyme separating from the surface of the electrode, we covered the DMSOR-CNTs/pyrolytic graphite electrode with an organic membrane that allowed through small molecules but blocked large molecules such as DMSOR. When CNT@SiO₂ was used as a working electrode instead of CNTs, the electrode was denoted as DMSOR-nanowire/pyrolytic graphite. For comparison, the DMSOR/pyrolytic graphite electrode without coating with CNT@SiO₂ or CNTs was also investigated in this study.

Electrochemical measurements were carried out with a BAS100B/W workstation. A three-electrode system which comprised of a DMSOR-CNT/pyrolytic graphite disk working electrode, a Pt wire counter, and a Ag/AgCl reference electrode was employed. The supporting electrolyte was a mixture of tris–buffer (50 mM, pH 8.0) and [Co(transdiammac)]³⁺ solution (30 μM) that was bubbled with argon prior to experiment. All electrochemical measurements were performed at ambient temperature.

3. RESULTS AND DISCUSSION

3.1. CNT@SiO₂ Nanowires. The synthesis procedure is shown in Scheme 1. First, carbon nanotubes were immersed into the mixture of HNO₃ and H₂SO₄ to make them soluble in water. The CNTs were then dispersed into a cationic surfactant (ODTMA) aqueous solution so that the

Scheme 1. Schematic Representation of the CNT/Mesoporous Silica Core–Shell Nanowires Preparation Process



hydrophobic parts of ODTMA interacted with the graphite sidewall of CNTs to achieve stable supramolecular assemblies at the CNT–liquid interface (26). Second, through a surfactant self-assembly templating and silica sol–gel reaction processes, a uniform mesostructured ODTMA/silica composite was deposited around the CNTs. Third, ODTMA templates were removed in a mild way by ethanol extraction to form a mesoporous SiO₂ shell, resulting in well-dispersed core–shell-structured CNT@SiO₂ nanowires.

The TEM and HRTEM images for CNTs are presented in Figure 1A and inset, respectively. As can be seen that the diameter of the CNTs is around 40–50 nm and the length ranges from hundreds of nanometers to micrometers. The lattice fringe of graphite is clearly observed from the HRTEM image (inset in Figure 1A), indicating that the carbon nanotubes exhibit graphite structure.

The TEM and HRTEM images of CNT@SiO₂ nanowires are shown in Figure 1B–D. The TEM image in Figure 1B reveals that core–shell nanowires have a relatively uniform shape along its entire length with a uniform silica-shell coated. HRTEM images of CNT@SiO₂ nanowires in images C and D indicate that the diameter of the core–shell nanowires is about 70 nm and the thickness of the shell is about 15 nm. The silica shell exhibits a uniform porous architecture. The SiO₂ in CNT@SiO₂ nanowires is amorphous, which is confirmed by electron diffraction results (see Figure S1 in the Supporting Information). Interestingly, the mesopore channels are found to be perpendicular to the CNTs surface (Figure 1C, D). It is believed the concentration of NaOH plays an important role in the nucleation and growth of the mesoporous silica shells because it significantly affects the hydrolysis rate of silica precursor. By controlling the concentration of NaOH, the reaction temperature and the ratio of CNTs/silica precursor, CNT@SiO₂ nanowires with a diameter of 70 nm and a 15 nm thickness uniform mesoporous shell were synthesized. The shell of this material is much thinner and the pores are more uniform than our previous work (23). Moreover, contrary to our previously published results, which showed randomly arranged periodic mesoporous silica shell (space group *p6mm*), the mesopore channels in this work are found to be perpendicular to the CNTs surface (Figure 1C, D). The mesopore orientation may have resulted from the preferable alignment fashion of the rod-shaped silicate/ODTMA complexes on the curved surface of the CNTs. This could effectively decrease the

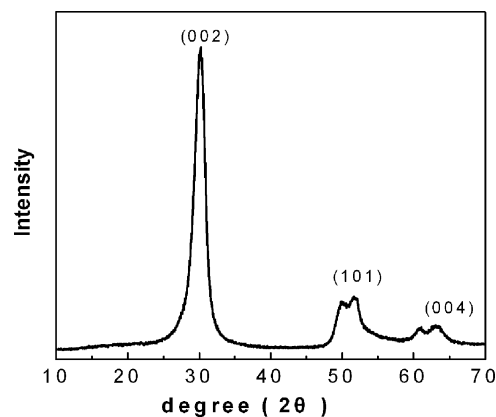


FIGURE 2. XRD pattern of carbon nanotubes.

surface energy in the synthesis system (Scheme 1). These results have also been evidenced by Deng et al. (27), where the perpendicularly aligned mesoporous SiO₂ was coated on the curved surface of the Fe₃O₄@SiO₂ microspheres.

Figure 2 shows the XRD pattern of carbon nanotubes, and these peaks located at 2θ values of 30.2, 51.8, and 63.3° corresponding to the (002), (101), and (004) reflections respectively. The *d* spacing calculated from (002) diffraction peak is about 0.34 nm, which is a typical distance of hexagonal graphite layer, which is consistent with the TEM results in Figure 1. These strong peaks show that the carbon nanotubes used here have well-graphitized walls. Its high conductivity is beneficial to the electron transfer in our experiment system. The low angle XRD pattern of CNT@SiO₂ nanowires in Figure 3A shows a high intensity diffraction peak of (100), which can be assigned to a two-dimensional hexagonal mesostructure. This suggests the synthesized core–shell nanowires possess uniform porous structure with well-formed hexagonal pore arrays and a short-range-ordered mesopore character. Nitrogen sorption result of the core–shell nanowire in Figure 3B exhibits a type IV adsorption isotherm with a uniform pore size distribution (inset of Figure 3B), which is characterized as characteristics of mesostructure. The pore size distribution exhibits a sharp peak centered at the mean value of 2.8 nm. BET surface area and total pore volume of the core–shell nanowires are estimated to be at 774 m²/g and 0.77 cm³/g, respectively. The high BET surface area, large pore volume, and perpendicularly aligned mesopores of CNT@SiO₂ nanowires can offer promising applications in adsorption, catalytic reaction, enzyme immobilizations, and biosensors.

The mesoporous silica shell would not only make the nanowires with good dispersibility in aqueous solutions and good biocompatibility, but also provide a versatile inorganic host material with high immobilization capacity for biomacromolecules. Mesoporous silicas is one of the most widely studied matrices for enzyme immobilization, this is due to a variety of factors including dispersibility in aqueous solution, high adsorption capacity, biocompatibility and facile functionalization. However because of its well-known insulating property, the mesoporous silica shells might restraint the electron transfer between the enzyme and the electrode. To overcome this problem, the CNT@SiO₂ nanowires with

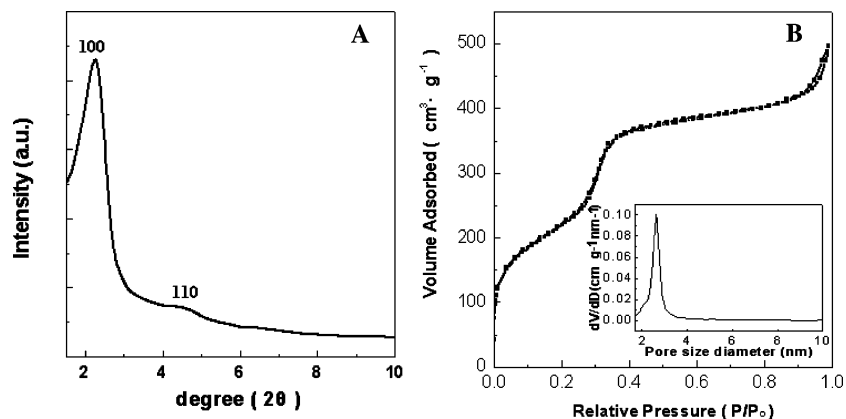
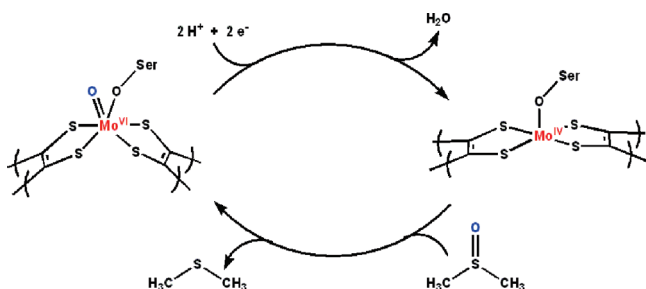
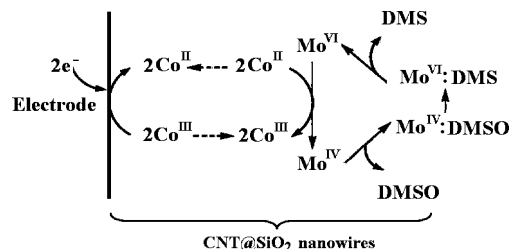


FIGURE 3. (A) Low-angle XRD pattern and (B) N_2 adsorption/desorption isotherms (inset: pore size distribution calculated from adsorption branch) of CNT@SiO₂ nanowires.

Scheme 2. Schematic Draw of the Reduction Reaction of DMSO to DMS Catalyzed by DMSOR



Scheme 3. Reduction Reaction of DMSO to DMS Catalyzed by DMSOR with Mediator



a very thin layer of perpendicularly aligned mesoporous silica shell (~ 15 nm) are synthesized in this work (Figure 1), which is achieved by controlling the ratio of CNTs and silica precursor. The unique perpendicular orientation together with the mesopore channels make the CNT@SiO₂ nanowires readily accessible, favoring the adsorption and release of guest objects triggered by external stimulus. Simultaneously, the biomolecules immobilized on mesoporous silica shells can interact easily with the CNTs, this is crucial to the electrical communication between the active sites of the enzyme and the surface of the electrode in the biosensing system (4).

3.2. Mediated Electrochemistry of Dimethyl Sulfoxide Reductase Promoted by CNT@SiO₂ Nanowires. The dimethyl sulfoxide reductase (DMSOR) from the bacterium *Rhodobacter Capsulatus* is a molybdenum-containing enzyme capable of reducing dimethyl sulfoxide (DMSO) to dimethyl sulfide (DMS). The schematic depiction of the reduction reaction of DMSO to DMS catalyzed by DMSOR was shown in Scheme 2. During this process, the

oxygen atom of DMSO is transferred to molybdenum of DMSOR, and then is subsequently removed from molybdenum as water. At present, all enzymes from the DMSOR family have been isolated from bacteria or archaea (28–30). Indeed, enzyme electrochemistry of DMSOR is an emerging area of interest in bioanalytical chemistry owing to the wide variety of substrates that are oxidized or reduced within this family, many which are chemically inert or not easily detected quantitatively by other methods. Hence, DMSOR is an ideal enzyme for the construction of a DMSO biosensor. To date, to the best of our knowledge, only a few papers have reported the electrochemical biosensing properties of DMSOR (28–30). The reason behind this is perhaps due to the high-molecular-weight (82 000) of DMSOR, which makes its active sites highly inaccessible (28–30). With the increase in the molecular weight of the enzymes, their active sites are more deeply buried into the large three-dimensional structure, hence their redox centers become more difficult to access. The employment of mediators have been regarded as an effective method to improve the electron transfer characteristics as they undergo simple heterogeneous electron transfer at the electrode while also reacting homogeneously with the enzyme (31, 32). In this study, we attempted to explore the applicability of CNT@SiO₂ nanowires for DMSO electrochemical biosensing test utilizing DMSOR as enzyme and the CNT@SiO₂ nanowires as an electrode for the immobilization of DMSOR. A mediator [Co(transdiammac)]³⁺, (the molecular structure is shown in Figure S2) was used to facilitate the electron transfer between DMSOR and the electrode. CNT@SiO₂ nanowires were randomly arranged on the electrode surface. An organic membrane was covered onto the DMSOR-nanowires/pyrolytic graphite electrode to allow small molecular through but blocked large molecule like DMSOR and most importantly to avoid the enzyme separating from the surface of electrode. On the basis of the size-exclusion mechanism (7), DMSOR is adsorbed on the external surface of the CNT@SiO₂ nanowires. DMSO reductase reacts with both DMSO (substrate, the electron acceptor) and the Co^{II} of the mediator ([Co(trans-diammac)]²⁺, the electron donor), which also undergoes diffusional heterogeneous electron transfer at the electrode (Scheme 3). It is likely that there are various

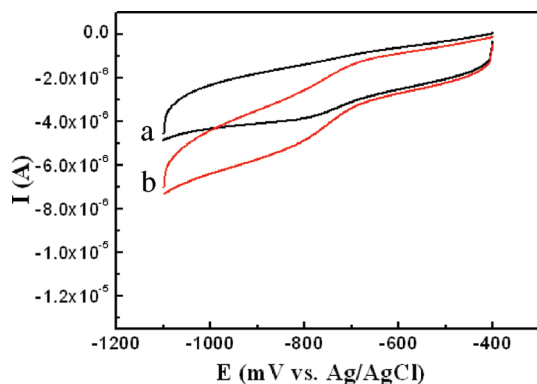


FIGURE 4. Cyclic voltammograms of the DMSOR/pyrolytic graphite electrode in 50 mM purged tris-buffe solution (pH 8.0) with $30 \mu\text{M}$ $[\text{Co}(\text{transdiammac})]^{3+}$ mediator in the (a) absence and (b) presence of $115 \mu\text{M}$ DMSO. Scan rate: 20 mV/s.

sites on the periphery of DMSO reductase where productive electron transfer from the mediator can be achieved. Heterogeneous electron transfer of DMSO reductase at the electrode can be improved by the employment of a mediator which may react homogeneously with the enzyme (30). The CNT@SiO₂ nanowires and the mediator can enhance the electron transfer between DMSOR and electrode, cooperatively.

Figure 4 shows the cyclic voltammograms of the DMSOR/pyrolytic graphite electrode in 50 mM purged tris-buffe solution (pH 8.0) with $30 \mu\text{M}$ of mediator ($[\text{Co}(\text{transdiammac})]^{3+}$) in the absence (curve a) and presence (curve b) of $115 \mu\text{M}$ DMSO at a scan rate of 20 mV/s. The catalytic current was clearly observed after the addition of substrate DMSO, but the catalytic current is very low. This result indicates that the reduction reaction of DMSO to DMS can be performed by immobilizing the DMSOR onto the surface of pyrolytic graphite electrode. Under the same experimental conditions the cyclic voltammetric results of the DMSOR-CNTs/pyrolytic graphite electrode and DMSOR-CNT@SiO₂ nanowires/pyrolytic graphite electrode have been obtained and shown in panels A and B in Figure 5, respectively. Comparing with DMSOR/pyrolytic graphite electrode, the catalytic current of DMSOR-CNTs/pyrolytic graphite electrode increases obviously, indicating that the CNTs can improve the electrode electron transfer characteristics. The electron transfer promotion effect of CNTs in this DMSOR

based electrochemical sensors is consistent with the results obtained in other enzyme electrode based electrochemical sensors (5, 12, 13). Interestingly, the catalytic current of DMSOR-CNT@SiO₂ nanowires/pyrolytic graphite electrode is extremely higher than that of DMSOR/pyrolytic graphite electrode and DMSOR-CNTs/pyrolytic graphite electrode, and keep raising with the increase of DMSO concentration (see Figure S3 in the Supporting Information). The experimental results reveal that the CNT@SiO₂ nanowires can enhance the electrical communication between the active sites of enzyme and the electrode surface. The immobilized DMSOR on core-shell nanowires may retain its bioelectrocatalytic activity very well.

As a DMSOR immobilizing matrix, the mesoporous silica shell of CNT@SiO₂ nanowires could incorporate many DMSOR enzymes through physical or chemical interactions because of its high specific surface area, large pore volume, and good biocompatibility. The mesoporous silica shell with the appropriate dimensions and functionalization adjacent to the enzyme redox center could act as a current nanocollector and electron capacitor/transactor to a macroelectrode (6). Simultaneously, the readily accessible perpendicular-orientation mesopore channels and the graphite CNTs core with remarkable electron conductivity of the CNT@SiO₂ nanowires can make the enzyme interact with the CNTs easily, and therefore enhance the electrical communication between the active sites of the enzyme and the electrode surface and promote electrochemical biosensing capacity.

4. CONCLUSIONS

We have presented the synthesis of CNT@SiO₂ nanowires with a CNTs core and perpendicularly aligned mesoporous SiO₂ shell. The core-shell nanowires possess high surface area, large pore volume, and uniform accessible mesopores. When DMSOR enzyme is immobilized on the nanowires, they can enhance the electrical communication between the active sites of the enzyme and the electrode surface at the presence of mediator. The toxicity of carbon nanotube is still a widely debated topic (33), and the coating of SiO₂ might reduce its toxicity due to the biocompatibility of SiO₂. Moreover, because of the unique properties of CNTs and uniform accessible mesopores, the CNT@SiO₂ nanowires

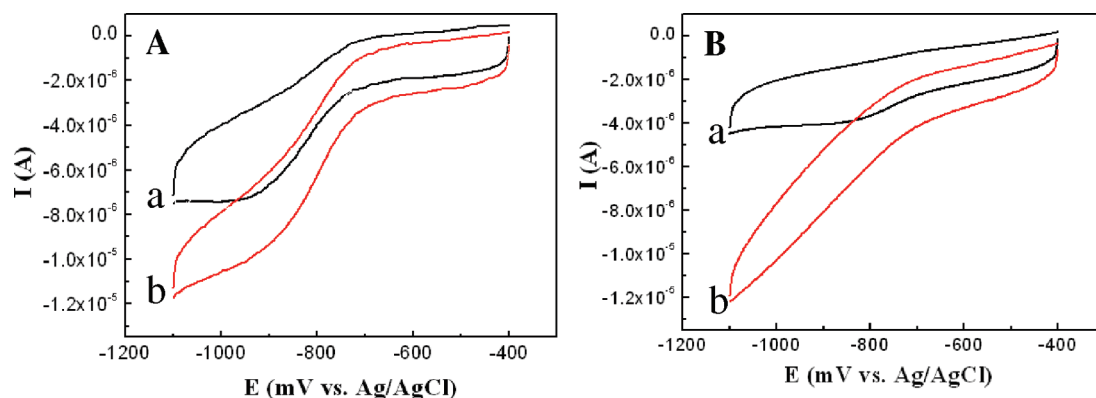


FIGURE 5. Cyclic voltammograms of (A) the DMSOR-CNTs/pyrolytic graphite electrode and (B) DMSOR-nanowires/pyrolytic graphite electrode in 50 mM purged tris-buffe solution (pH 8.0) with $30 \mu\text{M}$ $[\text{Co}(\text{transdiammac})]^{3+}$ mediator in the (a) absence and (b) presence of $115 \mu\text{M}$ DMSO. Scan rate: 20 mV/s.

may provide promising applications on carbon nanotube field-effect transistors, electrochemical detection, and biosensor.

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Supporting Information Available: Electron diffraction pattern of CNT@SiO₂ nanowires, molecular structure of the mediator, cyclic voltammetric of the DMSOR-nanowires/pyrolytic graphite electrode in the presence of increasing DMSO concentrations. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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