Electrochemical Functionalization of Single-Walled Carbon Nanotubes in Large Quantities at a Room-Temperature Ionic Liquid Supported Three-Dimensional Network Electrode

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Electrochemical functionalization of single-walled carbon nanotubes (SWNTs) was one of selective, clean, and nondestructive chemical methods. But in previous studies it met difficulties in homogeneous electrografting of SWNTs in large quantities because the reaction was often localized on a very thin film (ca. 2 μm). In this report, a room-temperature ionic liquid (RTIL) supported three-dimensional network SWNT electrode was first utilized to break through this barrier. In this work, large quantities of SWNTs were considerably untangled in RTILs so as to greatly increase the effective area of the electrode. N-succinimidyl acrylate (NSA), as a model monomer, was dissolved in the supporting RTILs and was electrografted onto SWNTs (SWNTs-poly-NSA). As an application example, glucose oxidase was directly covalently anchored on the SWNTs-poly-NSA assembly, and the electrocatalytic oxidation of glucose in this assembly was investigated. RTILs opened a new path in electrochemical functionalization of SWNTs.

Introduction

Single-walled carbon nanotubes (SWNTs), one kind of truly molecular entity, are of significant interest because of their unique properties and potential applications. In general, SWNTs are assembled and heavily entangled with each other, which makes them difficult to handle for further applications. Tailoring of SWNT hybrid systems is highly anticipated because of the bright and fascinating perspectives. Considerable attempts have been made, such as derivatization of tube ends and sides. Electrochemical functionalization via electro-generation of radicals in the vicinity of the SWNTs sidewall shows several advantages over those derivatization methods. For example, it is a clean and nondestructive chemical modification; it can be used for selective grafting of individual metallic nanotube. Hence, electrochemical functionalization has also been well-developed, such as covalent functionalization via electroreduction aryl diazonium salts. But, in a previous report, it has met difficulties in homogeneous electrografting SWNTs in large quantities because the reaction was often localized on a very thin film (ca. 2 μm) to get a homogeneous electrografting throughout the nanotube layer (as illustrated in Scheme 1a). In comparison with other derivatization methods, the electrochemical functionalization was not so satisfied, especially in homogeneous functionalization of large quantities SWNTs.

Recently, because of their specific properties, such as negligible vapor pressure, low toxicity, high chemical and thermal stabilities, and ability to dissolve a wide range of organic and inorganic compounds, room-temperature ionic liquids (RTILs) have been proposed as "green" alternatives to conventional organic solvents in a range of applications. RTILs have been utilized as a solvent and as a supporting electrolyte for various electrochemical processes. However, functionalization of large quantities SWNTs was not so satisfied, especially in homogeneous functionalization of large quantities SWNTs.

Scheme 1. Methods of Electrochemical Functionalization at the SWNT Paper Electrode (I) and Our Three-Dimensional Network SWNT Electrode (II).
of applications, such as synthesis, catalysis, liquid—liquid extractions, and so forth. Particularly in electrochemistry, they show a relatively wide potential window and high conductivity and allow studies to be undertaken without additional supporting electrolyte. SWNTs could be considerably untangled into much finer bundles that are physically cross-linked in RTILs. Thus, it provides new opportunities for the electrochemical functionalization of SWNTs. In this report, this concept was first utilized to fabricate a kind of RTIL-supported three-dimensional network SWNT electrode (as shown in Scheme 1b). It would greatly increase the effective surface area of the SWNT electrode, and the homogeneous electrochemical functionalization of the SWNTs performed well even in large quantities. N-succinimidy acrylate (NSA), as a model monomer, which bears an active ester group, was dissolved in the supporting RTILs and was electrografted and polymerized onto SWNTs (SWNTs-poly-NSA). As an example of its applications, glucose oxidase (GOx) was directly covalently anchored on the SWNTs-poly-NSA assembly, and the electrocatalytic oxidation of glucose in this assembly was explored.

Experimental Section

Materials. A kind of RTILs, 1-butyl-3-methylimidazolium hexafluorophosphate to BMIMPF₆, Acros, 97%, was prepared with water before use. The received SWNTs (MER Corp., U.S.A.) were refluxed in 3 M nitric acid for 24 h and washed thoroughly with water using a 0.45-µm nylon membrane filter before use. NSA was obtained from Acros (>99%). GOx (EC 1.1.3.4, 200 units/mg, from Aspergillus niger) was obtained from Fluka. 2-(N-Morpholino)ethanesulfonic acid (MES monohydrate, 99.5%) was obtained from Aldrich. All other reagents were of analytical grade and were used as received.

Instruments. All electrochemical experiments were performed in a conventional three-electrode cell with a platinum wire as the auxiliary electrode and an Ag wire or Ag/AgCl (saturated KCl) as the reference electrode with a CHI 832 Electrochemical Workstation (CHI, U.S.A.). Raman spectra were measured on a FT-Raman 960 spectrophotometer (Thermo Electron Corp., U.S.A.) at a resolution of 4 cm⁻¹ (λexc = 1064 nm). X-ray photoelectron spectroscopy (XPS) was conducted using a VG ESCALAB MK II spectrometer (VG Scientific, U.K.) employing a monochromatic Mg Kα source (hv = 1253.6 eV). Peak positions were internally referenced to the C(1s) peak at 284.6 eV.

Preparation of the RTIL-Supported Three-Dimensional Network SWNT Electrode. These preparation processes were schematically illustrated in Scheme 1 (method II). The liquid was added and ground thoroughly. Finally, the black gel was added into the cell on the conductive substrate, such as gold. For further use, NSA grafted SWNTs were collected from BMIMPF₆ and washed thoroughly. After electrografting, for further use, NSA grafted SWNTs were supported three-dimensional network SWNTs network electrode was fabricated. More direct evidence of covalent electrografting was provided using the theoretical hint. The electrochemical method can also initiate such free-radical coupleings just as other free-radical initiators do in the covalent anchoring of polymer to SWNTs. In this report, electrografting NSA, a model monomer, onto SWNTs was attempted. The RTIL-supported three-dimensional network SWNT electrode is in a manner similar to a carbon paste electrode, and the concept here did stem from the carbon paste electrode, however, here it was definitely different. The three-dimensional network SWNTs network electrode was supported with RTILs. Then NSA, which was dissolved in the supporting RTILs, could be considered in the vicinity of the SWNT network (Scheme 1b) and would be expected to be electrografted onto SWNTs homogeneously through the electrochemical reduction.

Preparation of the Enzyme Electrode. GOx suspension. One mg of SWNTs-poly-NSA was dispersed by ultrasonication in 1 mL of activation buffer (0.1 M MES, 0.5 M NaCl, pH 6.0) for 5 min, and 1 mg of GOx was added. After stirring at 4 °C for 24 h, the GOx modified SWNTs-poly-NSA (SWNTs-poly-NSA-GOx) was collected and washed thoroughly by repeated centrifugation and ultrasonication with phosphate-buffer saline (PBS, 0.05 M, pH 7.4). For the enzyme electrode, 3 µL of the SWNTs-poly-NSA-GOx suspension (1 mg/mL in PBS) was dropped on the surface of a gold electrode and allowed to dry at 4 °C for 24 h. For the control experiment, the SWNTs-poly-NSA modified gold electrode was prepared in a similar way but without the SWNTs-poly-NSA-GOx suspension.

Results and Discussion

Very recently, Mylvaganam et al. reported a quantum mechanics prediction which reveals that multiple covalent bonds between the polyethylene chain radical and the nanotube can be formed while proper free-radical generations are used. Such a prediction provided us with the theoretical hint. The electrochemical method can also initiate such free-radical coupleings just as other free-radical initiators do in the covalent anchoring of polymer to SWNTs. In this report, electrografting NSA, a model monomer, onto SWNTs was attempted. The RTIL-supported three-dimensional network SWNTs network electrode was fabricated. More direct evidence of covalent electrografting was provided using the theoretical hint. The electrochemical method can also initiate such free-radical coupleings just as other free-radical initiators do in the covalent anchoring of polymer to SWNTs. In this report, electrografting NSA, a model monomer, onto SWNTs was attempted. The RTIL-supported three-dimensional network SWNT electrode is in a manner similar to a carbon paste electrode, and the concept here did stem from the carbon paste electrode, however, here it was definitely different. The three-dimensional network SWNTs network electrode was supported with RTILs. Then NSA, which was dissolved in the supporting RTILs, could be considered in the vicinity of the SWNT network (Scheme 1b) and would be expected to be electrografted onto SWNTs homogeneously through the electrochemical reduction.

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to NSA. The disorder mode is the diagnostic of disruptions in the hexagonal framework of the SWNTs; the fact that the relative intensity of this mode increased after grafting confirmed this covalent modification of the SWNTs. For each sample, Raman spectra were collected at several different spots, where no distinctive difference was found. Hence, the functionalization was considered to be homogeneous. The experiment without NSA addition also confirmed that these conditions did not affect the nanotubes, as verified by Raman spectroscopy.

N(1s) XPS spectra provided us a further evidence of this successful grafting from the side of poly-NSA. Figure 3 shows the N(1s) XPS spectra of SWNTs-poly-NSA (a) and original NSA (b). The binding energy of N(1s) of succinimidyl groups almost did not change when NSA was grafted on SWNTs. It indicated that the active succinimidyl groups were retained; that is, NSA was modified on SWNTs. It agreed with the Raman result. Only a slight decrease of N(1s) binding energy (ca. 0.1 eV) was observed, which should be ascribed to the increase of electron density of N after polymerization. Finally, we can confirm that the NSA was successfully electrografted on SWNTs through a free-radical polymerization and the active succinimidyl groups were also retained. And such a product, SWNTs-poly-NSA, shows a benefit to anchor a large variety of nucleophiles, such as enzyme, through active succinimidyl groups.

Compared with heavily entangled SWNTs in a paper electrode (Scheme 1a), SWNTs in the RTIL-supported three-dimensional network electrode (Scheme 1b) are considerably untangled into much finer bundles. In this work, the dispersion of SWNTs in the RTIL network highly increases the effective area for electrografting. Then much larger amounts of SWNTs can be reacted, and it results in less critically in homogeneity. Figure 4 shows photographs of NSA-grafted SWNTs (a) and unreacted SWNTs (b) dispersed in dimethylformamide (DMF) solution for 3 h after ultrasonication (separated from the RTIL-supported three-dimensional network SWNT electrode after and before electrografting, respectively).
NSA-grafted SWNTs show much better solubility in DMF, suggesting that large amounts of SWNTs were electrografted.

Potential Applications of SWNTs-poly-NSA. Because SWNTs-poly-NSA bears an ester group, which is highly reactive toward nucleophiles, GOx, as an example, was directly covalently anchored on SWNTs-poly-NSA-GOx (solid) and SWNTs-poly-NSA (hollow) modified gold electrodes. Scan rate: 50 mV/s.

Figure 5. LSV curves of electrocatalyzed oxidation of glucose in 0.05 M PBS (pH 7.4) on the SWNTs-poly-NSA-GOx electrode at different concentrations of glucose: 0, 4, 8, 12, 16, and 20 mM from bottom to top. The inset is the calibration curve corresponding to amperometric responses at the SWNTs-poly-NSA-GOx (solid) and SWNTs-poly-NSA (hollow) modified gold electrodes. Scan rate: 50 mV/s.

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Role of RTILs. BMIMPF₆ plays a key role in the supported three-dimensional network SWNT electrode and homogeneous functionalization of SWNTs in large quantities via electrochemical reactions. Upon milling in BMIMPF₆, entangled high conductive SWNTs were considerably untangled as so as to form a cross-linking three-dimensional network electrode, while in other solvents such as dichlorobenzene, ethanol, and DMF, SWNTs do not. The relatively high viscosity and the delocalized π interaction between them provided us a possibility to fabricate this specific structure. And the high conductive BMIMPF₆ could also act as a supporting electrolyte itself. Furthermore, BMIMPF₆ shows a good solubility toward this monomer, NSA, which can be dissolved well in the vicinity of SWNTs. The large potential window of BMIMPF₆, which could bear such a relatively negative potential, also shows great favorableness in this electrochemical grafting. Besides, initiation of this free-radical polymerization in RTILs had been demonstrated to be advantageous over those in common solvents.

Conclusions

In summary, the application of the RTIL-supported three-dimensional network SWNT electrode overcame the difficulties of homogeneous electrochemical functionalization of SWNTs in large quantities. Such NSA-grafted SWNTs also provided a unique opportunity for biological applications of SWNTs. RTILs opened a new method in electrochemical functionalization of SWNTs. A similar concept would be useful for other applications of RTILs, such as electrosynthesis, chemical sensors/biosensors, electrocatalysis, and so forth.

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