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Carbon nanotubes/kraft lignin composite: Characterization and charge storage properties

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ABSTRACT

The results of this study demonstrate the spectral, microscopic and electrochemical properties of multi-walled carbon nanotubes (CNTs) surface-functionalized with kraft lignin (KL). XPS and FT-IR spectroscopy show that the biomolecule is effectively adsorbed on the surface of CNTs, leading to an increase in oxygen content and the appearance of spectral features characteristic of highly oxidized polyphenolic compounds. The presence of KL makes CNTs easily dispersible in organic (DMSO) and aqueous (0.1 M ammonia) solutions. Microscopic analysis (SEM and AFM) confirms the effective debundling of CNTs and the presence of densely packed globular structures on the surface of individual nanotubes. Deposition of the CNT/KL composite on the surface of a gold electrode facilitates its electrochemical characterization. This reveals that the CNT-supported biomolecule exhibits persistent reversible redox behavior attributed to KL-derived quinone moieties. Therefore the reversible redox activity of the lignin adsorbate can be utilized for charge storage, providing more than a 100% increase in the capacitance of KL-modified carbon nanotubes compared with unmodified ones.

1. Introduction

Carbon nanotubes (CNTs) have attracted a great deal of attention since their discovery, due to their exceptional electronic, mechanical and electrochemical properties [1,2]. Nevertheless, applications of CNTs are significantly limited due to their bundled structure, which results in poor if any solubility in common solvents, especially water. Various approaches have been proposed and studied to enable the debundling of CNT aggregates and thus facilitate the formation of stable CNT solutions. These include chemical (oxidative) treatment of CNTs to effect the partial destruction of the continuous sp^2-hybridized carbon lattice and to introduce ionogenic – mostly carboxylic – functionalities into it [3,4], or the grafting of certain solvent affinity groups onto the surface of CNTs [5,6]. The chemical routes used to modify the surface of CNTs are the subject of a review by Tasis et al. [7]. Such approaches may be considered covalent, since they alter the molecular structure of pristine CNTs or form new covalent bonds with them. By contrast, noncovalent functionalization routes are believed to be more promising, since the electronic structure of the tubes can be better preserved. It therefore becomes increasingly important to explore novel dispersants that might functionalize CNTs in easy and nondestructive ways. The approaches reported so far include uniform wrapping of CNTs with synthetic polyelectrolytes such as polyacrylic acid [8], siloxane polyethers [9], polydiallydimethylammonium chloride [10] and quaternized polyvinylpyridine [11], or polymers of biological origin, for instance DNA [12], polysaccharides [13], chitosan and its derivatives [14,15] or hyaluronic acid [16]. In the case of polymers containing aromatic moieties, the CNT-polymer interactions appear remarkably strong due to possible $\pi-\pi$ stacking. For this reason natural poly-phenolic biopolymers seem especially attractive, since they are easily obtainable from renewable resources, and offer low toxicity and a high degree of biocompatibility. Among these, humic substances [17] and tannic acid [18] are the most representative examples of such biopolymers. The structurally similar lignins are even more promising, since they are byproducts of the paper industry, obtained in vast quantities of over 45 million metric tons per year [19]. They are also available in different molecular weights and as chemically modified products tailored to certain applications [20,21].

Although lignins have found many applications outside the pulp and paper industry [22], they have only limited applications in practical electrochemistry. For instance, lignosulfonates have been used as poly-anions to dope chemically synthesized polyaniline [23] or to prepare molecular assemblies with poly(o-ethoxy)aniline [24,25]. The same type of lignin can be electropolymerized on steel for anticorrosion protection [26]. The addition of lignosulfonates to the negative paste of lead-acid batteries was reported to have a positive effect in terms of battery

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performance [27]. Recently we have shown that different sorts of lignins can be adsorbed on metallic [28,29] or glassy carbon electrodes [30,31] for the assembly of electrochemical sensors. We have also shown that the adsorbing capability of lignins can be extended to nanostructured carbons such as CNTs, and the nanocomposites eventually obtained exhibit high electrochemical activity and valuable electrocatalytic properties when deposited on pre-activated glassy carbon electrodes [32].

It is generally accepted that the redox chemistry of ortho- and para-quinones involves elementary steps comprising $2H^+$ and 2e for the quinone/hydroquinone (Q/QH_2) reaction. This means that two electrons and two protons are stored in a structure of 6 carbon and 2 oxygen atoms, giving a charge density of 2 faraday per 108 g, i.e. 1787 C/g or 496 mAh/g. This is a favorable value compared with standard electrochemical systems; in lithiated carbon materials a maximum doping level is 6 carbons per lithium, equivalent to 344 mAh/g, and in the olivine $FePO_4$ system the value is 170 mAh/g [33]. Hence it is desirable to use the quinone redox function in electroactive materials to enhance charge storage capacity. As a matter of fact, different approaches have been proposed to enable the reversible saving/extraction of electrons in quinone-type moieties. In the simplest cases, quinone was added to the electrolyte in a supercapacitor, leading to enhanced performance due to the pseudocapacitive effect occurring at the porous electrode/electrolyte interface [34]. Quite a similar effect was achieved using as the electrolyte additive sulfonated lignin derivative (lignosulfonate). The surfactant properties of this biopolymer along with the quinone moieties spread randomly throughout its structure led to increased wettability of the electrode materials, generating a higher double layer capacitance, and to the formation of a redox active biofilm responsible for measurable pseudocapacitance [35]. Finally, in a very recent report we showed that lignosulfonate incorporated into electrochemically grown poly-pyrrole can serve as an effective material for reversible charge storage, owing to the presence of highly active quinone moieties [36].

Here, we report a detailed study of the spectroscopic, microscopic and electrochemical properties of the kraft lignin (KL)/CNT nanocomposite. These will comprise XPS, FT-IR, SEM, AFM, cyclic and differential pulse voltammetry. We will also demonstrate the feasibility of the application of this novel nanocomposite as an energy storage material using galvanostatic charging/discharging.

2. Experimental

2.1. Materials

Multi-walled carbon nanotubes were synthesized by catalytic decomposition of acetylene on in situ formed cobalt nanoparticles. They had diameters of 10–15 nm [37]. Kraft lignin was obtained from Aldrich. Redistilled water was used to prepare all solutions. Dimethylsulfoxide (DMSO) was obtained from POCH (Gliwice, Poland).

2.2. Preparation of CNT/KL nanocomposite and its assembly on a gold electrode

A solution of KL at a concentration of 5 mg cm^{-3} was prepared using 0.5 M H_2SO_4/acetonitrile (1/3, v/v) as the solvent. The quantity of 2.5 mg CNTs was added to 5 ml of the KL solution, and the suspension was vigorously mixed for 15 min using an ultrasonic bath. Then the suspension was centrifuged at 5000 rpm for 10 min to separate the KL-modified CNTs from the KL-solution. After removal of the supernatant, the CNT/KL composite was re-dispersed in a KL-free solvent, sonicated and centrifuged again to wash away weakly bound KL from the composite. The washing/centrifuging protocol was repeated four times, and the suspension eventually obtained was vacuum-filtered. The collected modified CNTs were dried at 40 °C for 3 h. The powder thus obtained was re-dispersed in DMSO. The suspension was used to prepare cast films of the CNT/KL composite on a gold electrode by placing 2.5 μl of the suspension on the working surface of the electrode and allowing it to dry out at 60 °C.

2.3. Spectroscopic characterization

FT-IR spectra of parent and modified CNTs were recorded using a Bruker IFS66 v/S FT-IR spectrometer with KBr pallets (0.1 mg of sample per pallet).

XPS spectra of the CNTs and CNT/KL nanocomposite were obtained with a VSW photoelectron spectrometer (Vacuum Systems Workshop Ltd. England) using non-monochromatized Al Kα radiation (1486.6 eV). The radiation source operated at 15 kV and 14 mA. The vacuum pressure was always kept at around 3×10^{-8} mbar. The binding energy scale was corrected by referring to the aromatic peak of the C1s spectrum as 284.6 eV.

2.4. Microscopic analysis

The surface morphology of the cast films of unmodified CNTs and CNT/KL composite was investigated under a scanning electron microscope (Philips SEM 515).

AFM imaging was performed using a Nanosurf EasyScan 2 AFM microscope operating in tapping mode with a PPP-NCLR tip (Nanosensors^{TM}). The WSxM 4.0 software [38] was used to process the collected images.

2.5. Electrochemical characterization

Before its modification, the working electrode (polycrystalline gold, 1.0 mm diameter) was polished with alumina slurries of 1.0 and 0.05 μm on a Buehler polishing cloth with water as lubricant, rinsed with water, and sonicated in a water bath for 3 minutes. The electrode was then electrochemically activated in 1 M H_2SO_4 by cyclic voltammetry between −0.2 and 1.7 V for 15 scans at 0.1 V s^{-1}. The electrode was then surface modified with the CNT/KL composite (vide supra). The modified electrode thus obtained was pre-oxidized at +1.0 V for 5 minutes to transform some electroactive groups of the biopolymer into reversible redox couples [28,30,31]. All electrochemical measurements were carried out using a μAutolab electrochemical analyzer (EcoChemie, Utrecht, Netherlands) connected to a PC for control, data acquisition and storage. A standard three-electrode configuration, consisting of modified working, reference and counter electrodes, was incorporated into a glass cell (volume 20 cm^3). The supporting electrolytes were degassed with a stream of purified nitrogen for 20 min prior to the measurements. The counter electrode was a platinum wire. All potentials reported in this paper are referenced to an Ag/AgCl (3 M NaCl) electrode, with no account taken of the liquid junction potential.

3. Results and discussion

3.1. Spectroscopic studies of the CNT/KL composite

3.1.1. XPS spectroscopy

The chemical structure of pristine and modified CNTs was studied by the XPS and FT-IR techniques. XPS can yield information on the chemical structure of CNTs and the presence of defects, and has been routinely used to track different modification procedures [39].

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