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We report on the properties of electrochemically modified SWCNTs bearing a functional organic layer and a low density of noble metal nanoparticles, respectively. First, a novel approach to nanoscale pH sensors is demonstrated which involves the gentle modification of individual metallic tubes via covalent attachment of amino-substituted phenyl groups. Furthermore, gold particles with sizes of a few tens of nanometres deposited onto individual SWCNTs were found to locally enhance the Raman signals of the underlying nanotube. The enhancement imparted by individual gold particles was estimated to be two orders of magnitude.

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1 Introduction

Electrochemistry has proven to be a versatile approach to functionalize carbon nanotubes [1]. The electrochemical modifications (ECMs) explored so far consisted of the attachment of organic functional groups or electrodeposition of metals. To date, ECM has been mainly applied to bulk samples of multi-walled (MWCNTs) [2] and single-walled carbon nanotubes (SWCNTs) [3]. The few existing reports of individual tube functionalization via electrochemistry have focused on the nature of interfacial bonding between nanotube and deposited molecular layers [4] and the fabrication of single-molecule electronic devices [5]. A major advantage of electrochemical methods for chemical functionalization of individual tubes is the possibility to precisely control their functionalization degree. In the present contribution, we report two novel applications of ECM to individual SWCNTs, namely the covalent functionalization of metallic SWCNTs with the aim of realising chemical sensors, as well as the electrodeposition of gold onto SWCNTs in order to explore the Raman enhancement resulting from the presence of intimately attached gold nanoparticles.

Chemical sensors based upon SWCNTs normally comprise a semiconducting nanotube channel implemented into a field-effect transistor (FET) configuration. Such devices operate either as chemiresistors or in a CHEMFET mode [6]. In both cases, the tubes can be provided with suitable coatings that enable recognition of targeted analyte molecules [7]. Similar coatings can serve to enhance the sensor

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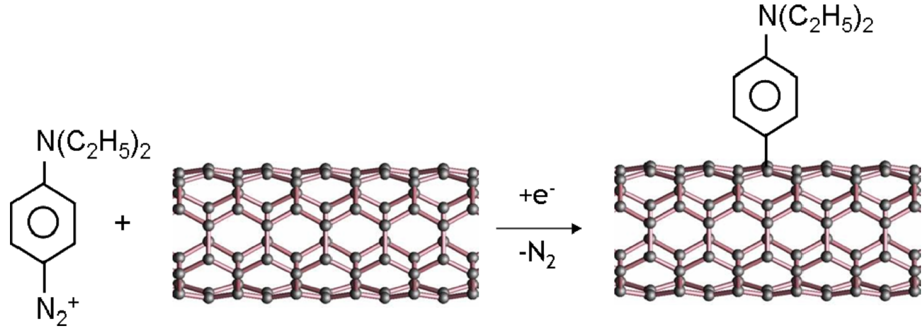

Fig. 1 (online colour at: www.pss-b.com) Schematic depiction of the covalent attachment of N,N-diethylaniline groups, using the corresponding diazonium salt as coupling agent, to a SWCNT for the purpose of rendering it sensitive towards protonation.

lifetime or the sensitivity of the sensors [8]. Here we describe a novel methodology to obtain chemical sensors from metallic SWCNTs, as exemplified by the fabrication of pH sensors [9]. It involves the covalent attachment of phenyl rings bearing basic amino groups (see Fig. 1), following the well-established diazonium coupling scheme [10]. For this purpose, the functionalization degree was controlled in order to achieve a useful sensor response without too strongly deteriorating the tube's carbon framework so that a minimum required electrical conductivity is preserved.

Regarding surface-enhanced Raman spectroscopy (SERS) of carbon nanotubes, previous investigations have mainly used bulk substrates like silver-coated filter paper [11] or metal colloid assemblies [12]. While these studies clearly revealed Raman enhancements attributable to strong local electromagnetic fields at the substrate surface, the detailed enhancement mechanism could not yet be clarified. As a first step towards this end, we have utilized ECM to decorate SWCNTs with gold nanoparticles (NPs) whose sizes range between 10 nm and 100 nm. The low NP coverage enabled us to directly compare bare and particle-modified sections on the same tubes.

2 Experimental

SWCNTs were synthesised on n^+-Si/SiO_2 substrates (100 nm oxide thickness) by chemical vapour deposition growth utilising iron nanoparticles as catalyst and ethanol as carbon feedstock. The tubes were provided with AuPd (60/40) electrodes (15 nm thickness) through standard e-beam lithography. Prior to ECM performed inside an electrochemical cell equipped with platinum wires as reference and counter electrodes, the samples were cleaned by thermal annealing at 250 °C for 60 min under argon atmosphere.

The covalent attachment of N,N-diethylaniline groups to metallic SWCNTs was accomplished by applying –0.45 V vs. Pt for 30 s in N,N-dimethylformamide (DMF) containing 0.1 mM 4-diazo-N,N-diethylaniline tetrafluoroborate and 0.1 mM $LiClO_4$ as supporting electrolyte. Measurements of the electrical resistance of the tubes during their electrochemical modification were performed with a lock-in amplifier. Electrodeposition of gold was carried out using an aqueous deposition solution (pH 2) containing 2 mM $KAuCl_4$, 5 mM poly-N-vinyl-2-pyrrolidone as stabilizer and 0.1 mM $LiClO_4$ as supporting electrolyte, by applying a potential of –0.8 V vs. Pt for 10–30 s.

The optical studies were performed on nanotubes covered with non-aggregated NPs, using a home-built confocal microscope operated under ambient conditions. For imaging and localization, the sample was scanned through the focus of a high numerical aperture objective (NA = 0.95), while the emitted light was collected with the same objective and guided through a monochromator to an Avalanche photo diode. Raman images were recorded by detecting the Raman G-line at 1595cm^{-1}. Raman spectra were recorded with laser powers of 0.1–1 mW at the entrance of the microscope and integration times between 1–300 seconds.

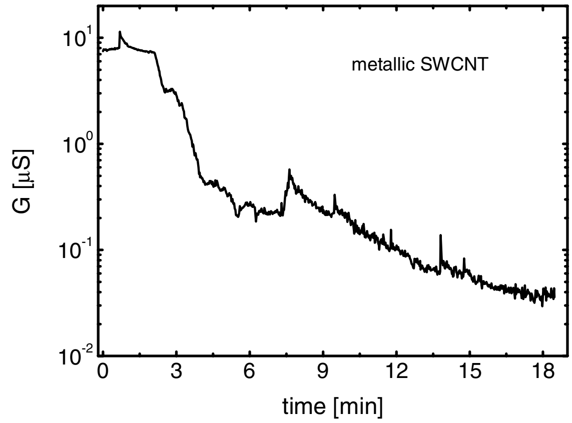

Fig. 2 Electrical conductance of an individual metallic SWCNT measured *in-situ* during the ECM involving the reductive coupling of 4-diazo-N,N-diethylaniline tetrafluoroborate.

3 Results and discussion

3.1 Chemical sensors from individual metallic SWCNTs

In Fig. 2, the *in-situ* measured electrical conductance of an individual metallic SWCNT is plotted as a function of electrochemical modification time, for ECM being performed according to the scheme in Fig. 1. As expected, the covalent modification decreases the nanotube conductance. The relatively slow time scale of this decrease allows precise stopping of the experiment when the tube has reached a desired conductance value.

The effect of covalently linking an increasing amount of amino-substituted phenyl rings is exemplified in Fig. 3, which displays the gate-dependent resistance of an individual metallic SWCNT before and after three consecutive ECMs. It is noteworthy that all three steps belong to a functionalization regime where the nanotube is not densely covered by the attached residues. At all functionalization degrees, the tube displays only weak gate dependence, indicating that the introduction of the groups does not open a gap in its electronic band structure. The slight resistance modulation by the gate voltage can be attributed to the attached moieties inducing impurity states near the Fermi level that act as scattering centres [13].

The pH response of metallic SWCNTs changes significantly after the covalent attachment of diethylaniline groups. Specifically, while the resistance of unmodified tubes remains essentially unaltered upon changing the pH of the aqueous solution, the resistance of aniline-modified tubes depends notably on the solution pH. The resistance of the modified tubes was found to increase by a factor of ~3 when the pH is raised from 4 to 10.

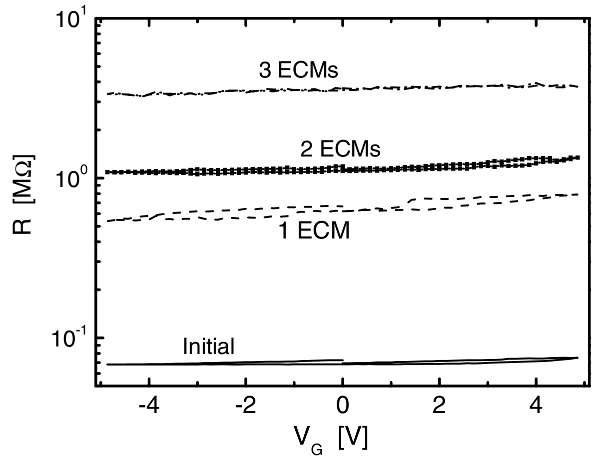

Fig. 3 Plot of electrical resistance (measured under ambient conditions) vs. back gate voltage of an individual metallic SWCNT before modification and after three consecutive electrochemical modification steps (ECMs) using 4-diazo-N,N-diethylaniline tetrafluoroborate.

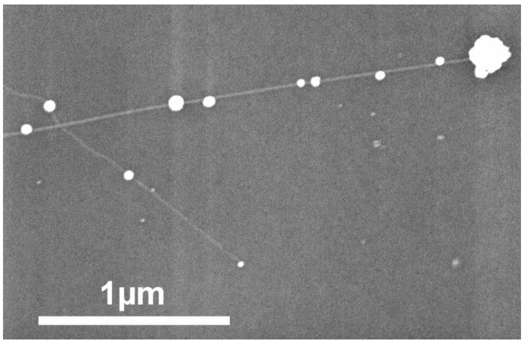

Fig. 4 SEM image of two SWCNTs after electrodeposition of gold. The electrode used for applying the potential is located on the left side, outside the scope of the image. The large particle agglomeration at the end of the upper tube demonstrates enhanced electrochemical activity at the highly curved tips or defective endings.

A range of control experiments, involving for example ionic strength variation, confirmed that the resistance change is indeed linked to the pH change. Although the detailed mechanism of the pH sensitivity remains to be determined, we propose a model according to which the scattering strength of the diethylaniline groups depends on their protonation degree. Future theoretical work is needed to test the viability of this model.

3.2 SERS study of gold nanoparticle-decorated SWCNTs

A representative example of SWCNTs bearing a low density of electrodeposited gold NPs is depicted in Fig. 4. Raman imaging of such samples revealed that many but not all of the present NPs lead to a local enhancement of the Raman peaks belonging to the underlying nanotube.

Figure 5 compares Raman spectra recorded from a bare section and a gold NP-decorated section on the same individual SWCNT. Both the RBM and the G-line of the tube show an enhancement by a factor of ~6 due to the presence of the metal particle.

In order to determine the effective Raman enhancement, it has to be taken into account that the local plasmon field decays rapidly with distance from the NP surface. By assuming that only a short nanotube section with a length on the order of a few nanometres experiences significant field strength, and considering that the diffraction limited laser spot has a diameter of ~500 nm, the local (effective) enhancement is estimated to be two orders of magnitude. Similar enhancement factors were observed on numerous other samples. The magnitude of enhancement is in good agreement with theory [14]. It should be emphasised that the intimate contact between the NPs and SWCNTs, as ensured by the electrodeposition procedure, turned out to be crucial for attaining Raman enhanced signals. This conclusion is based upon the absence of Raman enhancement in case of simply decorating the tubes by gold colloid particles from solution, despite the close physical association between tubes and particles discernable from AFM images.

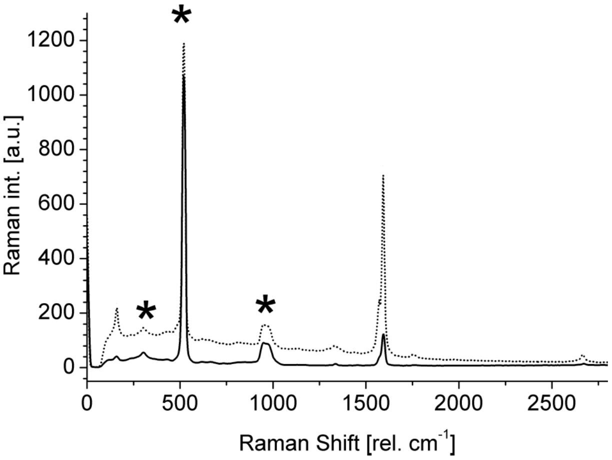

Fig. 5 Raman spectra acquired from an unmodified (full line) and a gold NP-decorated (dotted line) section on an individual SWCNT (λ_{exc} = 568 nm). Peaks originating from the Si/SiO$_2$ substrate are marked by a star.

4 Conclusion

With the aid of controlled electrochemical functionalization, we have successfully devised a novel approach to chemical sensors starting from individual metallic SWCNTs. The employed strategy of covalently linking a low density of functional groups to the sidewall of the tubes, which largely preserves their electrical properties, is promising for the development of nanotube-based sensors suitable for the detection of a wide range of (bio-)chemical species.

Furthermore, SWCNTs partially decorated by metal NPs have been proven as a valuable test bed for investigating the SERS effect arising from metallic nanostructures. Our current studies aim to unravel the factors determining whether a metal NP locally enhances the Raman response. Moreover, SWCNTs decorated with alternative metals like silver are examined in order to identify possible charge transfer contributions to the Raman enhancement.

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