Carbon nanotube stabilised emulsions for electrochemical synthesis of porous nanocomposite coatings of poly[3,4-ethylene-dioxythiophene]†

Chuang Peng,[a] Graeme A. Snook,[ab] Derek J. Fray,[b] Milo S. P. Shaffer[bc] and George Z. Chen*[ab]

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The amphiphobic nature of carbon nanotubes allows them to stabilise droplets of water-insoluble monomers dispersed in the aqueous nanotube suspension, leading to a flexible route to electrochemical synthesis of useful nanoporous composites of nanotube doped conducting polymers, and potentially to other chemistry involving reactants incompatible in the same medium.

Doping a conducting polymer with negatively charged carbon nanotubes (CNTs) enhances both electronic and ionic conductivity in the polymer, even at the fully reduced insulating state. It has been achieved by electrochemical co-deposition of negatively charged CNTs and polypyrrole or polyaniline from aqueous media.[1a] The resulting composite coatings have very high electrode capacitance in comparison with the polymer alone.[1b,1c] These successes have taken advantage of the good solubility of pyrrole and aniline in water. For many other monomeric compounds, an organic solvent is preferred, in which it is difficult to disperse CNTs. For example, poly[3,4-ethylene-dioxythiophene] (PEDOT) responds in a fast, reversible and stable manner to relatively large potential perturbations, and has been investigated for applications in supercapacitors.[2] However, EDOT (the monomer) is scarcely soluble in water, and no attempt has yet been made to use the co-deposition process to make the PEDOT–CNT composite; although such composites could be made by other methods, they are associated with some loss of electrochemical activity.[3]

In this work, 5 ml acetonitrile solution of EDOT (0.25 mol L^{-1}) were added to an equal volume of water, with or without a colour indicator (*e.g.* $CuCl_2$), and sonicated in a bath for 10 min. After sonication, phase separation occurred immediately, giving rise to an obvious, upper, organic phase with a golden colour due to dissolved EDOT; the volume, 2 ml, of the upper phase suggested that more than half of the acetonitrile remained partitioned in the water. Repeating this procedure but replacing the aqueous phase with an aqueous suspension of acid-treated multiwalled CNTs (0.3 wt%) led to a mixture that remained visually uniform for hours.† Acid treatment of CNTs was described previously.[4a]

This metastable organoaqueous emulsion was deaerated with argon and used directly for potentiostatic (1.0 V) polymerisation, without the addition of any other electrolyte. The working electrode was a 1.6 mm Pt or 6 mm graphite disc used in conjunction with a Ag/AgCl (3 mol L^{-1}) reference and a Pt wire counter electrode. After passing an appropriate charge, the electrolysis was terminated, and a smooth and coherent black coating was observed on the working electrode.

Under the scanning electron microscope, a series of shallow craters, up to a few hundreds of micrometers in diameter, were seen on the surface of the coating, see Fig. 1a. Also, smaller craters with or without a bank ring appeared at the bases of the large ones. Fig. 1b is a higher magnification image of the crater's base, and shows a network of nanofibrils with a degree of local alignment that has been reported previously in dried CNT suspensions.[4a] These nanofibrils were identified as PEDOT coated CNTs by their uneven surface, their diameter (30–50 nm *versus* 10–30 nm for the untreated CNTs), and also energy dispersive X-ray analysis.† The measured atomic composition of the crater base was typically of 81 at.% C, 15% O and 4% S. The sulfur confirms the presence of PEDOT but compared with the pure composition (6 C : 2 O : 1 S), there was excess C and O, apparently from the oxidised CNTs. The bank rings were found to be hollow in many cases, see Fig. 1c, and were also composed of PEDOT coated CNTs with atomic compositions more typically of 87 at.% C, 12% O and 1% S, indicating a lower PEDOT concentration.

The unique surface morphology of the PEDOT–CNT coating in Fig. 1a is new, and deserves more discussion. It is known that CNTs, particularly after acid treatment (partial oxidation), have both hydrophobic (graphene layer) and hydrophilic (hydroxyl and carboxylic groups) surface functionalities.[4b] This dual functionality (amphiphobicity) may stabilise CNTs at the interfaces between the aqueous and organic phases.[4c] Because of the small sizes of CNTs,

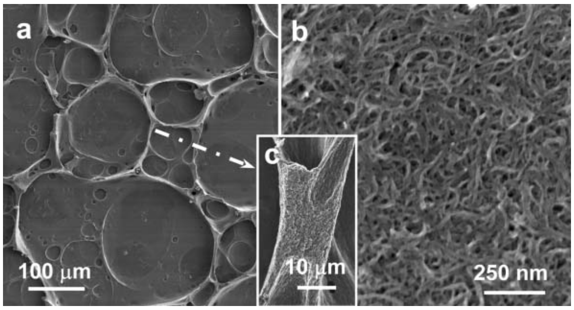

Fig. 1 SEM images: (a) the surface of the PEDOT–CNT coating, and typical enlarged images of (b) the base and (c) the bank of craters in (a). The coating was grown at a deposition charge of 0.3 C cm^{-2}.

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[a] *School of Chemical, Environmental and Mining Engineering, University of Nottingham, University Park, Nottingham, UK NG7 2RD. E-mail: george.chen@nottingham.ac.uk; Fax: +44-115-9514115; Tel: +44-115-9514171*
[b] *Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street, Cambridge, UK CB2 3QZ*
[c] *Department of Chemistry, Imperial College of Science Technology & Medicine, Imperial College Road, London, UK SW7 2AZ*

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formation of sufficiently stable or metastable droplets of one phase dispersed in another may be achieved with the CNTs functioning as an interfacial barrier hindering droplet coalescence.[4d,4e] Because the hydrophilic and hydrophobic groups are arranged along the surface, the CNTs are more likely to lie parallel with the interface, rather than perpendicular to the interface in the manner of conventional surfactant molecules with a hydrophilic head group and hydrophobic tail; it may also suggest that CNTs can only stabilise relatively large droplets and not micelles, due to their relatively high stiffness. Although the emulsion is stabilised, the electrodeposition process must introduce a number of dynamic changes, because EDOT cannot transport through the aqueous phase and CNTs are not able to enter the organic phase.

In the current experiments, the organic phase contained mainly EDOT and acetonitrile. During deposition, the organic droplets near the electrode surface presumably shrank as the EDOT was consumed by electropolymerisation, and the accompanying acetonitrile diffused into the neighbouring aqueous phase. Once the first round of droplets was deposited in this way, further droplets could move in from the solution, giving rise to subsequent craters. Note that the CNTs maintained the conductivity of the electrode surface, allowing the electrodeposition to continue.

The initial growth of the coating should result in small craters when the droplets of either aqueous or organic phase were relatively small. With electrolysis continuing, the aqueous droplets would grow larger, leading to larger craters on top of the earlier formed small ones, in accordance with what is shown in Fig. 1a. Because EDOT was less soluble in the aqueous phase (but may still polymerise to cover the small craters formed earlier), polymerisation was more likely to occur in the remaining organic phase between the large aqueous droplets, resulting in the observed hollow structure in the bank of the crater.

The relatively flat base of the crater, particularly of the larger ones, might have resulted from flattening of the aqueous droplets as they wet the surface of the composite coating. However, simple collapse upon drying is suggested by the fibrils in Fig. 1b which lie parallel to the electrode surface.[4a]

In this work, the CNT stabilised emulsions were used for several PEDOT–CNT composite depositions before phase separation occurred. The metastable emulsion could also be regenerated after phase separation by ultrasonication as long as the consumption of CNT and EDOT was not too great. Coatings obtained from these re-used or re-generated mixtures exhibited surface morphologies similar to that shown in Fig. 1a.

After deposition, the PEDOT–CNT-coated electrodes were rinsed in distilled water and transferred, together with the reference and counter electrodes, to an aqueous solution of 0.5 mol L^{-1} KCl for cyclic voltammetry and electrochemical impedance spectrometry. Fig. 2 compares the voltammograms of freshly and similarly made thin coatings of the composite and pure PEDOT in the same electrolyte. A voltammogram of the same composite coating recorded after 5000 charge–discharge cycles is also superimposed. In agreement with previous studies on co-deposition of composites of CNTs and other conducting polymers,[1] the PEDOT–CNT composite responded to the potential cycling with much larger currents than the pure PEDOT coating. When the potential scan was limited to a smaller but more positive range, where the polymers remained in the oxidised/doped state, typical capacitive behaviour, *e.g.* rectangular current–potential curves, was observed as shown in Fig. 2. Because the currents on such rectangular curves are directly linked to the capacitance (= current/potential scan rate), it is clear that the composite electrode was much greater in capacitance.

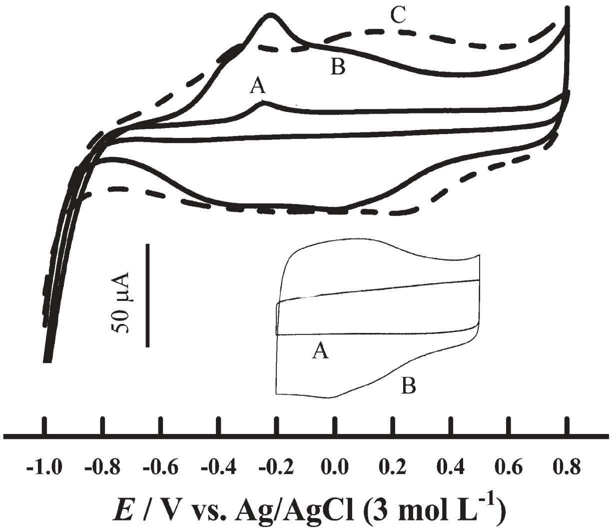

Fig. 2 Cyclic voltammograms of (A) first cycle of pure PEDOT prepared in 0.25 mol L^{-1} EDOT + 0.5 mol L^{-1} $LiClO_4$ in acetonitrile, and of (B) the fresh and (C) that after 5000 charge–discharge cycles of PEDOT–CNT prepared in the 1 : 1 (v/v) mixture of acetonitrile solution of 0.25 mol L^{-1} EDOT and aqueous suspension of 0.3 wt% acid treated CNTs. Deposition potential and charge: 1.0 V and 0.3 C cm^{-2}. Potential scan rate: 20 mV s^{-1}. Electrode substrate: 1.6 mm diameter Pt disc. Electrolyte: 0.5 mol L^{-1} KCl in water.

Besides the variation in peak currents, Fig. 2 also shows that the electrochemistry of the composite seems to have changed, particularly after continuous charge–discharge cycling. Although not yet fully explored, it is worth mentioning that the composite coating was doped, at least partially, by the large and negatively charged CNTs that were immobile. Thus, both cation (K^+) and anion (Cl^-) from the electrolyte may participate in the redox processes during potential cycling.[1a,1d] This mixed ion character is in contrast with pure PEDOT in which only the anion is involved during potential cycling.

Putting aside the larger scale porosity associated with emulsion templating, the local microstructure of the PEDOT–CNT composite coatings shown in Fig. 1b closely resembles that of previously reported CNT composites with other conducting polymers.[1,3] The larger voltammetric current and higher electrode capacitance can therefore be attributed to a number of effects from CNTs: (1) the provision of interconnected pathways for electrons through the CNTs and ions through the pore network, regardless of the conductivity of the polymer; (2) the thinness of the PEDOT layer on each CNT, minimising barriers both to ion transfer across the polymer/electrolyte interface and ion transport within the polymer phase; (3) the role of smaller cations in charge balancing due to the presence of the immobilised negatively-charged CNTs.[1,3]

The deposited coatings were scraped off the electrode and analysed by infrared (IR) spectrometry. It was found that the PEDOT–CNT composite retained the IR features of doped pure PEDOT even at very negative potentials where similarly prepared

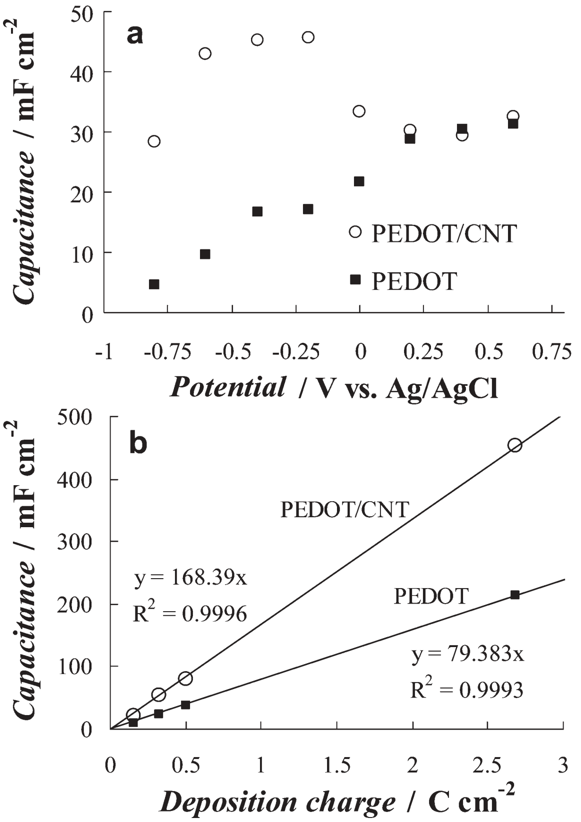

Fig. 3 Plots of electrode capacitance against (a) electrode potential for coatings with a deposition charge of 0.3 C cm^{-2}, and (b) deposition charge of PEDOT–CNT composite coatings (empty circles) and pure PEDOT coatings (filled squares) measured at 0.0 V *vs.* Ag/AgCl (3 mol L^{-1}) by electrochemical impedance spectrometry in 0.5 mol L^{-1} KCl.

pure PEDOT was already reduced (dedoped), exhibiting a noticeably different IR spectrum.† This IR property of the composites can be attributed to CNTs being capable of enhancing electron delocalisation along the polymer chains.[1c] This attribution also agrees with the capacitance measurement in this work by electrochemical impedance spectrometry, see Fig. 3a. The higher capacitance of the composite at more negative potentials reflects well the roles of CNTs as discussed previously.

The capacitance of the coatings would be expected to increase with increasing thickness (deposition charge), as more polymer is added to the electrode. The capacitance of a series of composite coatings, grown at larger deposition charge (for a longer time), was therefore measured by electrochemical impedance spectrometry in 0.5 mol L^{-1} KCl. Fig. 3b shows that the capacitance indeed increases linearly for both the composite and the pure polymer; more significantly, the composite again provides a significantly bigger capacitance.

This linear relationship does have a limit, although electropolymerisations can continue to very high deposition charges, up to about 60 C cm^{-2}. When the electrode was removed from the solution after passing high deposition charge, instead of a coherent coating, the electrode was covered by a large gel-like drop. After drying, the gel did form a coating, but it was not well defined, spreading beyond the area of the electrode disc (1.6 mm diameter) and onto the insulating sheath (5 mm diameter). Measurements on such coatings resulted in significantly lower capacitance than expected from an extrapolation of Fig. 3b. This behaviour was also encountered during the co-deposition of polypyrrole and CNTs, and can be attributed to the network forming abilities of the high aspect ratio CNTs.[4f]

In summary, we have reported a new CNT stabilised organoaqueous emulsion, and demonstrated, in such a metastable medium, the feasibility of electrochemical synthesis of novel PEDOT–CNT composites that are potentially applicable in supercapacitors. More importantly, the tactic communicated here may open a generic route for electrochemical synthesis of new composites of CNTs and conducting polymers from water-insoluble monomers of, for example, supramolecular nature with selective guest sensing functionality,[5] and also for other chemistry involving reactants that have incompatible solubilities in the same reaction medium.

In comparison with other methods for making polymer–CNT composites, as reviewed recently,[6] electrochemical co-deposition as described here is capable of direct formation of the CNT network supported porous structure in the as-deposited composite coating on the electrode, and uses the same or a similar dopant as in the charge–discharge tests. Therefore, there is no need for further processing steps that are typically used after chemical synthesis, including mixing with additives, pressing into thin films, exchanging dopant *etc.*[2,6] These post-synthesis steps could all compromise the charge–discharge performance of the composites.

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