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Facile template-free electrochemical preparation of poly[N-(2-cyanoethyl)pyrrole] nanowires

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ABSTRACT

In this paper the first synthesis of poly[N-(2-cyanoethyl)pyrrole] (PPyEtCN) in a nanowire morphology is reported. The method employed is a facile, one step electrochemical growth, which does not require the use of any templates or surfactants. Using optimised conditions the nanowires nucleate to give a homogeneous film across the electrode surface, with lengths of approximately 2 μm and diameters of approximately 150 nm. Structural information on the nanowires was obtained using vibrational spectroscopy. Evidence is presented to support an instantaneous 3-D nucleation and growth mechanism for the nanowires.

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1. Introduction

Polypyrrole (PPy) is one of the most extensively studied conducting polymers due to its facile preparation and its attractive range of properties, including redox activity [1], ion exchange capabilities [2] and biocompatibility [3]. However, there is currently much interest in using functionalised monomers to generate conducting polymers as novel materials, in particular, as biosensors [4–7]. When the functional group on the substituted pyrrole contains a terminal cyano group, supramolecular interactions between that group and other molecules are possible. Indeed, PPyEtCN modified electrodes have been used to immobilise specific antibodies for the fabrication of biosensors [8,9] and in the electrochemical sensing of dopamine [10].

In recent years a number of authors have reported template-free electrochemical methods for the formation of polypyrrole nanowires [11,12]. These nanowires possess a higher surface area and shorter diffusion lengths than the analogous bulk materials providing the wires with more attractive properties [13]. Although *N*-substituted polypyrrole has been employed for sensor applications, there are few studies on the preparation of these polymers in the nanowire morphology. Moreover, these studies have utilised either a template approach or coated already grown polypyrrole nanowires with the functionalised polypyrrole [14,15]. Here, we present results for the synthesis of novel PPyEtCN nanowires, and to the best of our knowledge this is the first report of a one-step preparation of *N*-substituted polypyrrole nanowires using a facile template-free electrochemical approach.

2. Experimental

All chemicals were purchased from Sigma-Aldrich and were of analytical grade. *N*-(2-cyanoethyl)pyrrole was distilled under vacuum and stored under nitrogen at $-40\text{ }^{\circ}\text{C}$. Electrochemical experiments were performed at room temperature using a standard three electrode cell. Potentials were referenced against a saturated calomel electrode (SCE) and a platinum wire was used as a counter electrode. The working electrode was a glassy carbon rod (4 mm diameter) embedded into a Teflon holder using an epoxy resin. Before each experiment the exposed surface was polished with successively finer grades of diamond paste (Buehler), sonicated in ethanol after each polishing step, and then finally sonicated in water. In a typical experiment the monomer (75 mM) was dissolved in EtOH (3 ml) while both LiClO_4 (20 mM) and $(\text{NH}_4)_2\text{H}_2\text{PO}_4$ (0.3 M) were dissolved in H_2O (7 ml). The two solutions were mixed, stirred for 10 min and finally a potential of 0.85 V vs. SCE was applied. SEM was performed using a Hitachi S-3200-N with a tungsten filament or a Hitachi S-4000 with a cold cathode field emission electron source (FE-SEM) and a JEOL 2000 FX, operating at 200 kV, was used for all TEM analyses. Raman measurements were performed with a LabRAM high resolution Raman spectrometer using a 660 nm solid state diode laser (100 mW). FTIR spectra were obtained using a Perkin Elmer 2000 FTIR spectrometer.

3. Results and Discussion

3.1. Electrochemical Growth of PPyEtCN Nanowires

Due to the different solubilities of the reagents used, the nanowires were electropolymerised from a 70:30 $\text{H}_2\text{O}/\text{EtOH}$ mixture. In accordance

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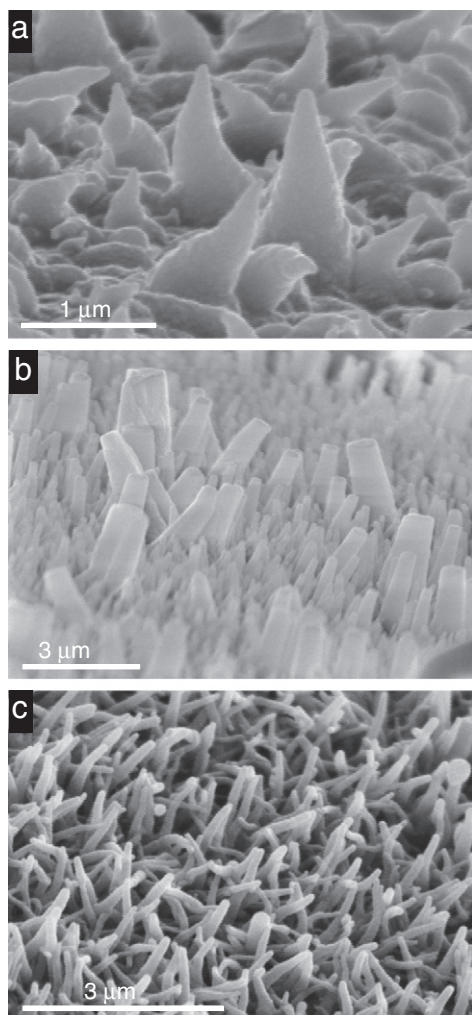


Fig. 1. SEM micrographs of PPyEtCN nanowires grown for 60 min at different molar ratios of monomer : $(\text{NH}_4)\text{H}_2\text{PO}_4$: LiClO_4 (a) 1:3:0.3 (b) 1:7:0.5 and (c) 1:4:0.3.

with previous studies nanowire formation was highly dependent on the growth conditions [16]. Their growth was only observed between the potential range of 0.8 to 1.0 V and the monomer to dopant ratio was critical (Fig. 1(a), (b) and (c)). Polymerisation using a low dopant concentration resulted in microwires which were significantly tapered towards the tip (Fig. 1(a)). Whereas, at higher dopant concentrations, vertical wires formed, but they possessed a wide distribution of sizes (Fig. 2(b)). Optimisation of these growth conditions led to a homogeneous and adherent nanowire film forming over the substrate (Fig. 1(c)).

FE-SEM micrographs recorded at various time intervals show that both the diameter and length of the wires were easily controlled by varying the electropolymerisation period. Only nodules are evident after 1 min of growth (Fig. 2(a)), after 5 min nanowire formation is clearly evident (Fig. 2(b)) and long slightly tapered wires are obvious after 60 min (Fig. 2(c)). Fig. 2(d) shows the relationship between electropolymerisation time and wire diameter and length.

3.2. Nucleation of the PPyEtCN Nanowires

Studies have shown that the preliminary stages of electrodeposition of conducting polymers occurs via diffusion controlled growth from nucleation sites [17,18]. A typical current-time transient recorded during the electropolymerisation period is shown in Fig. 3(a). Dimensionless $(I/I_{max})^2$ vs. (t/t_{max}) and (I/I_{max}) vs. (t/t_{max}) plots were produced from these data and compared to the theoretical 2-D and 3-D progressive and instantaneous models [19]. The resulting plots are shown in Fig. 3(b) and (c), and it is clear that for the early stages of growth the experimental data are consistent with the 3-D instantaneous phase of growth. Upon repeated experimentation we found that uniform nanowire films were only formed when the early stages of polymer growth followed the 3-D instantaneous growth model. This indicates that, even though a base layer of bulk polymer is formed before nanowire formation is observed, whether the polymer growth can result in the nanowire morphology is determined at the point of nucleation.

3.3. Structural Characterisation of PPyEtCN Film

A cross section of the PPyEtCN film is shown in Fig. 4(a), where it is clear that the wires are attached together at the base by a layer of bulk

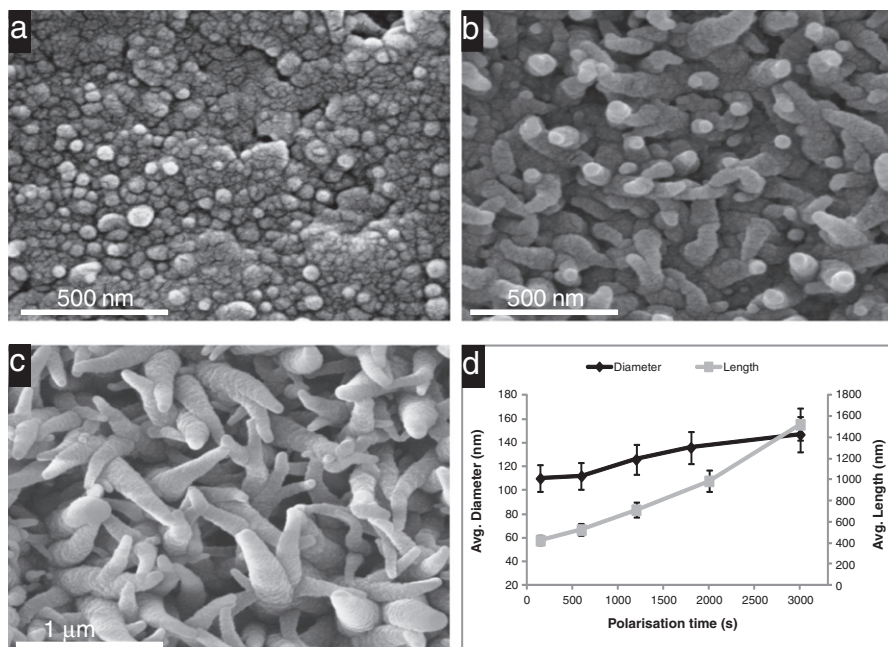


Fig. 2. FE-SEM micrographs of PPyEtCN nanowires at different growth stages (a) 1 min (b) 5 min and (c) 60 min. Average nanowire diameter and length as a function of time (d). Nanowires grown under the conditions given in Section 2.

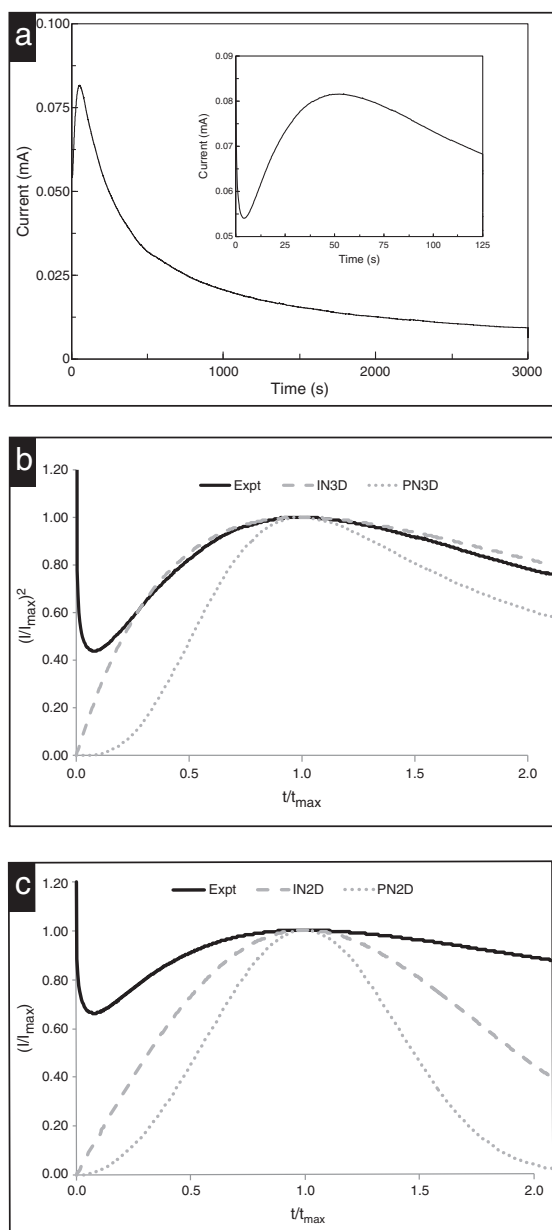


Fig. 3. A typical current-time transient for nanowire growth (a). Dimensionless plots of $(I/I_{max})^2$ or (I/I_{max}) vs t/t_{max} compared with (b) 3-D instantaneous nucleation (IN3-D) and progressive nucleation (PN3-D) (c) 2-D instantaneous nucleation (IN2-D) and progressive nucleation (PN2-D).

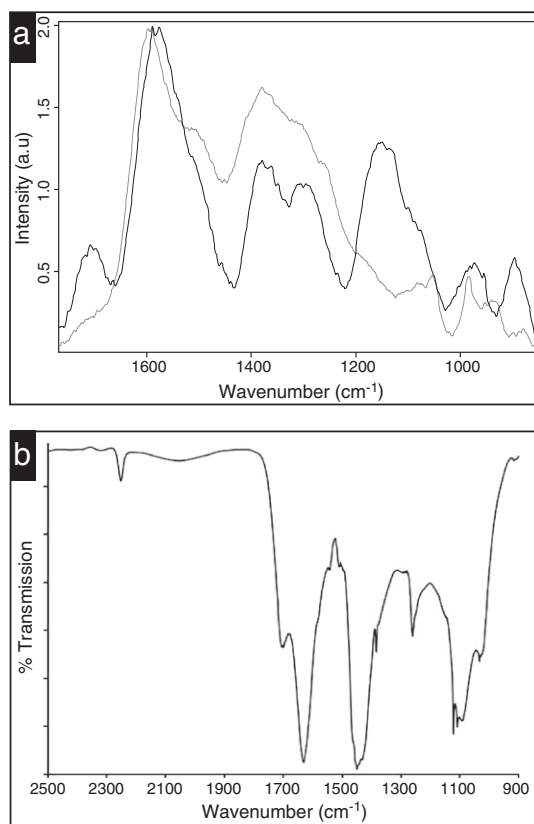


Fig. 5. (a) Raman spectra for bulk PPy (grey) and PPyEtCN nanowire film (black) and (b) FTIR spectrum of PPyEtCN nanowires in KBr disk.

polymer. It appears the polymer nucleates on the surface and grows to give a bulk-like layer. However, 1-D growth along the z-axis is eventually favoured giving the wires extended lengths above the base layer. A TEM micrograph of a single nanowire (Fig. 4(b)) shows a uniform contrast over the entire length, indicating a homogeneous solid structure. The tapering effect, which is common for the longer wires, is also clearly evident.

Direct evidence for the presence of the cyano group is obtained from the FTIR spectrum in which the characteristic $\nu(\text{C}\equiv\text{N})$ band at 2246 cm^{-1} is clearly observed (Fig. 5(a)). The Raman spectra of a PPy film and the PPyEtCN nanowires (Fig. 5(b)) show that the PPyEtCN retains the characteristic bands associated with PPy. The band at 1155 cm^{-1} is associated with the $\text{CH}_2\text{CH}_2\text{CN}$ moiety. The most intense band in the PPy spectrum at 1595 cm^{-1} is shifted to 1582 cm^{-1} for the PPyEtCN nanowires. This band is assigned as arising from the $\nu(\text{C}=\text{C})$ modes of both oxidised and neutral pyrrole units [20]. This shift to a lower wavenumber is indicative of a reduction in the amount of oxidised units in the nanowires compared to PPy. Furthermore, while

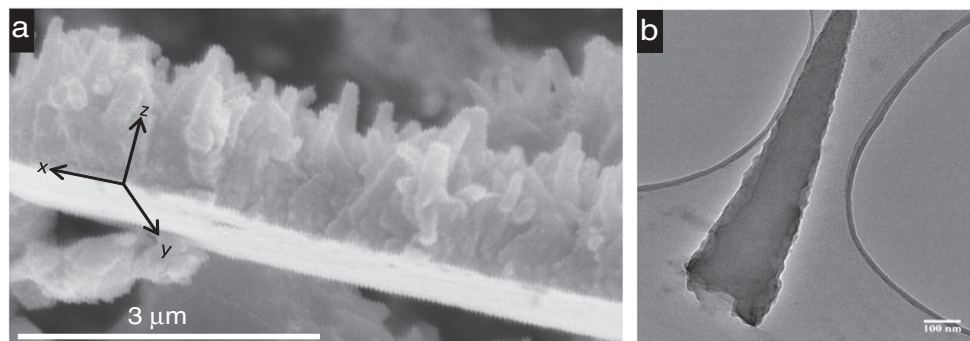


Fig. 4. (a) SEM image of a cross section of a nanowire film showing the base layer of bulk polymer and (b) TEM image of an individual nanowire removed from the electrode surface.

PPy exhibits bands due to the bipolaron and polaron species at 940 and 980 cm^{-1} respectively, only the latter is distinguishable in the PPyEtCN spectrum. The ratio of the intensity of the $\nu(\text{C}=\text{C})$ band to that of the skeletal band at 1503 cm^{-1} gives a measurement of the relative amounts of conjugation in the two polymers [21]. The ratios were determined to be approximately 2.7 and 2 for the PPy and PPyEtCN systems respectively, indicating the lower degree of conjugation in the PPyEtCN film. This finding is consistent with the presence of a band at approximately 1705 cm^{-1} in both the Raman and FTIR spectra which is indicative of a carbonyl stretching mode. Aradilla *et al.* observed a $\nu(\text{C}=\text{O})$ band in the FTIR of bulk PPyEtCN [22,23]. They proposed that this signal arose from the conversion of C–H moieties to carbonyls at the β positions of the pyrrole rings disrupting the conjugation of the polymer chains.

4. Conclusions

A one step method for the formation of novel PPyEtCN nanowire films was developed. Experiments, using vibrational spectroscopy, confirmed that the $\text{CH}_2\text{CH}_2\text{CN}$ group remains intact during the electropolymerisation and the data is consistent with the conjugation length in the PPyEtCN nanowires being relatively short. The initial growth of the nanowires follows a 3-D instantaneous nucleation and growth, leading to a uniform polymer film with a near homogeneous nanowire length.

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