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Electrochemical synthesis and one step modification of PMProDot nanotubes and their enhanced electrochemical properties†

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Poly (3,4-(2-methylene)propylenedioxythiophene) (PMProDot) nanotubes were synthesized within the pores of polycarbonate and were further modified with styrene and vinylcarbazole by a one step electrochemical method through the methylene functional group. The enhanced electrochemical and electrochromic properties of composite nanotubes were investigated using FTIR, UV/Vis absorbance spectroscopy, and AFM.

Conductive polymer nanostructures have always been of high interest because of their intrinsic electronic and physical properties, chemical stability, and significant potential in nano-sized electronic and electrochemical device applications.[1] More recently, due to the extensive range of applications, there has been more focus on the functionalization of conductive polymers. There are currently two main functionalization techniques found in the literature: pre- and post-polymerization.[2] In pre-polymerization, the additional functional group is introduced into a monomer of the conductive polymer prior to polymerization. However, the synthesis of the monomer derivative often involves multiple steps using harsh chemicals with limited production yields. In addition, this approach often fails due to additional redox interferences from the functional group.[3] Post-polymerization is often limited by chain stiffness and inter-chain interactions which cause physical and electrostatic crosslinking and branching.

Recently, Yoon *et al.* reported the chemical synthesis and electrochemical polymerization of (3,4-(2-methylene)propylene-dioxythiophene) (MProDot) films and the electrochemical grafting of polystyrene (PS) *via* methylene functional groups.[4] It is highly interesting to broad scientific community to investigate electrochemical properties of the electrochemically

grafted conductive polymer nanostructures because of their greatly enhanced performances in many applications such as displays, energy storage devices and drug deliveries. Nanotubular structures of conductive polymers have shown extremely fast electrochemical redox reactions, which have been systematically studied over well-controlled wall thickness of the nanotubes compared to the thin film structure.[1] Our group has reported the electrochemical polymerization of conductive polymer nanotubes in polycarbonate and anodic aluminium oxide (AAO) membranes and demonstrated the enhanced electro-chemical properties of nanotubes compared to thin film. The thin nature of the nanotube wall drastically decreases diffusion time (to tenths of milliseconds) of counterions through the conductive polymer during redox processes. In this communication, we report the facile synthesis of PMProDot nanotubes using a template synthesis method and one-step modification with PS and poly(vinylcarbazole) (PVK). This knowledge can be adapted to fine tune electrochromic displays and more recently, similar concepts can be applied to high power electrochemical energy storage devices currently emerging in renewable energy sources and other green systems.[5]

The template synthesis method of PMProDot nanotubes is performed in Anodisc 47 purchased from Whatman (Scheme 1). A gold working electrode was prepared by sputter-coating a thin layer of gold (*ca.* 500 nm) onto the branched side of the aluminium membrane. The Au-coated membrane was connected to an electrical circuit using copper tape (3 M). An electroactive window (0.20 cm^2 in area with a 60% porosity) was defined by using acid resistance tape. Electrochemical polymerization was performed by scanning the potential between -0.6 and $+1.3$ V (*vs.* Ag/AgCl) in 50 mM MProDot where Pt foil was used as a counter electrode and 100 mM of LiClO$_4$ in acetonitrile was used as the electrolyte solution, if not specified otherwise. The wall thicknesses of the nanotubes were controlled by adjusting the scan rate. During polymerization, the color of the observed electrode window changed from white to dark blue. After the electrodeposition of PMProDot, the AAO templates were dissolved in NaOH (3 M). The nanotubes were then rinsed with excess water and ethanol. Finally, the nanotubes were detached from the gold working electrode by sonication in ethanol solution where the nanotubes precipitated to the bottom.

For the modification of PMProDot nanotubes, the AAO template embedded with PMProDot nanotubes was dipped

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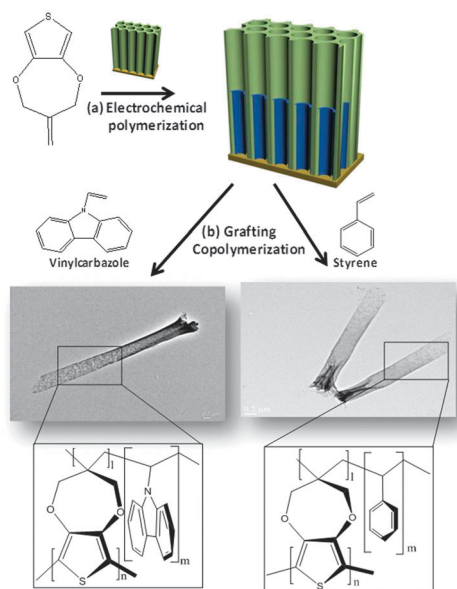
Scheme 1 Electrochemical synthesis of PMProDot nanotubes in (a) porous template; (b) proposed schematic for copolymerization of nanotubes with vinylcarbazole and styrene.

into a solution of styrene or vinylcarbazole. The coupling of PS with PMproDot nanotubes was achieved by scanning the potential between −0.6 and +1.5 V in 600 mM styrene.[4] Meanwhile the copolymerization of PVK with PMProDot was achieved by applying a potential of 0.75 V in 600 mM vinylcarbazole.

The structural characterization of the polymer nanotubes was investigated using electron microscopy. The transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images in Fig. 1a and b clearly show the hollow tubular structure of PMProDot nanotubes. The approximate length of the nanotubes was 4 μm. Fig 1b shows the aggregation of free standing nanotubes where the openings of the nanotubes are visibly noticeable. The outer diameter of nanotubes (200 nm–300 nm) well matched the diameters of the AAO membrane, while the wall thickness of the nanotubes was ca. 50 nm. The electrochemical synthesis of PMProDot in the AAO membrane provides remarkably uniform and smooth wall surfaces.

The IR spectrum of the PMProDot nanotubes shows a C=C stretching band of the thiophene ring at 1486 cm^{-1}, a C–S stretching at 853 cm^{-1}, and a C–O bending band at 934 cm^{-1}. The IR spectrum of PVK shows the C–H aromatic stretching at 3100 cm^{-1}, a characteristic ring vibration band
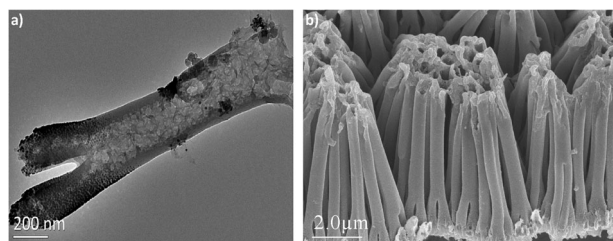
Fig. 1 (a) TEM and (b) SEM images of PMProDot nanotubes. The nanotubes were electrochemically synthesized by scanning the potential from 0.6 V to 1.3 V in 50 mM MProDot in Anodisc 47 membranes of pore size around 200 to 300 nm.
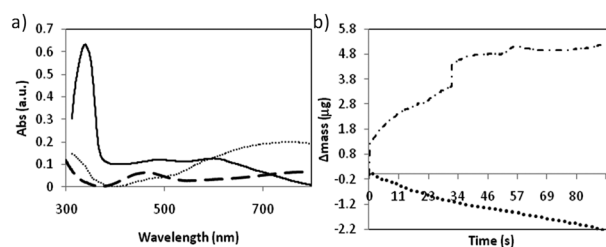
Fig. 2 All polymers were prepared on ITO glass. (a) The absorbance spectra of oxidized PMProDot (dotted), oxidized PMProDot composite with PS (dash) and oxidized PMProDot composite with PVK (solid). (b) QCM plot of mass change (polycarbonate/quartz crystal) versus time of electrochemical deposition of PVK on planar electrode (dotted) and on PMProDot surface (dashed) at 0.750 V.

at 1452 cm^{-1}, C–H deformation of vinylidene at 1329 cm^{-1}, and C–H plane deformation of aromatic ring at 1220 cm^{-1}, respectively (see spectra in ESI†).[6] IR analysis of the composite of PVK with PMProDot shows combinations of IR bands from individual polymers. Yoon et al. previously published the characteristic peak from sp^2 C–H of PS at 3020–3050 cm^{-1} for the FTIR spectrum of PS-treated PMProDot.[4] Fig. 2a shows the UV/Vis absorption spectra of oxidized PMProDot and PVK and PS on PMProDot. The spectrum of oxidized PMProDot shows a strong absorption band at ca. 700 nm. The absorption band blue-shifted following the coupling of PS to ca. 470 nm and to ca. 350 nm as a result of the coupling with PVK. It should be noted that the absorption of the carbazole group extends up to 370 nm.[7] These absorbance shifts are due to the shortening of the chain length following the addition of substituents to the polymer backbone.[8]

Quartz crystal microbalance (QCM) analysis was utilized to further investigate the accelerated graft copolymerization of PVK on PMProDot. Fig. 2b displays the plot of change in mass versus time for the electrochemical polymerization of vinylcarbazole on a bare gold working electrode and on a PMProDot surface at 0.75 V. During the electrochemical polymerization of vinylcarbazole at 0.75 V, a negative mass change was observed. This was caused by desorption of vinylcarbazole off the electrode surface which is normally observed at a lower positive potential than the polymerization potential.[9] In contrast, a mass increase was observed on the PMProDot surface at the same potential. This represents the accelerated polymerization of vinylcarbazole and confirms the facile coupling ability of the methylene group on PMProDot. TEM analysis of PVK-coupled PMProDot nanotubes shows a morphological variation between the bottom and top of the nanotube wall (see figures in ESI†).

To easily assess the enhanced electrochemical properties of PMProDot following modification, we investigated the variation in electrochromic properties of PMProDot coupled with PS and PVK. The evaluation of electrochromic response time is an easy and visible method to detect changes in electrochemical properties of conductive polymers. The strong coloration and color contrast between oxidized and reduced PMProDot is a visible assessment of the polymer's charging and discharging speed. We investigated on 200 mC of PMProDot deposited as a film on ITO glass and as nanotubes in flexible polycarbonate (PC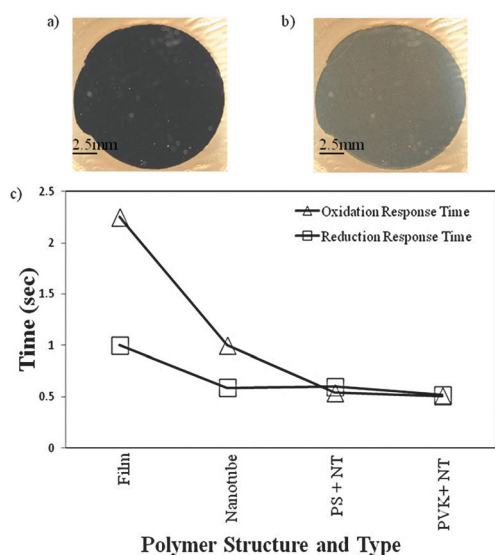) membranes. As seen in Fig. 3a and b, PMProDot in full