Electrochemical fabrication and characterization of poly(o-phenylenediamine) nanotubes by template method

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The fabrication of conducting poly (o-phenylenediamine) nanotube by electropolymerisation on alumina wafers (Whatman Anodisc 47 filter disk) is described. The nanotubes have been characterized by FTIR, UV-vis, SEM, TEM and AFM studies. SEM and TEM results reveal that the polymer nanotubes have uniform and well-aligned arrays and their diameter and length match with the aspect ratios of the anodisc aluminium oxide (AAO) membrane.

Keywords: Conducting polymers, Electropolymerization, Nanomaterials, Nanotube arrays, Template method, Poly o-phenylenediamine

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In recent years, one-dimensional nanostructures including nanofibers, nanotubes, nanorods and nanobelts of conducting polymers have been studied extensively. These 1D nanostructured materials have distinct geometries, and novel physical and chemical properties, which are probably applicable in nanodevices1. There are many methods to be developed for synthesizing 1D conducting polymers, for example, a hard-template based method to prepare 1D conducting polymers has been reported2-4. Micelles, surfactants, liquid crystals, thiolated cyclodextrins and polyacids have also been used as a soft-template to prepare nanofibers and nanotubes of conducting polymers5-11.

The template synthesis method has been widely used for preparing nanostructured materials, which involves the synthesis of the desired material within the pores of a membrane to generate nanotubes of cylindrical nature with uniform diameter12-19. Poly (o-phenylenediamine) (PoPD) is a polyaniline derivative which can be achieved through substituting hydrogens by an amino group in an aniline nucleus. PoPD is usually prepared by electrochemical polymerization. The PoPD obtained by this method usually has an irregular morphology as compared to that obtained by the conventional polymerization method. The detailed synthetic procedure of the template-synthesized poly (o-phenylenediamine) nanotube on Nafion and graphite are shown schematically in Fig. 1. The conventional synthesis of poly (o-phenylenediamine) was carried out in the same way without the alumina membrane as the template.

PoPD nanobelts can be synthesized from an o-phenylenediamine (oPD)-HAuCl4 or oPD-AgNO3 aqueous solution at room temperature without using any surfactant20,21. However, the resulting precipitates are not “pure”, and there are some Au or Ag particle byproducts, and therefore a post-separation process should be involved to obtain the pure 1D structure.

Herein, we report the preparation of PoPD nanotubes with uniform length and diameter using template assisted electrochemical synthesis. In this method the oxidizing agents, surfactants have not used and therefore, the obtained PoPD nanotube is “pure”.

Experimental

The present study was carried out in aqueous solutions. Purified water obtained by passing distilled water through a milli Q (Millipore) water purification system was used as solvent. o-Phenylenediamine (o-PD) was purchased from Aldrich. Sulphuric acid
was obtained from Fischer Chemicals. Nafion (5 wt %) solution was obtained from Dupont and used as received. Anodisc aluminium oxide (AAO) membranes were obtained from Whatman Anopore Filters.

All experiments were carried out in a conventional one-compartment cell with a Pt counter electrode and a saturated calomel reference electrode, at room temperature. First, the graphite electrode was coated with Nafion solution and the membrane is hot pressed with the graphite. Nafion not only acts as a binder but also provides both ionic and electronic contact and favours proton transport. Then the graphite electrode was used as current collector and contacted with the template membrane. The membrane together with the current collector was fixed between two teflon rings. The area of the membrane contacted to the electrode was \( \text{ca.} \ 1 \ \text{cm}^2 \). The solution was de-aerated by bubbling dry nitrogen gas for 15 min before electrochemical polymerization. The electropolymerization of \( o \)-Phenylenediamine (\( o \)-PD) was carried out with a BAS 100B Electrochemical Workstation (Bioanalytical Systems Inc., West Lafayette, IN). The poly \( o \)-phenylenediamine nanotubes were grown potentiodynamically between -0.2 V and 1.2 V containing 5 mM \( o \)-PD. The length of the nanotubes was controlled by the total charges passed in the cell.

The alumina membrane from graphite/Naf/PoPD\_Temp was removed by immersing the composite in 0.1 M NaOH for 15 minutes. The composite after the dissolution of the template was repeatedly washed with deionized water to remove the residual NaOH. It was subsequently immersed in 1% HBF\(_4\) for 10 minutes and then washed with deionized water again. The composite after the dissolution of the template was designated as graphite/Naf/PoPD\_Temp.

The schematic view of the homemade electrochemical cell for the preparation of template-synthesized poly (\( o \)-phenylenediamine) nanotube is shown in Fig. 2.

The scanning electron micrographs were obtained using JEOL instrument (model JSM-840), working at 15 kV. The nanotubes were sonicated in acetone for 20 minutes and then were dropped on the cleaned Si substrates. The AFM imaging was performed in air using the Nanoscope IIIA atomic force microscope (Digital Instruments, St. Barbara, CA) operated in contact mode. For transmission electron microscopic studies, the nanotubes dispersed in ethanol were placed on the copper grid and the images were obtained using Phillips Instrument (model 420), operating at 120 keV. The IR spectrum was recorded with Perkin Elmer (L-710) spectrophotometer.

**Results and discussion**

The electropolymerisation of \( o \)-Phenylenediamine (\( o \)-PD) monomer on the alumina template was carried out by cyclic voltammetry was shown in Fig. 3. A broad anodic peak is been in the potential range from \(-0.2 \ \text{V}\) to \(1.2 \ \text{V}\) in a solution of 0.5 M \( o \)-phenylenediamine in 0.5 M \( \text{H}_{2}\text{SO}_{4}\) solution. ([Scan rate: 50 mVs\(^{-1}\)].)
+0.2 V to 1.2 V, which indicates an oxidative process of o-PD. In all the cases no reduction peak is found in the reverse scans, thus suggesting that the oxidized oPD is involved in further chemical processes leading to non-reducible species in the potential range adopted.

The UV-vis absorption spectra of the poly (o-phenylenediamine) (PoPD) nanotubes were studied. A single, large absorption band around 364.3 nm is seen in the UV-vis spectra of PoPD. The band is due to inter-band charge transfer associated with excitation of benzenoid to quinoid moieties (optical absorption of the metallic polar on band of the conducting form).

The FT-IR spectroscopy was used to identify the structure of the PoPD. The absorption band in the FT-IR spectra of PoPD appears around 3400 cm\(^{-1}\), corresponding to the N-H stretching vibration. The absorption bands in the 650-900 cm\(^{-1}\) region are characteristic of the substitution pattern on the aromatic ring. The band at 812 cm\(^{-1}\) may be assigned to the vibration of the 1,4-disubstituted ring\(^{22}\). The intense band at 1450 cm\(^{-1}\) is attributed to the C=N stretching vibration. This suggests that a considerable portion of C=N bond existed in the PoPD nanotubes. It can be noted that the presence of this band in the PoPD backbone indicates that the polymer chain has an extensive \(\pi\) conjugation between polymer chain and all nitrogen atoms. This is consistent with the results of UV-vis spectroscopy and electrochemical experiments. Also the results of FTIR spectra of PoPD nanotubes agree well with previous reports\(^{23-25}\).

The SEM image of the conventionally synthesized conducting poly (o-phenylenediamine) is shown in Fig. 4a. The image shows ladder morphology and a dense coverage of poly (o-phenylenediamine) on graphite, which are not uniform in nature.
It is evident from Fig. 4b that the uniform, cylindrical, monodispersed nanotubes of PoPD after the removal of the template project perpendicularly to the graphite. The open ends of the uniform nanotube are clearly seen in this image. Figure 4c shows the picture of the conducting polymeric tubules taken at a tilted angle, in a different region. It is evident from the image that the density of nanotubes is quite high, in all the regions. These tubes are uniformly distributed in a regular array on the graphite with an outer diameter (200 nm) that almost matches the pore diameter of the template.

AFM images of the synthesized poly(o-phenylenediamine) nanotubes deposited on a silicon substrate were also studied and shown in Fig. 4(d). The AFM tip was carefully scanned across the tube surface in a direction perpendicular to the tube axis. AFM image shows the bunch of polymer nanotube on the silicon substrate further confirming the electropolymerization of o-phenylenediamine. A probable reason for this is that the polymerization inside the confined space of the pores, combined with electrostatic interaction, ensures the alignment of the resulting polymers on the walls of the pores of the template26.

References