Lyotropic Supramolecular Polymer Systems with Anisotropic Functional Properties

Sudha J. Devaki,* Neethu K. Sadanandhan, Rohini K. Narayanan

Summary: We have synthesized highly ordered nanostructured conducting PEDOT (poly (3,4-ethylenedioxythiophene)) through chemical and electrochemical polymerization of bio based liquid crystalline templates and modified transducer used for the detection of ascorbic acid and nicotine.

Keywords: conducting polymers; cyclic voltammetry; lamellar; self-assembly; sensors

Introduction

Lyotropic liquid crystalline (LC) materials exhibit concentration and temperature dependent mesophases with well-organized anisotropic channels that can be exploited for tuning the size and shape of functional nanomaterials. Self-assembled surfactant molecules in specific mesophases can serve as the templates during polymerization. Nanostructured conducting polymers (NCPs) have attracted tremendous attention in the past decade due to their extended \( \pi \)-conjugated chains, reversible doping and dedoping capability, good electrical conductivity and tunable electrochemical behaviours.[1] Poly(3,4-ethylenedioxythiophene) (PEDOT) has been identified as a reliable functional material for a wide range of applications because of its optical transparency, low band gap, flexibility and ease of preparation.[2] General strategies to achieve NCPs involves synthesis in micellar media, template guided polymerization using hard template like porous surfaces or soft templates formed from a variety of surfactants (cationic surfactants, anionic surfactants and nonionic surfactants).[3] Among them, the LC phase based soft template polymerization is interesting since it is a simple facile strategy for the preparation of shape/size controlled NCPs.[4,5]

Presently, the cost of petroleum based products is increasing due their scarcity arising from depletion. In this context, development of amphiphilic molecules derived from renewable resources based products are receiving significant importance. Amphiphilic molecules, like penta-decyl phenyl phosphoric acid (PDPPA) and pentadecyl phenyl sulfonic acid (PDPSA) derived from cashew nut shell liquid act as surfactant cum dopant for the preparation of NCPs.

In the present paper, we are reporting self-organized lyotropic LC template of EDOT-PDPSA and EDOT-PDPPA adduct for the nanostructured conducting PEDOT. LC phase formation is studied using PLM. Finally, we have demonstrated the modification of glassy carbon electrode with nanostructured PEDOT and their efficiency for the electrochemical detection of nicotine and ascorbic acid.

Experimental Section

EDOT-PDPSA was prepared by mixing the equimolar proportion of EDOT and PDPSA in ethanol-water mixture (3:7 ratio). PEDOT–PDPSA prepared by chemical polymerization using an oxidative initiator ferric chloride hexahydrate.[6] EDOT-PDPPA was prepared by mixing...
the equimolar proportion of EDOT and PDPPA in water. PEDOT–PDPPA was prepared by electrochemical polymerization using cyclic voltammetry.[7]

Instrumentation
Polarized light micrographs (PLM) were taken in an Olympus BX 51 microscope after drop casting the solution of the sample in a clean dry glass plate. The SEM images were obtained with SEM/EDAX (Scanning Electron Microscopy, JEOL JSM 5600 LV. EDS., EDAX, NJ, USA).

Results and Discussion
The stability of polymerizable LC the adduct EDOT-PDPPA and EDOT-PDPSA were theoretically confirmed by energy minimization using Gaussian software with the B3LYP method with a basis set 6-31G. The observed higher negative values of the binding energy −4.5 kcal and -5.04 kcal confirm the stability of the adduct EDOT-PDPPA and EDOT–PDPSA.

LC phase of EDOT-PDPSA showed spindle shape and is shown in Figure 1a. Oxidative polymerization of the liquid crystalline template EDOT–PDPSA was conducted in the presence of ferric chloride as the initiator. During the propagation process, color changes from brown to blue, green and finally to violet attributed to the variation in the electronic state of the PEDOT and the irregularity in the nature of aggregation. The morphological analysis of the prepared PEDOT-PDPSA showed the formation of nanospindles which preserve the shape of the mesophase of the adduct. The SEM image of PEDOT-PDPSA is shown in Figure 1b. GCE was modified with PEDOT-PDPSA used to study the electrocatalytic oxidation of ascorbic acid. It was found that the nature of oxidation process in phosphate buffer solution (pH = 7.4) proceeds through
diffusion control. Their good linear dependence and the low detection limit showed significant sensitivity of PEDOT-PDPSA/GCE for the detection of ascorbic acid.

EDOT-PDPPA showed concentration dependent LC phase like columnar and lamellar (Figure 2A and C). PEDOT-PDPPA was prepared through the electrochemical polymerization of the LC templates of EDOT-PDPPA. The morphological analysis of the prepared PEDOT-PDPPA exhibited web of peacock-like features, nanosheets that shown in Figure 2B and 2D. The observed structure results from the template directed polymerization of EDOT-PDPSA and PEDOT-PDPPA mimic the shape of the liquid crystalline templates.

Figure 3A represents Nyquist plots for GCE, PEDOT/GCE, CPEDOT/GCE, and LPEDOT/GCE. The charge transfer resistance (Rct) values of CPEDOT/GCE, and LPEDOT/GCE are measured as 83, and 68 Ω, respectively.LPEDOT/GCE exhibited a low value of Rct, and hence, it is taken as a model electrode for studying the performance of the transducer.

The electrocatalytic performance of LPEDOT/GCE in the electrochemical oxidation of nicotine was studied by CV in BR buffer (pH 8.0). At LPEDOT/GCE the oxidation of nicotine was observed at 0.83 V. Figure 3B shows the well resolved CV obtained during the successive additions of nicotine in BR buffer solution (pH 8.0). LPEDOT/GCE exhibited a linear relationship with nicotine in the concentration range of 0.1 μM to 320 μM, and the limit of detection of nicotine was calculated as 50 nM.

**Conclusion**

Self assembled liquid crystalline template of EDOT-PDPPA and EDOT-PDPSA exhibited concentration dependent lyotropic mesophases. During polymerization PEDOT preserved and locked the reordering of liquid crystalline template of EDOT-PDPPA and EDOT-PDPSA in the nanometer regime. Further the glassy carbon electrode modified with PEDOTs behaved as electrochemical transducer for the detection of nicotine and ascorbic acid in micromolar level. This simple low cost strategy for the preparation of conductive polymer with a desired ordering on the nanometer scale on the conventional electrode can be exploited for applications in plastronic devices.