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Sudha J. Devaki, Neethu K. Sadanandhan, Renjith Sasi, Hans-Juergen P. Adler, Andrij Pich

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Water dispersible electrically conductive poly(3,4-ethylenedioxythiophene) nanospindles by liquid crystalline template assisted polymerization†

Sudha J. Devaki,^{*a} Neethu K. Sadanandhan,^a Renjith Sasi,^a Hans-Juergen P. Adler^c and Andrij Pich^{*b}

In this work, we demonstrate an inimitable liquid crystalline template strategy for the preparation of water dispersible electrically conducting poly(3,4-ethylenedioxythiophene) nanospindles (PEDOTs). PEDOTs were formed during the polymerization of the spindle shaped liquid crystalline phase of "EDOT-PDPSA" which was formed by the specific interactions of 3,4-ethylenedioxythiophene (EDOT) with 3-pentadecyl phenol-4-sulphonic acid (PDPSA). Liquid crystalline phases were characterized by Polarized Light Microscopic (PLM) analyses, rheology and XRD. Morphology and solid state ordering of conducting nanospindles were characterized by SEM, TEM and XRD. PEDOTs exhibited an electrical conductivity of $\sim 2.79 \text{ S cm}^{-1}$ and a good thermal stability ($\sim 300^\circ\text{C}$), which suggests their applicability in fabricating high temperature electronic devices. Furthermore, electrochemical studies of PEDOTs modified glassy carbon electrodes (GCEs) showed an oxidation peak of ascorbic acid at a lower potential of 0.046 V with a peak current about 10 times ($91.68 \mu\text{A}$) higher than that of the bare GCE with excellent electrode stability, proposing that it can be used as a steady electrode for the electro-catalytic oxidation of similar molecules.

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1 Introduction

Nanostructured intrinsically conducting polymers (ICPs) have attracted tremendous attention in the past decade due to their extended π -conjugated chains, reversible doping and dedoping capability, good electrical conductivity and tunable electrochemical behaviours.¹ They have been used for fabricating organic light weight batteries, antistatic coatings, EMI shieldings, flexible photovoltaics, efficient sensors and memory devices.^{2–4} However, the development of nanoscopic conducting polymers with pointed ends such as nanospindles are receiving a huge amount of interest as it can facilitate the smooth transfer of charge carriers from end to end. Among the various ICPs, 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, ease of preparation, thermal stability, versatility for side chain

functionalization and bioconjugation.^{5–11} These properties make ICPs based on PEDOTs an unavoidable part in flexible organic photovoltaics.

Due to the scientific urge in creating ecofriendly materials in the nanoscopic regime for energy harvesting, there is remarkable research interest in the area of water dispersible PEDOT nanostructures.¹² In combination with polyelectrolytes such as poly(styrenesulfonate) PEDOT forms water dispersible highly conducting transparent films which have been utilized in solar devices as hole transport layers.¹³ Several promising strategies based on self assembly were reported for the preparation of nanoscale PEDOT materials by the manoeuvring of non-covalent interactions such as hydrogen bonding, van der Waals forces, π - π stacking and so forth.¹⁴ Major synthetic strategies involve conducting chemical or electrochemical template guided polymerisation. Templates can be micelles or liquid crystalline phases of anionic, cationic or non-ionic surfactants in aqueous solutions with concentrations greater than the critical micelle concentration (CMC).^{15–19} Self assembled surfactant molecules in specific mesophases can serve as the templates during polymerization. The well-ordered channels present in the mesophase could be utilized as the structure-directing strategy for tuning the size and shape of the targeted functional nanomaterials. Recently, Stupp *et al.* have utilized the lyotropic hexagonal mesophase as a template for the electrochemical polymerization of PEDOT, which could imitate the texture and birefringence of the LC template.²⁰ A. Pich *et al.*

^aChemical Sciences and Technology Division, National Institute for Interdisciplinary Science and Technology (NIIST), CSIR, Thiruvananthapuram 695 019, India. E-mail: sudhaid2001@yahoo.co.in

^bDWI Leibniz-Institute for Interactive Materials, Functional and Interactive Polymers, RWTH Aachen University, D-52056 Aachen, Germany. E-mail: pich@dwil.rwth-aachen.de

^cDepartment of Macromolecular Chemistry and Textile Chemistry, University of Technology, Dresden, Germany

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reported the use of microgel particles as microreactors for the deposition of functional conducting polymers.²¹ H. Mao *et al.* synthesized nanospindles of β -akaganeite containing PEDOT using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ as an oxidant initiator in aqueous solution in the presence of the template formed by cetyl trimethyl ammonium bromide and poly(acrylic acid).²²

Recently petroleum based surfactants have become expensive due to their increased demand and depletion of resources. So researchers are looking for renewable resource based low cost and abundantly available molecules for their research. Among these cashew nut shell liquid (CNSL) can be considered as an alternate source for unsaturated long chain phenols. It is a low cost, abundantly available industrial byproduct obtained from the cashew industry. The main constituent of CNSL is cardanol (3-pentadecyl phenol), which can be separated by a distillation process. 3-Pentadecyl phenol-4-sulphonic acid, denoted as PDPSA is a sulphonic acid derivative of cardanol. It has a unique built-in amphiphilic design consisting of the hydrophilic sulfonic acid head group and a hydrophobic tail made up of a 15 carbon long alkyl chain. Development of a nanostructured conducting polymer-clay nanocomposite using PDPSA as the structure directing agent cum intercalating agent was earlier reported by our group.^{23,24} In the present work, the unique amphiphilic nature of the EDOT-PDPSA adduct is utilized for the generation of a thermodynamically stable self-organized lyotropic liquid crystalline template both in water and water-ethanol media. Liquid crystalline phase formation of EDOT-PDPSA was studied by polarised light microscopy, rheology and XRD. Later, EDOT-PDPSA in its liquid crystalline phase was polymerized to form PEDOTs. Effects of temperature, solvent and reaction time on the molecular weight, electrical conductivity, morphology and crystalline order were studied. Then the glassy carbon electrode was modified with PEDOTs and its efficiency in the electrocatalytic oxidation of ascorbic acid was studied.

2 Experimental

2.1 Materials and methods

3-Pentadecylphenol-4-sulfonic acid was prepared from 3-pentadecyl phenol as per the reported procedure (ESI).²⁵ 3,4-Ethyleneedioxythiophene and ferric chloride hexahydrate were purchased from Aldrich and used as such. All solutions were prepared in doubly distilled water.

2.2 Preparation and characterisation of the liquid crystalline template, EDOT-PDPSA

Lyotropic liquid crystalline behavior of EDOT-PDPSA was studied both in water and ethanol-water mixture (3 : 7). The critical micelle concentration (CMC) and liquid crystalline phase formations were studied by adjusting the amount of the EDOT-PDPSA both in water and ethanol-water mixture. CMC was evaluated by conducting UV-vis absorption measurements of solutions with varying concentrations. The concentration corresponding to the inflection point in the absorbance vs. the concentration plot was taken as the CMC. The typical curve is

given in the ESI (Fig. S1†). The concentration of EDOT-PDPSA was further increased both in water and water-ethanol media to observe liquid crystalline phases under PLM and was confirmed by rheological analyses using the same solutions.

The typical procedure for the preparation of the LC template is given below.

0.5 g of PDPSA (1.3×10^{-4} mol) was mixed with 0.02 g of EDOT (1.3×10^{-4} mol) and then dispersed in 10 mL of doubly distilled water with heating and stirring for 1 h at 60–70 °C.

2.3 Synthesis of PEDOT-PDPSA

Polymerization experiments were performed in a liquid crystalline phase of the self-organized “EDOT-PDPSA” using the oxidative initiator, ferric chloride hexahydrate. Experiments were performed both in water and ethanol-water mixture (3 : 7) at 20 and 60 °C. Typical procedure: 0.52 g of EDOT-PDPSA (1.3×10^{-4} mol) in the LC phase was taken in a 25 mL three necked round bottomed flask provided with a magnetic stirrer. To this solution, ferric chloride hexahydrate (0.23 g) (1.3×10^{-4} mol) was added dropwise with stirring at 20 °C. As time passes the resultant solution changed its color from orange red to brown and then to green. The reaction was allowed to continue for 24 h. Then the residue was collected under centrifugation using an ultra-centrifuging apparatus operating at 20 000 rpm for 20 minutes at 20 °C. The filtrate was removed using a dropper and again redispersed in water using an ultrasonicator. Washing and centrifugation were repeated several times for the complete removal of the byproducts and the unreacted oxidants until the filtrate become colourless. The solid product was dried in a vacuum oven at 60 °C for 24 h. Experiments were also performed using EDOT without a template. PEDOTs prepared under different conditions were designated as PEDOTS1 (ethanol-water at 20 °C), PEDOTS2 (ethanol-water at 60 °C), PEDOTS3 (water at 20 °C), PEDOTS4 (water at 60 °C) and PEDOT (control sample prepared without a template).

2.4 Fabrication of a PEDOTS modified GCE for electrochemical analysis

Aqueous dispersion of PEDOTs (2.5 mg mL^{-1}) was prepared and dropped on the surface of a pre-cleaned GCE and kept under vacuum for the evaporation of water to form a uniform film over the GCE. This modified GCE was used as the working electrode for studying the electrocatalytic activity during the oxidation of ascorbic acid.

2.5 Instrumentation

UV-vis absorption spectra were studied using a UV-vis spectrophotometer [Shimadzu model 2100, Japan] in the range of 300–1100 nm. FT-IR spectral measurements were made using a fully computerized Nicolet impact 400D FT-IR spectrophotometer (Czech Republic, EU). X-ray diffraction studies were done using a powder X-ray diffractometer (Philips X'Pert Pro, Netherlands) with $\text{CuK}\alpha$ radiation ($\lambda \sim 0.154 \text{ nm}$) employing an X'celerator detector and a monochromator at the diffraction beam side. Thin films cast on glass plates were used employing a standard sample holder. Electrical conductivity (σ_{dc}) of pellets were

measured using the standard spring loaded pressure contact four-probe method using a Keithley 6881 programmable current source and a 2128 A nano-voltmeter at 30 °C supplied by Keithley (Germany) as per the standard procedure ASTM F 43-99. For conductivity measurements, the samples were pressed into a 5 mm diameter disk using a hydraulic press operated at a pressure of 200 MPa. The conductivities of the samples were measured at three different positions, and at least three pellets were measured for each sample: an average of nine readings was used for conductivity calculations. Polarised light micrographs (PLM) were taken in an Olympus BX 51 microscope after drop casting the solution of sample on a clean dry glass plate. For SEM measurements, samples were subjected to thin gold coating using a JEOL JFC-1200 fine coater. The probing side was inserted into a JEOL JSM-5600 LV scanning electron microscope for taking photographs. Transmission electron microscopy was performed in a FEI, TEC NAI 30G2 S-TWIN microscope with an accelerating voltage of 100 kV. For TEM measurements, the water suspensions of samples were fully dispersed under ultrasonication. Then they were deposited on a formvar coated copper grid and dried at room temperature before observation. The rheological property of various phases was measured using Anton Paar Modulated Compact Rheometre-150 Physica (Germany). A parallel plate sensor with a diameter of 50 mm and a gap size of 0.25 mm was used and measurements were done in dynamic oscillatory mode. Thermal stability measurements were performed at a heating rate of 10 °C min⁻¹ in a nitrogen atmosphere using Shimadzu, DTG-60 equipment. The molecular weight was measured using a MALDI TOF mass spectrometer (AXIMA CFR, Shimadzu) equipped with a nitrogen laser emitting at 337 nm and α -cyano-4-hydroxy cinnamic acid as the matrix. All cyclic voltammetry studies were performed in an Electrochemical CH Analyser. Experiments were done at ambient temperature in a one-compartment electrochemical cell with a three electrode system. The saturated Ag/AgCl electrode was used as the reference electrode and platinum wire with 0.5 mm diameter and 50 mm length were used as the auxiliary electrode. All the experiments were carried out at 25 ± 5 °C. Before performing the experiments, the solution was purged with nitrogen gas for 10 minutes and current was passed.

3 Results and discussion

3.1 Structure and properties of EDOT-PDPSA

The stability and formation of the adduct was theoretically confirmed by energy minimization using Gaussian software with a B3LYP method using a basis set 6-31 g and the energy minimised structure shown at the inset in Fig. 1. The higher negative value of binding energy (−5.04 kcal) confirms the stability of the formed adduct EDOT-PDPSA. Results showed that the adduct was formed by the charge transfer interaction between the thioether group of EDOT and the sulfonic acid group of PDPSA. Formation of the adduct was confirmed by measuring the shift in the characteristic bands of EDOT and PDPSA in EDOT-PDPSA in the FTIR spectra. The band corresponding to the O–H stretching frequency of PDPSA is observed at 3439 cm⁻¹ and is shifted to 3286 cm⁻¹ in EDOT-PDPSA,

Fig. 1 FTIR spectra of EDOT, PDPSA and EDOT-PDPSA.

which confirms the inter-molecular hydrogen bonding and the ion-dipole interaction in EDOT-PDPSA. PDPSA exhibited a peak at 1228 cm⁻¹ attributed to the C–O vibration which is shifted to 1224 cm⁻¹ in EDOT-PDPSA revealing the extensive interaction between the lone pair of electrons on –CO with EDOT. The characteristic asym (C=C) stretching peak of EDOT observed at 1460 cm⁻¹ is shifted to 1459 cm⁻¹ in EDOT-PDPSA. The characteristic peak of C–S observed at 976 cm⁻¹ in EDOT is shifted to 876 cm⁻¹ in EDOT-PDPSA. These shifts in the wavenumber of characteristic peaks of EDOT and PDPSA in the EDOT-PDPSA suggested the presence of various types of molecular interactions between these two molecules during the formation of the adduct.

The CMC and liquid crystalline phase formation of the self-assembled adduct “EDOT-PDPSA” was studied both in water and ethanol–water media by mixing EDOT and PDPSA in an equimolar ratio. The critical micelle concentration of the EDOT-PDPSA in water and water–ethanol mixtures were determined using UV-vis absorption measurements as 1 × 10⁻³ M and 5 × 10⁻³ M respectively.

Polarized light microscopy (PLM) is a very useful technique for the characterization of the LC phase since it is possible to observe mesophases with distinct bands as a function of the “EDOT-PDPSA” concentration. The PLM images showing the formation of birefringent micelles of complex shapes of discs, rods and spheres are shown in Fig. 2a.

The richness of structures with various shapes of micelle results from the weak ordering attributed to the various non-covalent interactions between EDOT-PPSA and water through a self-assembly process.²⁶ Internal energy of this micelle is important as it enables transitions between shapes with different degrees of order. It was theoretically predicted that the intensity of inter-micellar attraction decreases in the sequence, disc > rod > sphere.²⁶ Normally aqueous suspensions containing surfactants exhibited a strictly spherical shape of micelles corresponding to a minimum size (shown in Fig. S2†). As micelles grow beyond a certain aggregation number, they are forced to turn into some kind of non-spherical shape to avoid hole

Fig. 2 PLM images of EDOT-PDPSA showing the formation of (a) micelles in water, (b) spindle shaped LC phase in ethanol-water, (c) gel phase in ethanol-water and (d) hexagonal lamellar phase in water.

formation at the micellar core.²⁷ Under conditions of spatial confinement in a cavity, surface and bulk elastic properties compete to minimize the overall free energy.^{28,29} An elastic membrane may form on the surface of the micelle by the crystallization of micelle *via* surface freezing to form 2D discs. When the medium of EDOT-PDPSA is changed into an ethanol-water mixture, the mode of crystallization of the micelles from the surface to the centre changes and a layered structure is formed inside the disc. Magnus *et al.*³⁰ experimentally and theoretically demonstrated that charged surfactant layers may grow both with respect to length and width to form a disc like micelle and eventually the shape of the disks could become biconcave through bending elasticity and take the shape of a thermodynamically stable spindle with layers inside. This is supported by the work reported by Andres F. Mejia *et al.*³¹ At a higher concentration (5×10^{-2} M); the lamellar phase with micro spindle morphology has been identified under PLM. A typical PLM photograph showing the formation of a micro-spindle shaped phase in ethanol-water is given in Fig. 2b. At a higher concentration (~ 0.1 M) EDOT-PDPSA formed a gel phase which appeared as a fractograph under PLM. The typical image of the same is shown in Fig. 2c. Fig. 2d shows the formation of a lamellar smectic phase in water. Different phases were formed due to the self-organization of the interdigitated bilayers of EDOT-PDPSA through various noncovalent interactions as shown in Scheme 1 and are supported by XRD and rheological analyses which are described in the later part of the discussion.

Further formation of the liquid crystalline phase was confirmed by rheological measurements of both EDOT-PDPSA solutions under oscillatory and rotator modes. In oscillatory mode keeping constant strain (1%) elastic and viscous moduli were measured under the angular frequency sweep (Fig. 3i). It can be observed that the elastic modulus (G') dominates over the viscous modulus (G'') and maintains a constant value over a large frequency spectrum. Since a low frequency crossover is not observed in the frequency range considered, it exhibited a

Scheme 1 Formation of nanospindles of PEDOT through various steps: formation of EDOT-PDPSA adducts → micelle formation → LC phase → polymerisation to form nanospindles (top). Various non-covalent interactions present in EDOT-PDPSA to form self-organized EDOT-PDPSA through various noncovalent interactions such as alkyl chain interdigitation and π - π stacking ion-dipole interaction (bottom).

saddle like increase in the modulus at a higher frequency, indicating the occurrence of dissipation mechanisms. The structure of the lamellar liquid crystal phase is built from one by one bimolecular leaflets. During the action of outside force (higher frequency), they can slide between the bilayers into the flowing state in a similar manner showing plastic fluid like behavior. These two findings in the rheogram together suggest the presence of a lamellar phase. This is supported by the observation made by Montalvo *et al.*²⁹ In rotatory mode shear rate dependent viscosity measurements were made and the diagram showing the change in viscosity under a varying shear rate from 300 to 1000 s^{-1} for isotropic and liquid crystalline phases (EDOT-PDPSA in water) is given in Fig. 3ii. The isotropic

Fig. 3 (a) Viscoelastic properties of EDOT-PDPSA in the liquid crystalline phase as a function of angular frequency. G' and G'' represent elastic and viscous moduli, respectively. (b) Viscosity as a function of the shear rate, (a) liquid crystalline phase and (b) isotropic phase.

system showed Newtonian behavior whereas the viscosity profile of the LC system exhibited the non-Newtonian variation with large shear thinning behavior at a lower shear rate. Secondly, the magnitude of the viscosity in a liquid crystalline phase was measured to be remarkably larger than the isotropic system (1238.4 Pa S and 43.9 Pa S). Later, on increasing the shear rate, it exhibited a relaxation type behavior similar to viscosity dependence typically observed in smectogenic fluids as reported by Larson *et al.*³²

3.2 Synthesis of PEDOT-PDPSA by oxidative polymerization

Oxidative polymerization of the liquid crystalline template 'EDOT-PDPSA' was conducted in the presence of ferric chloride as the initiator. A series of color change effects were observed subsequent to the addition of the initiator, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. During the propagation process, color changes from brown to blue, green and finally to violet owing to the progress of the oxidation-reduction process leading to a high molecular weight PEDOTS as shown in Scheme 1. The change of the color is attributed to the variation in the electronic state of the PEDOT and the irregularity in the nature of aggregation. The polymerization process was driven by the intrinsic properties of the self-organized lamellar phase of "EDOT-PDPSA" which act as a soft anisotropic template and drives the shape and size of the formed PEDOTS. The self-assembly of EDOT-PDPSA through bilayer interdigitation forming micelles, its transformation into a liquid crystalline phase and its action as a soft template for the generation of PEDOTSs are illustrated in Scheme 1.

PEDOTS particles were observed to be highly dispersible in water. The particle size and polydispersity index measurement of the PEDOT dispersions were carried out using a DLS technique and details are given in Table 1. Results showed that the particle size of the prepared PEDOTS nanospindles varied with the change of experimental conditions. The particle size of PEDOTS1 was measured to be in the range of ~ 48 nm with a polydispersity index of 0.3–0.2. However, when the polymerization temperature was increased to 60°C , the particle size was raised to ~ 69 nm. Increase in temperature may accelerate the aggregation behavior, which in turn enhanced the particle size. This observation was further strengthened during molecular weight determination and morphological analysis. The particle size of PEDOTS3 was observed to be ~ 80 nm at room temperature and ~ 100 nm at 60°C (PEDOTS4). Particle sizes of polymer nanostructures are affected by the solvent used for their preparation.^{33,34} In the ethanol-water mixture EDOT-PDPSA adopts a spindle type micellar assembly which retains its shape on polymerisation and has a size of ~ 48 nm. But in water, due

to increased polarity EDOT-PDPSA impulsively associates to form 2D ordered lamellar self-assembly. Growth of polymeric chains from lamellar self assembly in polar medium leads to aggregation of polymeric nanostructures with an approximate size of 80 nm. PEDOT prepared in the absence of the template exhibited a particle size of ~ 300 nm. The molecular weight of PEDOTS was measured using MALDI TOF and found to be in the $\sim 50\,000$ Da, $\sim 55\,000$ Da, $\sim 40\,000$ Da, $\sim 45\,000$ Da, and $\sim 30\,000$ Da with a narrow molecular weight distribution of PEDOTS1, PEDOTS2, PEDOTS3, PEDOTS4 and PEDOT, respectively.

The chemical and electronic structures of the PEDOTSs were confirmed by FT-IR and UV-vis spectroscopy. The FTIR spectrum of PEDOT and PEDOTS1 is shown in Fig. 4i(a–b). PEDOT showed a band at 1380 cm^{-1} which can be ascribed to the quinoid C–C structure in the thiophene ring. The band observed at 1205 cm^{-1} can be assigned to the C–O–C bond stretching, and the bands corresponding to the C–S bond vibrations in the thiophene ring were found at 1004 and 750 cm^{-1} . The band observed at 1054 cm^{-1} is associated with the stretching vibrations in the ethylenedioxy group. The band at 1629 cm^{-1} can be attributed to the doped level of PEDOT. The bands at 2850 – 2980 cm^{-1} are associated with the characteristic $-\text{CH}_2-$ stretching of the ethylenedioxy bridge. The chemical structure of the formed PEDOTS1 exhibited similar peaks to those of PEDOT with additional bands at 1305 and 1195 cm^{-1} due to the presence of $(-\text{SO})$ and the band at $1032, 574\text{ cm}^{-1}$ attributed to $(-\text{SO}_3)$. All these results are consistent with the reports made by other researchers.^{35,36}

UV-vis absorption spectroscopy is a very sensitive tool for studying the nature of protonation in conducting polymers and showed obvious differences between the conducting and non-

Fig. 4 (i) FT-IR spectrum of (a) PEDOT, (b) PEDOTS and (ii) UV-vis spectra of (a) PEDOT, (b) PEDOTS1, (c) PEDOTS3, (d) PEDOTS2 and (e) PEDOTS4.

Table 1 Properties of PEDOT nanostructures prepared in the presence and absence of PDPSA

Sample	Conditions solvent/T	Particle size (nm)	Conductivity (S cm^{-1})	Mol. wt Da
PEDOTS 1	Et-H ₂ O/20 °C	48	2.92×10^{-1}	50 000
PEDOTS 2	Et-H ₂ O/60 °C	69	2.79	55 000
PEDOTS 3	H ₂ O/20 °C	80	1.69×10^{-1}	40 000
PEDOTS 4	H ₂ O/60 °C	100	1.35	45 000
PEDOT	H ₂ O/20 °C	300	3.5×10^{-5}	30 000

conducting state of the polymer.^{37,38} The UV-vis spectra of PEDOT, PEDOTS-1, PEDOTS-2, PEDOTS-3, and PEDOTS-4 are shown in Fig. 4ii(a-e), respectively. PEDOT, PEDOTS1 and PEDOTS3 showed absorption maxima at 420 nm which can be ascribed to the π - π^* electronic transition of the thiophene units. However, PEDOTS2 and PEDOTS4 showed a red shift to 480 nm showing a high level of doping at high temperature. PEDOTS1 and PEDOTS3 exhibited a broad absorption band at about 800–900 nm, a feature typically seen in the doped state of conducting polymers and the absorption band at a wavelength greater than this band is referred to as a “free carrier tail.” This tail was observed in conducting polymers with highly delocalized bipolarons. Intensity of this tail in this region in PEDOTS2 and PEDOTS4 was observed to be higher revealing the formation of more number of bipolarons at high temperature. These observations are supported by the measured high conductivity of the PEDOTS2 and PEDOTS4.

3.3 XRD measurements

The nature of solid state ordering in PDPSA, liquid crystalline phase of EDOT-PDPSA, PEDOT and PEDOTS prepared under different conditions were studied by an X-ray diffraction technique and are shown in Fig. 5a-f, respectively. PDPSA exhibited well-ordered sharp peaks with high intensity at $2\theta = 2.3^\circ$, 4.6° and 7.1° revealing the presence of a high degree of crystalline order due to the intermolecular hydrogen bonding between the -OH and -SO₃H and also due to the ordering arising from the interdigitation of the hydrophobic layer stacking. The highest peak observed at $2\theta = 2.3^\circ$ with a d -spacing of 36.2 Å corresponds to the dimension of the self-assembled bilayered PDPSA molecule (Fig. 5a). The XRD pattern of “EDOT-PDPSA” in the lamellar phase given in Fig. 5b showed a sharp peak at $2\theta = 2.75^\circ$ (32.1 Å) and a broad peak at $2\theta = 3.62^\circ$ (24.38 Å) revealing the presence of supramolecular organization with a liquid crystalline hexagonal phase. It also exhibited sharp peaks at $2\theta = 5.08^\circ$ (17.37 Å), $2\theta = 9.67^\circ$ (9.13 Å) and $2\theta = 12.00^\circ$ (7.37 Å). The peak observed at $2\theta = 23.83^\circ$ corresponds to the d -spacing of 3.73 Å corresponding to the inter-planar distance of the adjacent ethylene dioxithiophene centres. The observed d -spacing in “EDOT-PDPSA” was found in good correlation with the dimensions of the optimized interdigitated structure of EDOT-PDPSA obtained from Gaussian software with a B3LYP method using a

basis set of 6-31g (Fig. 5 given inset). It showed the head to tail distance of EDOT-PDPSA as ~ 22.34 Å, the distance between the interdigitated alkyl chains as ~ 2.4 Å, length of the extended hydrophobic chain as ~ 16.27 Å, and the distance between the interdigitated thiophene head groups as ~ 8.31 Å.

All PEDOTSs exhibited a high intense peak at $2\theta = 2.8$ – 3.5° with an average d -spacing of ~ 26.36 Å corresponding to the dimension of the self-assembled supramolecular PEDOTS structures. The XRD pattern of PEDOTSs prepared from both water and ethanol-water at 20°C showed a peak at $2\theta = \sim 3.35^\circ$ (26.34 Å). But for PEDOTS2 it is shifted to 3.26° with a d -spacing of 27.07 Å revealing a higher dimension for the aggregated self-assemblies. PEDOTS3 exhibited this signal at $2\theta = 2.82^\circ$ with a d -spacing of 31.29 Å. The diffraction peak at $2\theta = 25.5^\circ$ (d -spacing 3.5 Å) corresponds to the inter-planar ring stacking distance. However, it was noted that the XRD pattern of PEDOTS prepared in water exhibited weak broad peaks, compared with the batches prepared in the ethanol-water mixture which suggest less ordering for PEDOTSs prepared from aqueous medium. However, PEDOTS3 (Fig. 5d) prepared at a higher temperature showed a peak at $2\theta = 25.5^\circ$ with a higher d -spacing suggesting a loose molecular interaction between the stacked ring and the larger size for stacking aggregates. Here inclusion of the dopant ion pulls polymeric chains apart making necessary room for solvent inclusion. These will facilitate more water molecules to intrude the polymeric matrix, making it more water dispersible. PEDOT prepared in the absence of PDPSA showed a broad weak signal between $2\theta = 19$ – 25° , revealing amorphous nature.

3.4 Morphology and mechanism of PEDOT nanospindle formation

The energy minimized structure of the adduct “EDOT-PDPSA” using Gaussian program suggested an extended conformation with a bent structure for the “EDOT-PDPSA” indicating its propensity for the formation of self-assembled supramolecular structures through various noncovalent interactions. XRD of aggregated “EDOT-PDPSA” showed a d -spacing of ~ 32.1 Å which is slightly less than twice the molecular length of “EDOT-PDPSA”, suggesting the presence of interdigitated molecular layers in the supramolecular aggregates as shown in the scheme. At a low concentration, they were observed to form micelles of various shapes, which will be randomly dispersed in the solvent and the PLM picture (Fig. 2a) showed the presence of a mixture of spherical and disc shaped micelles. Above the critical micellar concentration, “EDOT-PDPSA” exhibited the formation of a lyotropic phase. This might have formed by coalescence of various micelles and later they reorganized to form a thermodynamically stable spindle shaped lamellar phase in ethanol-water and a thread like hexagonal phase in water. The spindle shape of the liquid crystalline phase may be attributed to the strong intermolecular interaction among the charged ions present in the head groups and the counter charge in EDOT, hydrophobic tails and also inter planar π - π stacking. The interdigitated bilayers formed by the “EDOT-PDPSA” ensembles as shown in Scheme 1.

Fig. 5 (i) Powder XRD patterns of (a) PDPSA, (b) EDOT-PDPSA, (c) PEDOT, (d) PEDOTS2, (e) PEDOTS1 and (f) PEDOTS3. Energy minimized double layer geometry of EDOT-PDPSA is given in the inset and (ii) the magnified lower angle portion of powder XRD.

These supramolecular assemblies are thermodynamically stable and may take the shape of a spindle as shown in Fig. 2b. The lyotropic phase of “EDOT-PDPSA” in water exhibited a lamellar smectic phase as shown in Fig. 2d. Morphological variations during polymerization of “EDOT-PDPSA” in ethanol-water and water were followed by taking TEM images in definite time intervals. Initially nanoscopic spindle shaped PEDOTS were observed under TEM. In the propagation step, PEDOTS aggregates which are in the lyotropic mesophase may lose molecular order on a nanometer scale due to the thermodynamic influence of the growing chain. They form thermodynamically stable spindles of inherent nanoscale dimensions *via* self-assembly.

The TEM pictures showing the formation of sub-nanospindles and later aggregation to form nanospindles through side-wise etching are shown in Fig. 6a. PEDOTS1 exhibited uniform nanospindles of 20 nm width and 200 nm lengths after 6 h (Fig. 6b). However, when the polymerization time was increased to 12 h, PEDOTS1 were observed as slightly elongated spindles of 30 nm width and 300 nm lengths and after 24 h spindles of 50 nm width and 300 nm length were observed (Fig. 6c and d). Similar observations were made by O'Brien *et al.*³⁹ They successfully prepared varieties of liquid crystalline assemblies with the preservation of the shape of the meso-structures of the monomers. These observations were further strengthened by the studies made by Stup *et al.*²⁰ They proposed that the observed structure results from the template directed aggregation of the oriented polymer chains which preserve the shape of the liquid crystalline template.

The TEM image showing a single nanospindle composed of subnanofibrils is shown in Fig. 6e. It further confirms the

formation of nanospindles from micelles of lower dimensions having disc or fibrillar morphology. It has been observed at high temperature, the oriented nanofibrils confined inside the nanospindles blossoms out with fibrils of a high aspect ratio due to the changes in the thermodynamic properties and the mode of molecular packing at high temperature. The TEM image of PEDOTS2 synthesized at 60 °C showed nanowhisker/fibrillar morphology as shown in Fig. 6f. TEM images of PEDOTS3 prepared from water dispersion at 20 °C for 6 h showed networks of nanofibrils as shown in Fig. 6g. However, after 24 h these nanofibrils transformed into a more ordered nanofibers with a high aspect ratio (Fig. 6h). PEDOTS4 prepared at 60 °C in water exhibited nanowires of 20–30 nm diameter and several orders of micrometer length attributed to the hierarchical aggregation of the self-assembled nanofibrils as shown in Fig. 6i. SEM analyses of PEDOTS also confirm the formation of nanofibrils and nanowires (Fig. S3a–S3c†). The SEM image of PEDOT prepared in the absence of PDPSA showed no specific morphology (Fig. S3d†) revealing the contribution of PDPSA in the formation of a template. SAED patterns showing the presence of well-ordered nanospindles and nanowires are given in the ESI as Fig. S4a and S4c.† Our observation is contrary to the reports made by Mao *et al.*²² They prepared PEDOT nanospindles using FeCl₃ as the initiator in the presence of CTAB and PAA as templates. They reported that the observed nanospindles are attributed to the co-crystallization of PEDOT and β-akagenite and they observed their characteristic crystalline peaks in XRD and the stoichiometric amount of iron in EDAX spectra. However, we could neither observe the characteristic crystalline peaks of β-akagenite in XRD nor the stoichiometric amount of iron in EDAX confirming that the spindle formation is ascribed exclusively to the imitation of a liquid crystalline template and not by the simultaneous occurrence of polymerization of EDOT and crystallisation of Fe³⁺. Nevertheless, EDAX of PEDOTS1 prepared from ethanol-water showed the presence of some amount of iron, which may be contributed from the free iron hydroxide retained during the purification step. The typical EDAX profile of PEDOT nanospindles and nanowires are given in the ESI (Fig. S4b and S4d†). The size of the nanospindles and nanofibrils could be adjusted by controlling the reaction conditions.

3.5 Conductivity studies and thermal stability

DC conductivity of pelletized samples of PEDOTS was measured using a four-probe conductivity meter. Details regarding the composition and conductivity are depicted in Table 1. Conductivities of PEDOTSs prepared under different experimental conditions showed significant variations. PEDOT prepared in the absence of the template exhibited conductivity in the order of $3.5 \times 10^{-5} \text{ S cm}^{-1}$. However, PEDOTS1, PEDOTS2, PEDOTS3 and PEDOTS4 have conductivity of $2.96 \times 10^{-1} \text{ S cm}^{-1}$, 2.79 S cm^{-1} , $1.69 \times 10^{-1} \text{ S cm}^{-1}$ and 1.35 S cm^{-1} respectively. Sulphonate ions acts as smooth relay bridges in between the polymeric chains for charge carriers and thereby enhancing the conductivity in a significant manner. In a recent report, PEDOT:PSS films prepared by the template method

Fig. 6 Morphological evaluation of PEDOTSs during the course of polymerization: (a) sideways etching of subnanospindles to nanospindles. PEDOTS1 (b) after 6 h, (c) after 12 h, (d) after 24 h, and (e) single nanospindle showing subnanofibrils or discs; (f) PEDOTS2 after 24 h; (g) PEDOTS3, (h) nanofibrils of PEDOTS3 after 24 h; and (i) nanofibrils of PEDOTS4.

exhibited a conductivity of 2 S cm^{-1} which is less than that of PEDOTS.⁴⁰ This also supports the utility of PEDOTS in photo-voltaic devices as a charge transport layer. Any nano-formulations with pointed ends are capable of accumulating charges and transfer to other parts. T. P. Lodge *et al.* showed that their nanoporous PEDOT fibrous film has a conductivity of $5.4 \times 10^{-4} \text{ S cm}^{-1}$ which is comparatively lower than that of PEDOT hexagonal rods prepared by Remita *et al.* (0.4 S cm^{-1}).^{41,42} Kim *et al.* reported PEDOT nanofibers with a higher conductivity of 1 S cm^{-1} .⁴³ M. H. Lee *et al.* reported PEDOT/PSSA spherical nanoparticles with a conductivity of 0.11 S cm^{-1} .⁴⁴ These observations suggest that bulk aggregated films have lower conductivity in comparison with distinctly separated nanostructures. Also, elongated nanostructures with tapered ends have more conductivity than spherical particles. In our case we got a maximum conductivity of 2.79 S cm^{-1} due to the nanospindle morphology. Nanospindles with pointed ends facilitate smooth transfer of charge carriers resulting in higher conductivities which can be applied in different fields as anisotropic conductors. It may also find place by replacing PEDOT/PSS as a charge carrier for various energy devices. Further, a comparative study showing the effect of shape on the electrical conductivity PEDOT nanoparticles is illustrated in Table S1.†

Conducting polymers with good conductivity and thermal stability are desirable for the high energy applications.⁴⁵ Thermal stability studies were carried out in a DTG analyzer under nitrogen atmosphere. PEDOTS1, PEDOTS3 and PEDOT were observed to be decomposing at 310°C , 315°C and 290°C with a char yield of 6.9%, 6.5% and 4.1%, respectively. The higher thermal stability exhibited by PEDOTS compared with PEDOT may be due to the high molecular weight and also due to the presence of doped ions. Thermograms of PEDOTS1, PEDOTS3 and PEDOT are shown in Fig. S5a–S5c,† respectively in the ESI.

3.6 Electrochemical behavior and CV responses of L-ascorbic acid using a nanospindle PEDOT modified GCE

The electrochemical behavior of PEDOTS was studied by cyclic voltammetry (CV). CV response of the PEDOTS1 modified GCE in $0.1 \text{ M H}_2\text{SO}_4$ with a scanning rate of 0.05 V s^{-1} is shown in Fig. 7. It exhibited weak redox peaks at 0.562 V (oxidation) and 0.37 V (reduction) referred to as a standard Ag/AgCl electrode, which is a characteristic feature of PEDOT.

Experiments were performed for studying the electro catalytic activity of a modified GCE with PEDOTSs on the oxidation of ascorbic acid. Fig. 8i shows the cyclic voltammograms of the PEDOTS modified GCE and bare GCE in phosphate buffer solution (PBS) ($\text{pH} = 7.4$ at 27°C with a scanning rate of 0.05 V s^{-1}). The bare GCE did not give any CV response (Fig. 8ib) and current obtained is much lower than the modified GCE (Fig. 8ia). The CV measurements have been carried out in PBS with 1 mM L-ascorbic acid. The oxidation potential of L-ascorbic acid appeared to be around 0.357 V with a peak current of $4.7 \mu\text{A}$. It was found that the oxidation peak was broad and no peak in the reverse scan was observed, which indicated that the

Fig. 7 Cyclic voltammogram of PEDOTS3 in $0.1 \text{ M H}_2\text{SO}_4$. Scan rate 0.05 V s^{-1} .

oxidation of ascorbic acid at the bare electrode is totally irreversible (Fig. 8iib). However, the CV diagram of the PEDOTS modified GCE showed the oxidation peak of ascorbic acid at

Fig. 8 Cyclic voltammetric responses in the presence and absence of L-ascorbic acid (AA) in PBS buffer ($\text{pH} = 7.4$) (i) without AA (a) PEDOTS modified electrode and (b) bare GCE. (ii) In the presence of 10^{-3} M AA (a) PEDOTS modified electrode and (b) bare GCE. (iii) Effect of the AA concentration on CV responses of the modified electrode in PBS buffer (a) $5 \times 10^{-5} \text{ M}$, (b) 10^{-4} M , (c) 10^{-3} M and (d) $5 \times 10^{-3} \text{ M}$ AA. (iv) Effect of the scan rate on the cyclic voltammetric responses of the PEDOTS modified GCE (a) 10; (b) 20; (c) 30; (d) 40; (e) 50; (f) 60; (g) 70; (h) 80; (i) 90; and (j) 100 mV s^{-1} in PBS with 1 mM L-AA. (v) Plot of the square root of the scan rate vs. the peak current.

0.046 V compared to the bare GCE, the peak current was about 10 times (91.68 μA) higher than that of the bare GCE, which revealed the electro-catalytic oxidation of ascorbic acid at the modified GCE (Fig. 8iia). This is supported by the work done by other researchers.⁴⁶ According to the literature, the large cathodic shift in the oxidation potential and the enhanced oxidation current may be due to the electrostatic attractions between the cationic charged PEDOTS backbone on the modified GCE and the ascorbate anions in the solution. Also from the FTIR data, it is evident that the doped PEDOT contains sulphate anions, which could be partly exchanged by the ascorbate anions and might accumulate at the interface of the modified GCE. Fig. 8iii shows the CV responses of the modified GCE in PBS with different concentrations of L-ascorbic acid. The effect of the scanning rate and the CV responses of the electro-catalytic oxidation of ascorbic acid using the modified GCE are shown in Fig. 8iv. It was found that the nature of the oxidation process in PBS proceeds by diffusion control as evidenced from the plots of the square root of scan rate vs. the peak current. Their good linear dependence and the low detection limit showed significant sensitivity of PEDOTS nanospindles modified GCE for the detection of ascorbic acid in aqueous solutions.

Conclusions

Water dispersible PEDOTSs with controlled size, shape and microstructure were prepared using polymerization of the liquid crystalline template EDOT-PDPSA. It was observed that the morphology of PEDOT could be tuned from nanofibrils to nanospindles and wires by controlling the experimental conditions. Solid state ordering in the template monomer and polymer was confirmed by XRD and SAED patterns. The formation of nanospindles and nanowhiskers was confirmed by SEM and TEM. Nanospindles of conducting PEDOTS with pointed ends are a suitable candidate for charge transfer in nanoelectronic devices. Studies on the electrochemical stability and electrocatalytic activity of the PEDOT nanospindle modified GCE suggest its application in the electrocatalytic oxidation of ascorbic acid and similar molecules. The electrical conductivity of PEDOTS observed as $\sim 2.79 \text{ S cm}^{-1}$ and its high thermal stability of $\sim 300^\circ\text{C}$ suggest that these water dispersible nanomaterials can be used as a hole transport layer in photovoltaics.

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