Improved performance of PEDOT aqueous dispersion and film with poly (sodium styrene sulfonate) graft poly (ethylene glycol) as a template and hexafluorobutanol as a polymerization additive

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In this study, we have successfully synthesized a poly(3,4-ethylenedioxythiophene): poly(sodium styrene sulfonate)-*graft*-poly(ethylene glycol) (PEDOT:PSS-*g*-PEG) aqueous dispersion with enhanced film conductivity. A graft copolymer template of poly(sodium styrene sulfonate)-*graft*-poly(ethylene glycol) was synthesized via free radical polymerization of sodium styrene sulfonate and allyl polyethylene glycol. Stable PEDOT water dispersions with low surface tension were successfully synthesized using PSS-*g*-PEG as a template and hexafluorobutanol (HFB) as a polymerization additive. Results showed that the poly(sodium styrene sulfonate)-*graft*-poly(ethylene glycol) when used as the template increased the stability of PEDOT water dispersion and lowered the surface tension. And HFB lowered the polymerization rate of EDOT. The conductivity and transparency of PEDOT films can be increased with HFB as a polymerization additive. The square resistance of PEDOT:PSS-*g*-PEG film with HFB was about 34 times lower than that of PEDOT: PSS-*g*-PEG film without HFB. The improvement of conductivity can be attributed to the better phase separation between PEDOT and PSS-*g*-PEG and HFB enhanced this phase separation.

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1. Introduction

Poly(3,4-ethylenedioxythiophene) (PEDOT) has excellent electrical conductivity and receives much attention both in academic and industrial fields [1]. But the insoluble property of PEDOT prevents it from further applications. With poly(styrene sulfonate) (PSS) as a template, PEDOT:PSS can be dispersed in water and some polar organic solvents [2-4]. PEDOT:PSS films show good conductivity, high transparency in the visible range, mechanical flexibility, excellent thermal stability and can be processed through conventional solution processing technologies [5]. PEDOT:PSS is the most successful conducting polymer and finds many applications, such as antistatic coatings [6-7], capacitors [8], solar cells [9], light emitting diodes [10], and touch panel displays [11].

However, the conductivity of PEDOT:PSS film is normally less than 1S/cm, much lower than that of pure PEDOT films prepared by vapor polymerization. The main reason for the low conductivity of PEDOT:PSS film is that the PSS, which is used as the charge compensator and template for PEDOT, is an insulator [3,7]. It is essential to enhance the conductivity of PEDOT:PSS film effectively by reducing the negative effect of PSS. Three methods to improve PEDOT:PSS film conductivity have been proposed [12]. Vapor polymerization of EDOT is an effective method to prepare high conductivity PEDOT film. In this kind film, no insulate template is used and the film with conductivity as high as 1500 Scm^{-1} has been reported [13]. "Secondary doping" is another widely used method to enhance the conductivity of PEDOT:PSS film. Polar organic compounds, such as dimethyl sulfoxide (DMSO), *N,N*-dimethyl formamide (DMF), ethylene glycol, ionic liquid and even anionic surfactant are added into PEDOT:PSS water dispersions [14-21]. By addition of secondary dopants to the PEDOT:PSS water dispersions, larger phase separation between PEDOT and PSS was observed. This lowers screening effects of PSS leading to better connection between the conducting PEDOT domains and enhances the conductivity of the film. Post-treatment of PEDOT:PSS film is also a way to improve the conductivity of PEDOT:PSS film. Treating the PEDOT:PSS films with polar organic solvents, acids and zwitterions can remove excess PSS from film surface, change the morphology of PEDOT and improve the conductivity [22-26]. Recently, Yijie Xia et al [27]

proposed that highly conductive PEDOT:PSS films can be obtained through a treatment with amphiphilic fluoro compounds. The square resistance of treated film is as low as 46 Ω/square, which is close to that of ITO (50 Ω/square).

However, vapor phase polymerization is not so easy to be widely used in mass production. The post-treatment of PEDOT:PSS film will cause the film to be crack and not smooth. Here, we report a PEDOT water dispersion with better wettability and enhanced film conductivity through changing structure of the template and introducing an additive. Allyl polyethylene glycol (APEG) is copolymerized with styrene sulfonate to produce PSS-*g*-PEG template to increase the stability and wettability of the PEDOT aqueous dispersion. Hexafluorobutanol (HFB), as a polymerization additive, is introduced to enhance the conductivity of PEDOT film.

2. Experimental

2.1. Materials

Sodium styrene sulfonate (SSNa), 3,4-ethylenedioxythiophene (EDOT), ferric sulfate ($Fe_2(SO_4)_3$), ammonium persulfate ($(NH_4)_2S_2O_8$, APS), hexafluorobutanol (HFB), isopropanol (IPA) and other chemicals are purchased from Sinopharm Chemical Reagent Co., Ltd. and used as received unless otherwise noted. Allyl polyethylene glycol (APEG，M_n=2400) was obtained from Jiangsu Haian Petrochemical Plant, China. Deionized water was used throughout the work.

2.2. Synthesis of PEDOT:PSS-*g*-PEG aqueous dispersion with HFB as the additive

Synthesis of poly(sodium styrene sulfonate)-g-poly(ethylene glycol) copolymer (PSS-g-PEG)

The template polymer of PSS-*g*-PEG was synthesized via free radical polymerization in water. 20.38 g SSNa and 2.038 g APEG (M_n=2400) were dissolved in 88.38 g deionized water, then 0.1 g APS was added into the solution. The reaction was kept at 90 °C for 6 h under nitrogen atmosphere. Finally, the obtained product (PSS-*g*-PEG) was precipitated in ethanol and dried in vacuum oven under 50 °C for 24h.

Synthesis of PEDOT:PSS-g-PEG water dispersion with HFB as an additive

The synthesis of PEDOT: PSS-*g*-PEG water dispersion with HFB was carried out using PSS-*g*-PEG as the template and charge-balancing counterion and the HFB as an additive. 3 g PSS-*g*-PEG, 1 g EDOT, 1 g isopropanol (IPA) and 196 g deionized water were mixed in a three-neck flask and stirred for 0.5h. Then, 0.0056g iron sulfate and 2.4168g APS were sequentially added into the solution to start the polymerization. The reaction was kept under nitrogen at 40 °C for 24 hours. Samples were taken at specific time intervals to measure the monomer conversion using gas chromatography (GC) method.

2.3. Characterization

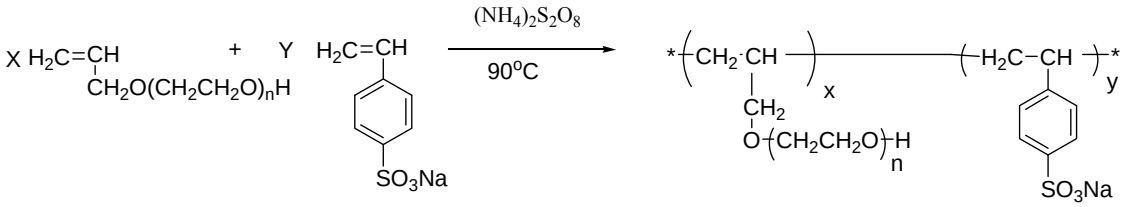
Monomer conversions were analyzed using gas chromatography (GC) method via GC-1690 (Beijing Kexiao Chemical equipment Co. Ltd.) with isopropanol as an internal standard. Nuclear magnetic resonance (NMR) spectra were obtained using a Bruker DMX 500 MHz spectrometer with D_2O as a solvent and tetramethylsilane as an internal standard. Molecular weights and polydispersities of the copolymers were obtained via gel permeation chromatography (GPC) utilizing a Waters 1515 with dimethylformamide as an eluent, at a flow rate of 1.0 ml/min, and polystyrene as a standard. Thermo-gravimetric analysis (TGA) of the polymers was carried out on an SDT Q600 (TA Instruments) under nitrogen and at a rate of 20 °C/min. UV-visible absorption spectra were recorded on UV-vis spectrometer (Shimadzu UV-2450). The film samples were prepared by spin-coating the dispersions on glass substrates with the thickness of the film of 80 nm. The particle size and size distribution of the PEDOT dispersion were analyzed by dynamic light scattering technique using Malvern Nano-ZS, Particle Size and Zeta Potential Analyzer. The surface square resistances (Ω/sq) of PEDOT films were measured using a standard four-point probe method (RTS-9, Guangdong Four-Point Probe Technology Company，China) under ambient conditions. For the film formation, the synthesized PEDOT dispersion was poured into a plastic (PET) sheet and dried in the oven at 60 °C to form the conductive PEDOT thin film. The thickness of PEDOT film was controlled to be about 100 μm. The TEM images were recorded on JEM-2100 from Japan Electron Optics Laboratory Co., LTD. The samples were prepared by drop-casting the diluted PEDOT dispersion on a TEM grid. Nanoman VS Atomic Force Microscope were used to obtained the surface morphology of the PEDOT films. The films were prepared by spincoating the PEDOT dispersion on clean glass substrate. Cyclic voltammetry was conducted on a CHI660C electrochemical work station (Chenhua Instrument Co., Shanghai) in an electrolyte water solution of 0.1 M sodium chloride. Pt wires were used as both counter and working electrodes, and Ag/AgCl was used as a reference electrode. The scan rate was 50 mV/S.

3. Results and discussion

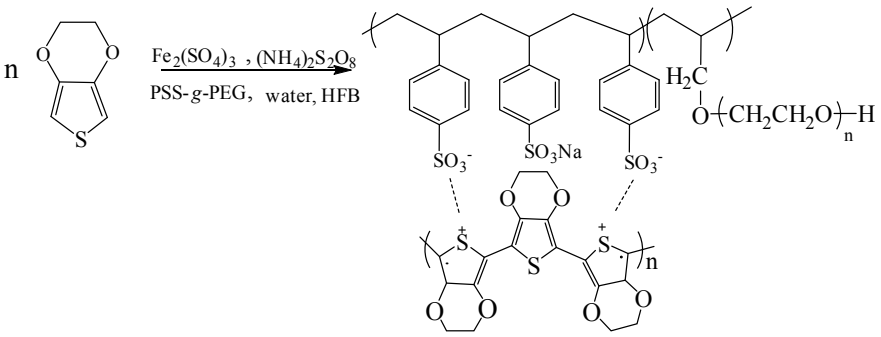
3.1. Synthesis of PEDOT:PSS-*g*-PEG water dispersions with HFB as an additive

PSS-*g*-PEG copolymers were synthesized by free radical polymerization with sodium styrene sulfonate and allyl polyethylene glycol as monomers, as shown in scheme 1. And the reaction scheme of preparation of PEDOT: PSS-*g*-PEG water dispersions is shown in

scheme 2.



Scheme 1 Synthetic route for PSS-g-PEG.



Scheme 2 Reaction scheme for preparation of PEDOT:PSS-g-PEG

Fig. 1 shows the ^{1}H-NMR spectrum of copolymer PSS-*g*-PEG, where the M_n of PEG is 2400. Typical protons are indicated in the figure. The protons a at chemical shift of δ(ppm)= 6.5~7.5 ppm are the protons from phenyl rings of the polymer. The protons b at the chemical shift of δ(ppm)= 3.5 ppm are the protons on methylene attached to oxygen of PEG branched segment. These indicate that the target copolymer of PSS-*g*-PEG was obtained. The integration ratio of a to b is 1:0.8 and the molar ratio of SSNa to APEG can be estimated to be 65:1. The molecular weight of the copolymer (M_n) is about 45200, which was determined by GPC. Thus on average, one PSS-*g*-PEG macromolecule chain contains approximately 2.86 grafted PEG chains.

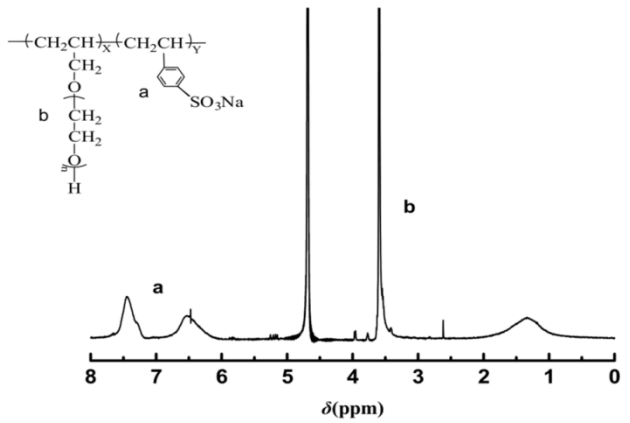


Fig. 1. ^{1}H-NMR spectrum of the copolymer of PSS-g-PEG

PEDOT:PSS-*g*-PEG water dispersion was synthesized using the above PSS-*g*-PEG copolymer as the template and hexafluorobutanol (HFB) as an additive to enhance the performance of the PEDOT dispersion and films. We first investigated the effect of HFB on the polymerization kinetics of EDOT and the conversion curves are shown in Fig. 2. The amount of HFB used was based on the total weight of EDOT and PSS-*g*-PEG and slightly low polymerization rate was observed. This may attributed to the dilute concentration of EDOT droplet by HFB. But after about 8 hour polymerization more than 90% conversion of EDOT can be achieved.

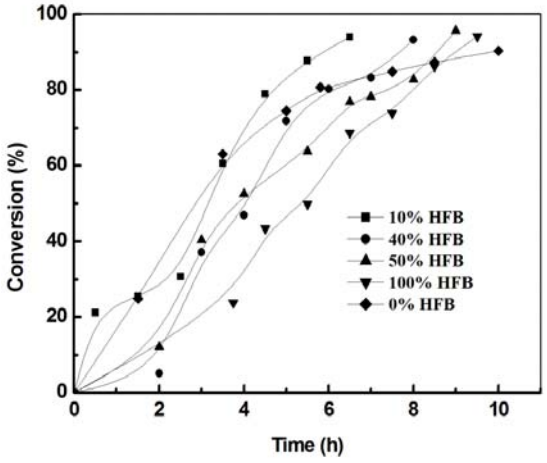


Fig. 2. Conversions of EDOT with different amount of HFB

3.2. Characterization of PEDOT: PSS-*g*-PEG water dispersion and film

Table1 lists the particle sizes of PEODT:PSS-*g*-PEG aqueous dispersions with different amount of HFB. The particle sizes of PEDOT aqueous dispersions slightly increased after the addition of HFB, which may be due to the insolubility of HFB in water and the PEDOT particles were swelled by HFB. The swelled small particles were

easy to aggregate and formed bigger particles.

From TEM images (Fig.3), it can be seen that PEDOT particles are the aggregation of smaller ones. And the particles prepared with HFB (Fig.3 b) seemed to be composed of much smaller particles than that of without HFB (Fig. 3a). This can be explained by the emulsified effect of HFB. HFB has an OH group which is hydrophilic and has some emulsifying effect in the system.

Table 1. Particle sizes of PEDOT:PSS-g-PEG aqueous dispersions with different amount of HFB

HFB/(PSS-*g*-PEG+EDOT) （wt%）	0	10	40	50	100
Average Particle Sizes (nm)	556	593	642	806	945

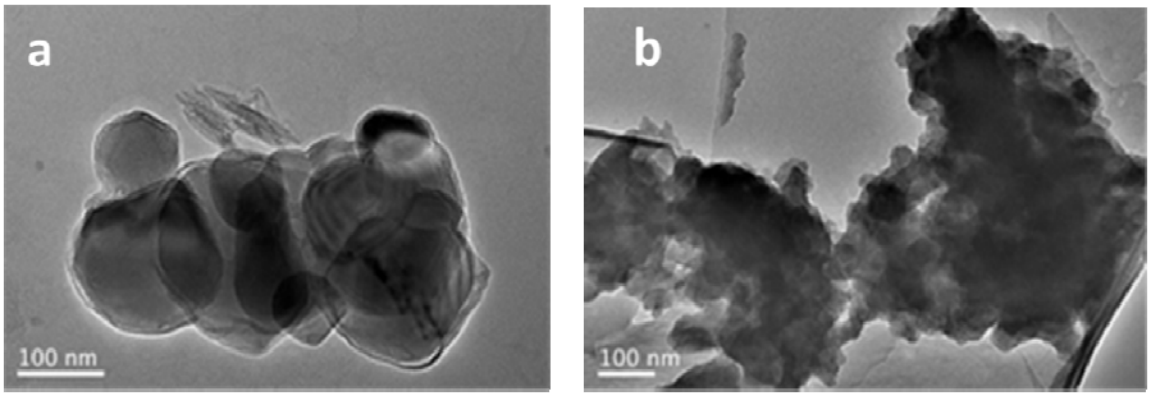


Fig. 3. TEM images of PEDOT:PSS-g-PEG particles. (a) PEDOT particles without HFB (b) PEDOT particles with HFB

Large surface tension of commercial PEDOT:PSS water dispersions with PSS as the template causes difficulties in coating the PEDOT:PSS on substrates such as glass and PET by spin-coating or other wet processes without surface treatment. However, when PSS-*g*-PEG was used as the template, the surface tension of the dispersion was reduced from 54.95 mNm^{-1} for PEDOT:PSS to 39.43 mNm^{-1} for PEDOT:PSS-*g*-PEG, increasing the wettability of PEDOT dispersion on the substrate.

Cyclic voltammetry is an effective method to characterize the electrochemical stability and capacity of semiconductors. CV curves of PEDOT:PSS-*g*-PEG without and with 40% HFB are presented in Fig.4. The cyclic voltammograms of the PEDOT was conducted in 0.1 M NaCl with repeated potential scans between -1 V and 1V vs Ag/AgCl at a scan rate of 50 mVs^{-1}. The good repeatability of CV curves after several scans indicates the good electrochemical stability of the materials. Comparing Fig.4a and Fig.4b, PEDOT prepared with 40% HFB (Fig.4b) showed better electrochemical stability than PEDOT prepared without HFB (Fig.4a). This could be contributed to better aggregation of PEDOT segment because of the existence of HFB. On the other hand, the integral area of the CV curves in Fig.4b is much greater than that of Fig. 4a, which suggests the introduction of HFB can increase the electric capacity of PEDOT:PSS-*g*-PEG.

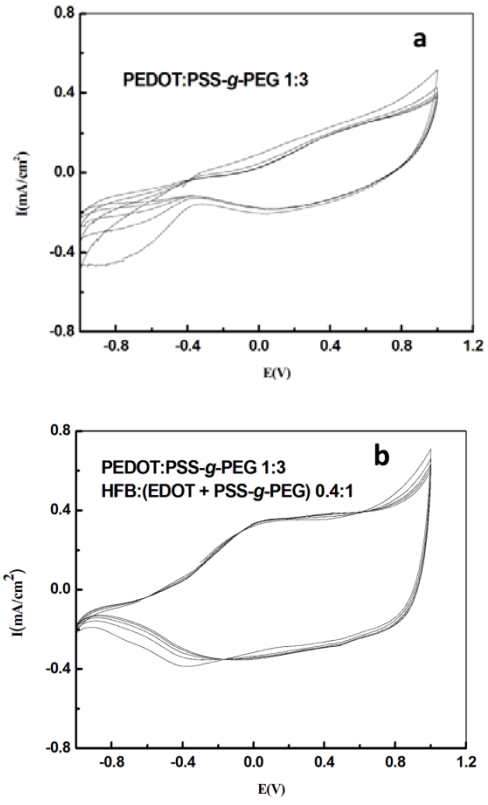


Fig. 4. Cyclic voltammograms of PEDOT:PSS-g-PEG films in 0.1 M NaCl at a scan rate of 50 mVs^{-1} with Ag/AgCl as a reference electrode.
(a) PEDOT:PSS-g-PEG without HFB
(b) PEDOT:PSS-g-PEG with 40% HFB.

The transparency of the PEDOT films in visible range is not greatly affected by the addition of HFB, as seen from Fig.5. After adding HFB into PEDOT dispersions, the transmittance of the PEDOT was even slightly higher than that without HFB. This can probably be ascribed to the dilute effect of HFB on the PEDOT phase which makes the PEDOT phase more uniform.

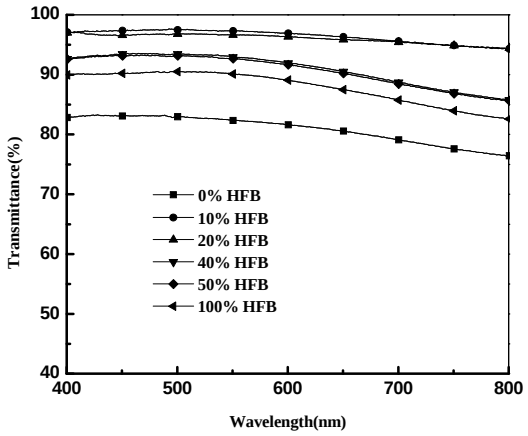


Fig. 5. Transmittance spectra of PEDOT:PSS-g-PEG films. (Thickness of the film was approximately 80 nm)

3.3. The conductivity enhancement of PEDOT: PSS-*g*-PEG films with HFB

As many researchers reported, polyhydric alcohols could significant enhance the conductivity of PEDOT:PSS films, whether these were added into PEDOT:PSS aqueous dispersion as a second doping agent or used to post-treat the films of PEDOT:PSS. Recently, Ouyang Jianyong [5] presented that highly conductive PEDOT:PSS films could be obtained through a film treatment with germinal diols or amphiphilic fluoro compounds. Here, we introduced HFB into the synthetic process to prepare the PEDOT:PSS water dispersion containing HFB. And it was found the square resistances of PEDOT:PSS films were greatly decreased after addition of HFB in the process. Fig 6 shows that the square resistance of PEDOT film with HFB was about 34 times lower than that of PEDOT:PSS-*g*-PEG film without HFB when the mass ratio of HFB to (EDOT+ PSS-*g*-PEG) was 0.5:1. The conductivity enhancement of PEDOT film with HFB was not caused by film crystallinity change; the XRD curves of PEDOT film with and without HFB were compared in Fig. 7. The two XRD patterns are similar, only a big diffraction peak existing, which reveals that the addition of HFB did not change of crystallinity of the film.

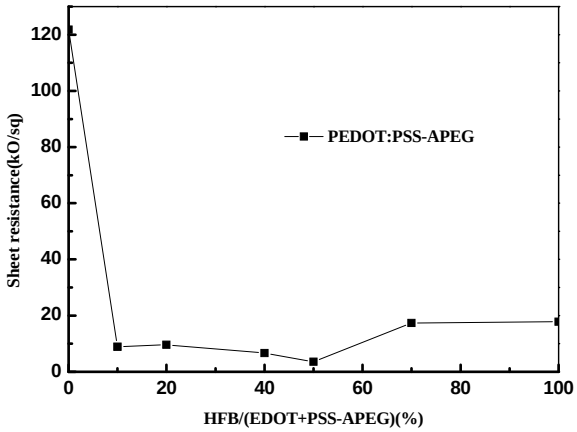


Fig. 6. The square resistances of PEDOT:PSS-g-PEG film with different amount of HFB

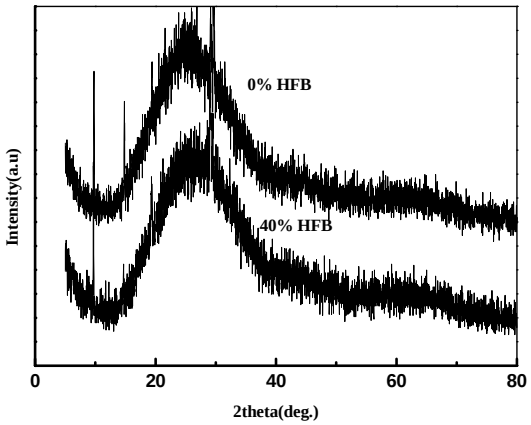


Fig. 7. XRD patterns of PEDOT:PSS-g-PEG films without and with 40% HFB on a glass substrate

The conductivity enhancement of the film can be ascribed to the better phase separation between PEDOT region and PSS-*g*-PEG region. Fig.8 shows the AFM images of the PEDOT films without and with 50% HFB. In Fig. 8, the bright area in the images corresponds to PEDOT rich regions while the dark area corresponds to PSS-*g*-PEG rich regions [28]. The PEDOT:PSS-*g*-PEG film without HFB has a quite smooth surface (Fig.8a), but after adding HFB into the system, the PEDOT film shows much rougher surface (Fig.8c). Apparent phase separation can be observed in the phase images. The incompatibility between PEDOT and PSS-*g*-PEG is the reason for the phase separation and HFB enhances the phase separation because of the incompatibility of HFB with other species. Better phase separation between PEDOT and templates (PSS-*g*-PEG) favors to form conductive networks of PEDOT matrix and enhance the conductivity of the PEDOT films.

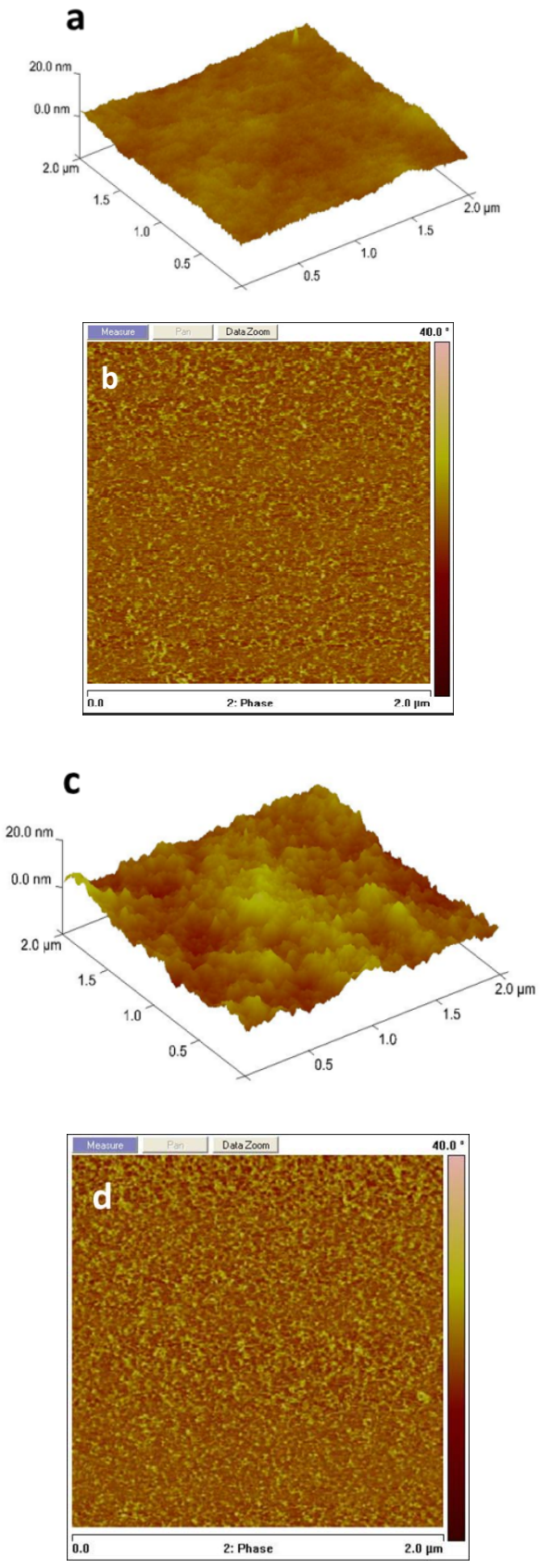


Fig. 8. AFM images of PEDOT:PSS-g-PEG without (a and b) and with (c and d) HFB. All the images are in 2µm×2µm region

4. Conclusions

In conclusion, we have successfully prepared stable PEDOT: PSS-*g*-PEG water dispersions with enhanced film conductivity. The new template copolymer, PSS-*g*-PEG, was synthesized via free radical polymerization and characterized. Stable PEDOT water dispersions with good wettability were synthesized with PSS-*g*-PEG as a template and HFB as a polymerization additive. HFB slightly lowered the polymerization rate of EDOT. The conductivity of PEDOT films can be significantly increased with HFB as a polymerization additive. The improvement of conductivity can be attributed to the better phase separation between PEDOT and PSS-*g*-PEG and HFB enhanced this phase separation.

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