

OPTICAL BAND GAP AND CONDUCTIVITY MEASUREMENTS OF POLYPYRROLE-CHITOSAN COMPOSITE THIN FILMS

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Abstract Electrical conductivity and optical properties of polypyrrole-chitosan (PPy-CHI) conducting polymer composites have been investigated to determine the optical transition characteristics and energy band gap of composite films. The two electrode method and *I-V* characteristic technique were used to measure the conductivity of the PPy-CHI thin films, and the optical band gap was obtained from their ultraviolet absorption edges. Depending upon experimental parameter, the optical band gap (E_g) was found within 1.30–2.32 eV as estimated from optical absorption data. The band gap of the composite films decreased as the CHI content increased. The room temperature electrical conductivity of PPy-CHI thin films was found in the range of 5.84×10^{-7} – 15.25×10^{-7} S·cm⁻¹ depending on the chitosan content. The thermogravimetry analysis (TGA) showed that the CHI can improve the thermal stability of PPy-CHI composite films.

Keywords: Polymer composite; Electron transition; *I-V* characteristic technique; Optical band gap; Polypyrrole.

INTRODUCTION

Since polypyrrole can be prepared easily by electrochemical polymerization on electrodes, numerous works have been made on the characterization and finding application of this polymer in sensors, electronic and optical devices^[1–4]. The electronic conductivity of conducting polymers is unusual and results from mobile charge carriers introduced into the conjugated π -system through doping. A bonding band (π) and an antibonding band (π^*) are generated from π bonds in the electrical density-of-states described by two Gaussian functions separated by a gap^[5]. The electrical conduction in conducting polymers is due to the formation of non-linear defects such as solitons, polarons or bipolarons during doping or polymerization process. In conjugated polymers, all states are localized and therefore electrical transport occurs mainly by hopping process, while the conduction in inorganic materials occurs through a multiple trapping process in which most of the electrical transports occur at the mobility edges.

Khor and Hee Whey^[6] prepared chitosan-polypyrrole hybrid biomaterials by chemical method and they reported low conductivity for this hybrid. Yalçınkaya *et al.*^[7] prepared polypyrrole/chitosan composites on the platinum electrode in the presence of oxalic acid dopant by using cyclic voltammetry. Bredas *et al.*^[8] showed that there was a correlation between UV-Vis absorption bands of polypyrrole at different oxidation levels and formation of polaron and bipolaron species. They studied the band-structure evolution of polypyrrole at different

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levels of oxidation using theoretical calculations. This evolution is supported by electron resonance measurements on oxygen-doped polypyrrole^[9]. Electron spin resonance (ESR) measurements has showed that polarons have spin $S = 1/2$, whereas bipolarons are spinless^[10]. During the oxidation and doping process, intermediary energy levels are created between the valance band (VB) and conduction band (CB); these new electronic levels cause a decreasing in the energy required for the electronic transition and leading to a red shift in the UV-Vis spectrum. The optical absorption and particularly the absorption edge study is a useful method to investigate the band structure and energy gap of both crystalline and non-crystalline materials. Conductivity within conducting electroactive polymers (CEPs) is a complex issue^[11]. The electrochemical conditions, the solvent, the nature/concentration of electrolyte or counterion, doping level, the electrode material, synthesis temperature and the monomer all influence the nature of the polymerization processes occurring and; hence influence the conductivity and optical properties of polymer^[12–14].

In our previous work^[15], it was shown that incorporation of chitosan in the PPy structure led to increasing the electrical conductivity and thermal diffusivity of PPy-CHI composite films. In the present research, UV-Vis spectroscopy was used to investigate the oxidation states of PPy-CHI composite films with the aim of determining the band gaps of these materials. This technique allows monitoring of electronic property changes in polymer films upon oxidation at different doping levels. The main purpose of this work is to study and measure the band gaps and conductivity of composite thin films and their changes as a function of polymerization conditions.

MATERIALS AND METHODS

PPy-CHI thin films were prepared using chemicals and procedure described in our previous work^[15]. The electrochemical deposition of PPy-CHI was performed using a potentiostat (Model: PS 605, USA). All the polymers were potentiostatically prepared in solution containing different concentrations of pyrrole (monomer), chitosan (insulating polymer) and *p*-toluene sulfonate (*p*-TS) at 1.2 V (versus SCE) for 60 s. For the comparison purposes, a PPy film without chitosan was also prepared. A black thin layer of the composite film formed on the ITO glass which could be seen with bare eye. Similar works on the electrodeposition of conducting polymers in short time has also been reported by others^[11]. Martel *et al.*^[16] electrodeposited PPy on different substrates for 70 s. He showed that the substrate nature had a striking effect on the optical properties of PPy films. To measure the conductivity of the PPy-CHI thin films prepared in 1 min, the two-electrode method and *I-V* characteristic technique were used. Four point probes or two probes could not be used for conductivity measurements because the composite films were very thin and the probes could penetrate inside the films which caused some errors in conductivity measurements.

A Keithley Measure Unit Two-probe (236) was used to provide the necessary voltage and measure the resulting currents. As it was mentioned before the probes could penetrate inside the thin film. Thus, this technique was modified to two electrode method. Two wires were used instead of the two probes and they were connected to the thin film on the ITO substrate by using silver paint and circled stickers with a known surface area. The set-up is shown in Fig. 1. In this instrument by applying different voltage, V , and measuring the current, I , resistance (R) and conductance (G) were simply obtained by Ohm's law:

$$R = V/I \quad (1)$$

$$G = 1/R \quad (2)$$

Clearly, if the surface area (a) and thickness (t) of the sample are known, then resistivity (ρ) and conductivity (σ) can be obtained by:

$$\rho = R \times a/t \quad (3)$$

$$\sigma = 1/\rho \quad (4)$$

The thickness of the thin films on the ITO glass was measured by ellipsometry and surface area of the circled sticker was simply measured and finally, the conductivity of the films was obtained using Eq. (4).

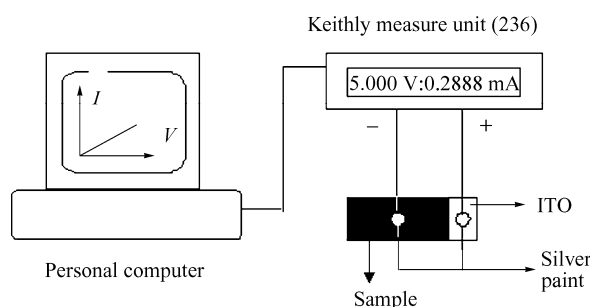


Fig. 1 Experimental set up of the two-electrode method and I - V characterization technique

The optical properties of the thin films were studied using UV-Vis spectrometry. A Perkin-Elmer UV/Vis Lambda 20 spectrophotometer was used to obtain the optical absorption data and an ITO glass was used as the reference for optical absorption measurements. In order to clean the ITO glass surfaces, they were washed with detergent, rinsed thoroughly with distilled water, and then washed with acetone ultrasonically for 10 min following by rinsing the surface with distilled water and drying at 50°C.

The band gap in insulators/semiconductors is classified into direct and indirect band gaps. If the k -vector (momentum) of the minimal-energy state in conduction band and maximal-energy state in the valance band are the same, it is called a “direct gap”. If they are different, it is called an “indirect gap”. Generally the optical band gap (E_g) in an amorphous semiconductor is determined by Tauc Eq. (5).

$$[\alpha h\nu]^{2/n} = K(h\nu - E_g) \quad (5)$$

where n represents the nature of the transition, K is a constant and $h\nu$ is the energy of photon^[17]. The absorption coefficient $\alpha(\nu)$ at various wavelength (or frequencies) is calculated from absorbance (A) and thickness (t) of the sample Eq. (6)

$$\alpha(\nu) = \frac{2.303}{t} A(\nu) \quad (6)$$

The plot of $(\alpha h\nu)^{2/n}$ versus $h\nu$ would give a two-region straight line or a sigmoid shape graph with high value of correlation coefficient. The optical band gap (E_g) can be obtained by extrapolation of the linear portion of the plot of $(\alpha h\nu)^{2/n}$ versus $h\nu$ ^[18]. For a direct transition ($n = 1$), equation becomes (7):

$$[\alpha h\nu]^2 = K(h\nu - E_g) \quad (7)$$

Dutta and De^[18] also obtained the band gaps for SiO₂-polypyrrole nanocomposites using direct transition.

RESULTS AND DISCUSSION

UV-Vis spectra of PPy and PPy-CHI films prepared from solutions containing 0.3 mol/L pyrrole, 0.1 mol/L *p*-TS as dopant and different concentrations of chitosan at 1.2 V (versus SCE) are shown in Fig. 2. These spectra showed two broad bands, centered approximately at 460 and 900 nm. These peaks are related to the electron transition from the valence band to the antibonding polaron state (VB-ABP) and valance band to the bipolaron band (VB-BB), respectively. UV-Vis spectra of organic semiconductor are not so sharp and same spectra for PPy films prepared by chemical method have been reported by Lei *et al*^[14]. The wavelength of VB-ABP transition showed redshift with an increase in CHI concentration till 7 g/L CHI. It means that the band gaps decreased and conductivity increased, indicating a longer conjugation length for the composite film^[19]. This has been confirmed by band gap and conductivity measurements.

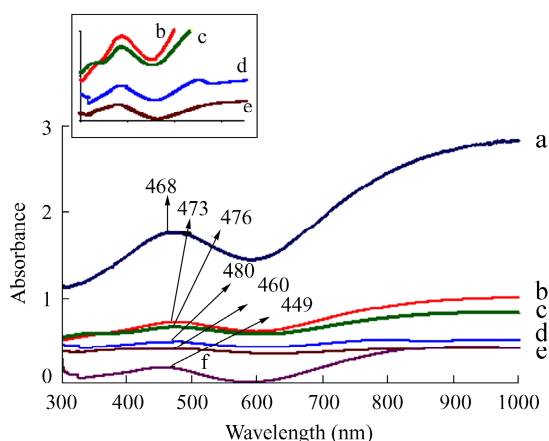


Fig. 2 Absorption spectra for (a) PPy and PPy-CHI films with various CHI content: (b) 3 g/L CHI, (c) 5 g/L CHI, (d) 7 g/L CHI, (e) 9 g/L CHI and (f) 11 g/L CHI

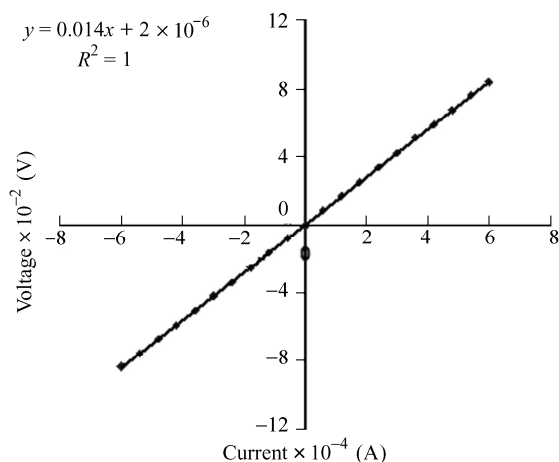


Fig. 3 I - V characteristic graph for the PPy-CHI thin film prepared from 7 g/L CHI

Electrical conductance of the PPy-CHI thin films prepared in 1 min was measured by the two electrode method and I - V characteristic technique, and a typical result of the I - V measurement is shown in Fig. 3. The conductance of the composite film was obtained from the slope of the I - V dependence. The surface area (a) of the sticker which was used for connecting the wires to the thin films was 0.196 cm^2 and the thickness (t) of the samples was obtained by ellipsometry. The resistivity and conductivity were obtained by using Eqs. (3) and (4), and the results are shown in Table 1.

Table 1. Optical band gap (E_g) and conductivity of PPy and PPy-CHI films prepared from various concentrations of CHI

CHI concentration (g/L)	Thickness (nm)	Conductance $\times 10^{-3}$ (S)	Conductivity $\times 10^{-7}$ (S $\cdot\text{cm}^{-1}$)	E_g (eV)
0.0	197	8.2	8.24	2.05
3.0	170	14.0	12.14	1.75
5.0	161	15.6	12.81	1.69
7.0	155	18.8	14.86	1.65
9.0	140	9.9	7.07	1.77
11.0	125	12.4	7.91	2.32

0 g/L of CHI represents PPy without CHI.

The band gaps of the films were determined by extrapolation of the plot of $(\alpha h\nu)^2$ versus $h\nu$, and the results are shown in Fig. 4. Extrapolation of the line to the base line, where the value of $(\alpha h\nu)^2$ is zero, produced a band gap value of 2.05 eV for PPy film which was in good agreement with the results obtained by Santos *et al.*^[20]. They showed that PPy prepared on gold substrate as working electrode at 0.8 V had a maximum absorbance which corresponded to the band gap between 1.7 eV and 2.3 eV. This energy could be related to the transition from the valence band to the antibonding polaron state^[7]. The optical band gaps of the chemical prepared PPy doped with HCl and H_3PO_4 were also determined by Saxena *et al.*^[21]. They reported that the band gap values for PPy doped with HCl and H_3PO_4 were 2.29 eV and 2.43 eV, respectively. Comparison of these values with our results, confirms the fact that electrochemically prepared PPy shows much better electrical properties compared with chemically prepared polymers.

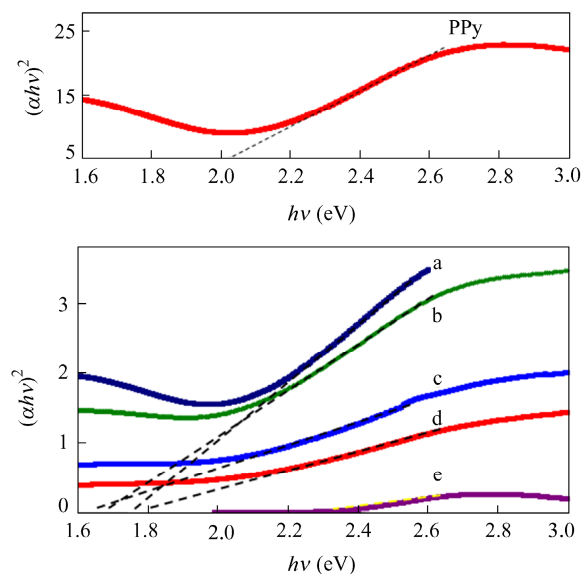


Fig. 4 Determination of the band gaps from a plot of $(\alpha h\nu)^2$ versus $h\nu$ for PPy and conductive polymer composite films with (a) 3, (b) 5, (c) 7, (d) 9, (e) 11 g/L chitosan

It has been shown that with the increase in conductivity, intermediary energy levels are created between the VB and the CB^[13, 20] and it is expected that the polymer with higher conductivity shows higher absorbance, and consequently the absorbance of composites should be higher than that of PPy without CHI. In contrast to these results, in our study, the composite films with higher amount of CHI (higher conductivity) showed less absorbance and PPy film (lower conductivity) had absorbance higher than that of all composite films (Fig. 2).

The reason is that in the CHI free solution, the rate of oxidation is high and there is not enough time for formation of long chain polymers, hence the short chains of the polymers deposit layer by layer which results in shorter chain, higher thickness, lower conductivity and absorbance in UV-Vis spectra. In the presence of a certain amount of CHI (7 g/L), polymer with longer chain is formed. As Yang & Lu^[22] reported, it seems that chitosan as a useful steric agent with amino and hydroxyl groups can promote the interaction between pyrrole monomers and its oligomers. They used chitosan as a stabilizer to prepare hollow nanometer-sized polypyrrole capsules and observed that without chitosan the core/shell structure could not form and chitosan could induce growing polycationic PPy chains on the AgCl core. It means that in the presence of certain amount of chitosan, PPy with longer chains and lower thickness is formed and it causes higher conductivity and lower absorbance for resulting polymers. Another reason for forming longer polymer chains in the presence of chitosan is the hydrogen-bonding interaction between the acetylamino groups of chitosan and hydrogen atoms on nitrogen of PPy chain. This interaction plays a role of offering the active sites for the formation of polypyrrole on ITO glass. In other words, ITO glass has a hydrophilic native surface and it is a little difficult to form hydrophobic PPy on the ITO surface, but it can be modified by chitosan to allow polymerization of pyrrole to PPy with long chain length. In addition, the FTIR results in our previous work^[23] confirmed the higher conjugation chain length of PPy-CHI composite films in presence of certain amount of chitosan.

In the concentrations more than 7 g/L of CHI, in highly viscous solutions, the rate of oxidation and polymerization is very low and the amount of deposited polymer is much lower which leads to low conductivity and absorbance. The results of the thickness of PPy-CHI obtained from ellipsometry confirmed this fact and PPy (without chitosan) was the sample with the highest thickness. Figure 5 shows a schematic view of growing polymer's chains on the surface of ITO glass in the presence of CHI and in CHI free solution. These results have also been confirmed by the empirical measurement of the band gaps. The change of band gaps with CHI concentration implies that electronic structure of PPy is affected by CHI. The composite films prepared from

7 and 11 g/L CHI showed the lowest and highest values for band gap, respectively. It is notable that in most previous literatures, it has been shown that through the use of planar dopants based on aromatic units (such as *p*-TS), electrically conducting polypyrrole films can be prepared in which the planes of the pyrrole rings lie preferentially parallel to the growth surface^[24, 25].

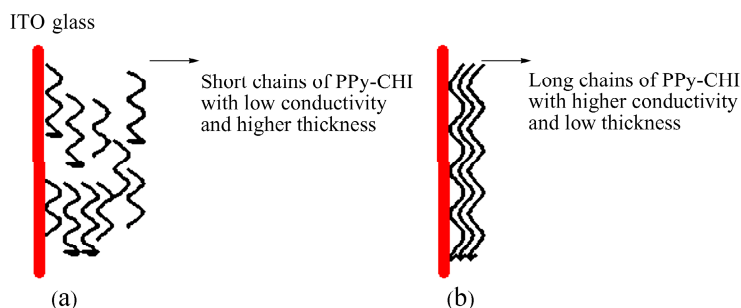


Fig. 5 Schematic view of partially formed chains at the surface of electrode (a) without chitosan (short length and high thickness) and (b) with suitable concentration of chitosan (long length and low thickness)

As it can be seen from Table 1, the conductivity increased as the band gap decreased, but there was one exception. The conductivity of composite film prepared from 11 g/L CHI was higher than the value obtained for composite film prepared from 9 g/L of CHI, even though its estimated band gap was higher. Since the conductivity of ITO substrate was higher than that of all the films and the film prepared from 11 g/L CHI had the lowest thickness (it even could be seen with bare eyes), it seems that the silver paint penetrated inside this thin film and ITO substrate contributed in conductance measurements.

To investigate the effect of monomer concentration on the electrical conductivity and optical band gap of PPy-CHI thin films, the samples were prepared with concentration of pyrrole ranging from 0.1 mol/L to 0.5 mol/L. All of the films were grown at 1.2 V (versus SCE) from the solution containing 0.1 mol/L *p*-TS and 7 g/L CHI. The absorption spectra of PPy-CHI composite films synthesized from different concentration of pyrrole are compared in Fig. 6.

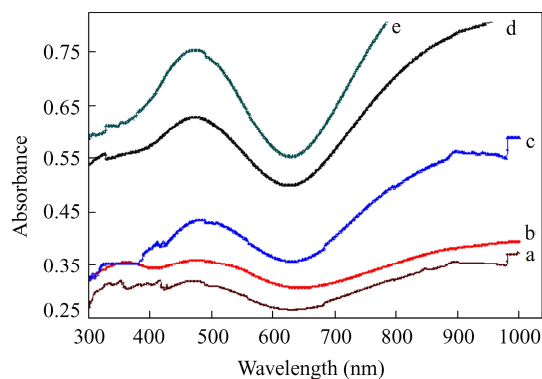


Fig. 6 Absorption spectra for PPy-CHI composite films prepared from (a) 0.1, (b) 0.2, (c) 0.3, (d) 0.4 and (e) 0.5 mol/L pyrrole

It can be seen that the absorbance increased with the increase in pyrrole concentration. It has already been found that the electrical conductivity is strongly influenced by the molecular structures of the dopant and the doping level^[26]. The doping level of PPy is 0.25–0.33 per pyrrole unit depending on the type and the charge of the incorporated anion^[27]. In this research, by increasing the concentration of pyrrole above 0.3 mol/L (higher than doping level), it seems that some neutral PPy's were produced and inserted between the planer PPy chains which led to forming a film with higher thickness and absorbance. This effect prevented the intersoliton

hopping, a mechanism for conductivity by charge-hopping between different polymer chains, resulted in lower electrical conductivity. The estimated band gaps for the composite films prepared from different concentration of pyrrole were determined from the plot of $(\alpha hv)^2$ versus $h\nu$ and are shown in Table 2. The composite films prepared from 0.3 mol/L pyrrole showed the lowest band gap which also corresponded to the highest conductivity and was confirmed with the results obtained from conductivity measurements.

Table 2. Optical band gap (E_g) and conductivity of PPy-CHI composite films prepared from various concentration of pyrrole

Pyrrole concentration (mol/L)	Thickness (nm)	Conductance $\times 10^{-2}$ (S)	Conductivity $\times 10^{-7}$ (S·cm ⁻¹)	E_g (eV)
0.1	133	1.25	8.48	1.65
0.2	141	1.00	7.19	1.52
0.3	151	1.98	15.25	1.30
0.4	159	1.32	10.70	1.85
0.5	171	0.67	5.84	1.90

It can be observed that the composite film synthesized from 0.1 mol/L pyrrole, compared to the film prepared from 0.2 mol/L pyrrole, represented the higher conductivity, even though it had higher band gap. As it was mentioned before this could possibly due to the fact that the film prepared from 0.1 mol/L pyrrole was very thin and the ITO substrate contributed in conductance measurements.

Thermal Stability

Thermogravimetric analysis measurements were used to investigate the influence of chitosan on thermal stability of conducting polymer composites, and the results are shown in Fig. 7. The samples were prepared from the solution containing 0.3 mol/L pyrrole, 0.1 mol/L *p*-TS at 1.2 V (versus SCE), in 2 h. The films peeled off from the electrode and dried in an oven at 45°C for 24 h. The first weight loss for PPy (without CHI) occurred at temperature between 34°C and 150°C and showed 3.5% mass loss. Since PPy is hygroscopic, during the heating to 150°C the polymer may lose the residual water^[28]. The rapid loss which corresponded to polymer degradation occurred in the range 172–598°C. PPy showed a residue of 62% weight retention at 598°C. The first weight loss corresponding to loss of water for chitosan was around 5.7%. This might be due to having more functional groups (OH) in CHI structure compared to PPy film. The second step starting around 183°C, corresponded to the CHI degradation, and only 46.8% mass remained for CHI at 456°C. The comparison of TGA curve for PPy-CHI with the curves of PPy and CHI is also shown in Fig. 7. The evaluated mass loss of PPy-CHI during heating to 150°C decreased with the increase in CHI content. These results indicated that the affinity of composite toward humidity decreased with increase in CHI content. The second mass loss for composite film prepared from 7 g/L of CHI started at 185°C, and the residual sample mass increased as the CHI content increased. The composite of 11 g/L CHI showed a weight loss of only 24% indicating that the CHI can improve the thermal stability of PPy-CHI composites.

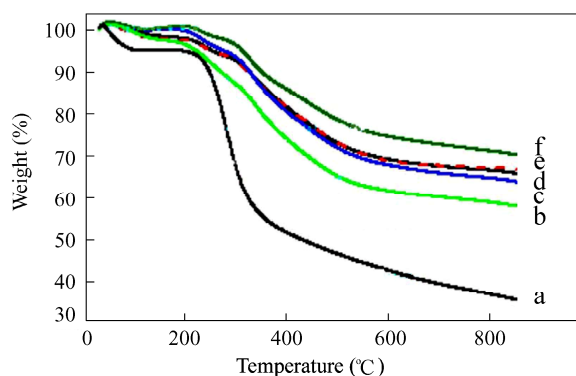


Fig. 7 TGA curves of (a) chitosan, (b) polypyrrole, composite films with: (c) 3, (d) 5, (e) 7 and (f) 11 g/L chitosan

CONCLUSIONS

It is interesting to note that the conductivity follows a mid-concentration maxima trend, in all of the experiments. The optical and electrical study on the PPy-CHI composite films revealed the enhanced electrical properties of composite films in the presence of a certain amount of CHI. Electrical conductivity decreased in the presence of extra amount of chitosan and monomer. The band gaps between VB and CB decreased with the increase in CHI content, and hence the wavelength of electron transition increased. The results revealed that the composite film prepared from solution containing 0.3 mol/L pyrrole, 0.1 mol/L *p*-TS and 7 g/L CHI at 1.2 V (against SCE) had the lowest optical band gap and the highest conductivity, respectively. Chitosan was found to improve the thermal stability of the PPy film.

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