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Development of dendritic growth patterns of polythiophene copper composite during electropolymerization: Characterization and bidirectional sensing applications

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The development of three dimensional dendritic growth patterns of conductive polythiophene and its copper composite by electrochemical method from systems containing (A) thiophene, perchloric acid, acetonitrile and (B) thiophene, perchloric acid, cupric chloride and acetonitrile have been studied. Height of three dimensional hyper branched polymer aggregates is measured at different time of polymerization. Morphology and growth kinetic studies have been made and aggregates have been characterized by electrical conductivity, FT-IR, X-ray diffraction and TGA/DTG analysis. ESR and SEM-EDS studies confirm the presence of metal ion in the polymer composite. SEM studies show the formation of globular aggregates while TEM studies reveal the formation of nanosized polythiophene particles in the range 20-50 nm which increase on addition of copper salt. Solid-state potassium ion sensor with conductive polythiophene copper composite as novel matrix for assembling ion sensing membrane has been demonstrated. Cyclic voltammetric and amperometric studies show excellent electrocatalytic ability for H_2O_2 sensing at lower operating potential.

Keywords: Composite, Conducting Polymer, Electrochemical Polymerization, Electrochemical properties, Nanomaterials, Prussian blue (PB), Sensing applications

Interest in conducting polymeric materials is growing rapidly due to their ease of preparation, mechanical processibility, and ability to become electrically conductive upon chemical and electrochemical doping[1,2]. Nanoscale conducting polymers can be used for biosensors[3], electrochemical devices, single electron transistors[4], Conductive textiles and fabrics[5] and Chemical sensors[6]. Dendrimers are synthetic macromolecules with globular or ellipsoidal shaped, nano scale, tree -like topological structures and large number of surface functionalities[7-11]. Astruc *et al.*[12] have reviewed various aspects of dendritic structure, dendrimers, their application as catalyst, also emphasized on dendrimers encapsulation, bio medical applications etc. Star burst dendrimers have a defined molecular composition[13].

The development of chemistry of clusters and aggregates has lead to interesting applications in the field of catalysis owing to the high reactivity that they show towards various small molecules[14]. A different type of encapsulation, involving the formation of metal nanoparticles within dendrimers, has been used to prepare inorganic-organic composite structures that are also useful in catalytic applications[15]. Such materials have been widely used in many fields including electrochemistry, photochemistry, nanoparticle synthesis, ion sensing etc. Among the numerous conducting polymers, polythiophenes are the subject of considerable interest. It is one of the most studied and important class of linear conjugated polymers. Perepichka *et al.*[16] have reviewed the applications of thiophene –based polymer and oligomers as electroluminescent materials. Although work on electropolymerization of thiophene and its zinc composite has been done earlier by Das *et al.*[17] using 4- Toluene sulphonic acid silver salt and perchloric acid in the presence and absence of $ZnSO_4$ and reviewed by Roncali[18]. Later polythiophene cobalt composite was electrochemically synthesized and used as charge storage device[19].

In the present investigation, we report results on the development of three dimensional dendritic structures during electropolymerization of polythiophene and its copper composite using a different electrode setup consisting of vertical anode and circular cathode and characterized by XRD, ESR, TG/DTG, SEM-EDS, TEM, SEM, FTIR and electrical conductivity measurements. Growth kinetic studies at different experimental conditions were also carried out. Polythiophene copper composite provide an excellent platform for assembling ion sensing membrane impregnated with dibenzo-18-crown-6 allowing the fabrication of solid-state potassium ion sensor. In addition to that polythiophene composite also combined with Prussian blue (PB) through adsorption process. The polythiophene composite modified electrode facilitates the electrochemical sensing of H_2O_2 as compared to that of on Prussian blue modified electrode justifying the potential application of the materials.

Experimental Section

Materials

Thiophene (Spectrochem Pvt. Ltd India), Perchloric acid 70% (s. d. fine chem. Ltd., AR), cupric chloride (Qualigens A.R), acetonitrile (s.d.fine chem. Ltd., L.R). Poly vinyl chloride (PVC) powder, dibenzo-18-crown-6 (Aldrich), sodium tetraphenyl boron (SISCO, India), dibutyl phthalate (Qualigens fine chemicals), Tetra Hydro Furan (THF) (Molychem, india) and milli- Q water were used in the experiment. The potentiometric measurements were made in a 0.1 M Tris-HCl buffer *p*H 7.0 using a double junction calomel electrode. Electrochemical experiments were performed on an electrochemical workstation Model CHI660B, CH Instruments Inc., TX, USA, with three electrode configurations and a working volume of 3 mL. Graphite powder (particle size 1-2 mm) and Nujol oil (density 0.838 g mL^{-1}) were obtained from Aldrich Chemical Co., India. Potassium ferricyanide and ferrous sulphate were purchased from Merck, India. Ag/AgCl electrode (Orion, Beverly, MA, USA) and a platinum plate electrode served as the reference and counter electrode, respectively. All potentials given in the text are relative to the Ag/AgCl electrode. The working electrode was a modified graphite paste electrode (GPE). All experiments and measurements were conducted at room temperature.

Electrochemical synthesis of dendritic polymers

Polythiophene and its copper composite were electrochemically synthesized by anodic oxidation from the systems A and B under potentiostatic condition. The electrochemical synthesis of polymer was carried out using an experimental set-up described earlier[21]. 10 mL of a solution of thiophene and perchloric acid
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in presence and absence of cupric chloride in acetonitrile medium was taken in petri dish. Cleaned Platinum vertical anode (diameter 0.4 mm) and a circular platinum cathode were used in electropolymerization. The vertical anode was put at the centre of circular cathode such as to touch the air / liquid interface. These electrodes were attached to a potentiostat (Scientific India). The digital image of experimental setup is shown in Fig. 1 (a). Polymerization started at the anode as soon as the potential was applied across the electrodes and three dimensional growth patterns were obtained. The aggregates were washed properly and dried in vaccum desiccator. Heights of the three dimensional polymer aggregates were measured at different time intervals for both systems A and B. Two dimensional views of patterns were also taken using a Nikon camera. Morphologies of systems A and B at different field intensities and corresponding weight of the polymer aggregates of systems A and B were obtained. Growth of polymerization was studied by

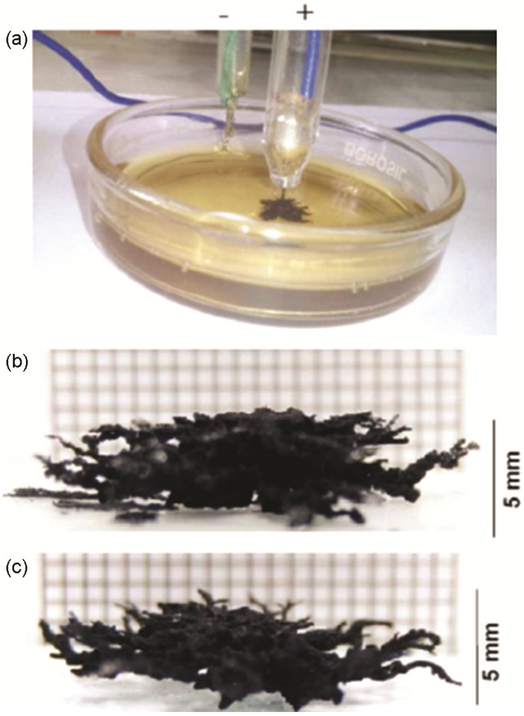

Fig. 1 — The digital image of (a) experimental setup with platinum electrodes (vertical anode and circular cathode) for electropolymerization of polymer aggregates.(b) three dimensional views of polymer aggregates obtained from systems thiophene- perchloric acid- acetonitrile and (c) thiophene- perchloric acid- cupric chloride- acetonitrile. Conditions: [Thiophene] = 1.5 M, [$HClO_4$] = 0.1 M, [$CuCl_2.2H_2O$] = 0.0008 M, field intensity = 4.8 *V*/cm, time of polymerization = 30 min.

recording weight of polymer aggregates at different time and concentrations of cupric chloride, thiophene and perchloric acid for system B.

Construction of a K^+ -selective electrode

The electrode body used for the construction of the electropolymerized polythiophene copper composite and subsequently, the ion-sensor based on dibenzo-18-crown-6 impregnated PVC membrane was made from a Teflon cylinder. The gold disk on the brass rod was screwed within the hollow screwed Teflon cylinder resulting in an electrode body with a cavity of a recessed depth of 2 mm. The exposed diameter of the gold disk to be used as an active surface for sensor construction was 2 mm. The electropolymerization of polythiophene was carried out in acetonitrile in presence of $CuCl_2.2H_2O$ and perchloric acid at the constant potential resulting into excellent film. The electropolymerized polythiophene copper composite film was washed with milli- Q water and dried over night at 25ºC. The solution of the PVC casting membrane was made in dried THF with the following compositions; PVC fine powder (11.2 mg), dibenzo-18-crown-6 (1 mg), dibutyl phthalate (30 µL), sodium tetraphenyl boron (0.8 mg), THF (300 µL).

After complete dissolution of the membrane material, 20-30 µL of the solution was added to the recessed depth of the electrode body covered with the polythiophene copper composite film. The solvent (THF) was allowed to evaporate slowly over a 20 hr period at room temperature. On the complete evaporation of the solvent, a transparent smooth layer of the sensing membrane remained at the surface of the polythiophene copper composite modified electrode. The resulting electrode was conditioned for 6-8 hr in 1 M KCl solution.

Potentiometric operation of polythiophene copper composite modified ion-sensor

The potentiometric responses of the ion-sensor constructed above were carried out in 0.1 M Tris-HCl buffer, *p*H 7.0 and using a double junction calomel electrode. The ion-sensor together with a double junction reference electrode was dipped in the stirred electrochemical cell with a working volume of 15 mL the electrode potential was monitored Keithley Multimeter connected to a personal computer through RS 232 interface. At the steady- state potentiometric response, varying concentrations of the ionic solution was injected into the cell and the new steady- state potential was recorded.

Adsorption of prussion blue nanoparticles on polythiophene copper composite

Prussian blue nanoparticles (PBNPs) were prepared as described earlier[22]. 2.0 mg of powder polythiophene copper composite was mixed with 10 mL suspension of PBNPs sol in a small conical flask fitted with stopper and the mixture was shaken on magnetic stirrer for 20 min. The PBNPs were adsorbed on polythiophene copper composite with 92% color removal. The color removal % was calculated as described earlier[23] using a Double Beam microprocessor UV – vis. spectrophotometer (Model: LI – 2802).The PB adsorbed polythiophene copper composite was then separated out from PB solution and dried at 35°C in an incubator for overnight.

Electrode fabrication

Graphite paste electrode (GPE) body used for the construction of the modified electrode was obtained from Bioanalytical system (West Lafayette IN; (MF 2010). For fabrication of the electrode the well was filled with an active paste of following composition: graphite powder, 67.5% *w/w* PBNPs- polythiophene copper composite, 2.5% *w/w* and nujol oil, 30% . Finally the paste electrode was made smooth on a clean butter paper to get the flat surface. This resulted in the formation of a GPE of PBNPs- polythiophene copper composite system. Similarly graphite paste electrode of PBNPs was also fabricated following the same procedure containing only Prussian blue.

Electrocatalytic reduction of H_2O_2 at the modified electrode

The mixed polythiophene copper composite electrode was also for use as a sensing platform to determine H_2O_2 cathodically through the involvement of PB character in polyhiophene copper composite. The cyclic voltammograms at the scan rate of 10 m*V*/s in 0.1 M phosphate buffer (*p*H 7.0) in absence and the presence of 1 mM H_2O_2 were obtained.

Characterization

Powder X-ray diffraction patterns of polymer aggregates were taken using CuK_α radiation by Bruker AXS D8 Advance from STIC Cochin. Intense lines of both the samples are recorded Table 1. Electrical conductivity of polymer aggregates were measured by using an experimental setup as employed earlier[20]. TG/DTG studies of polymer aggregates obtained from systems (A) and (B) were made by Mettler Toledo DSC 822e from STIC Cochin and TG data is recorded. The FT-IR spectra of the polymer aggregates were taken using a Thermo

Table 1 — Powder X- ray diffraction data for polymer aggregates obtained from systems A and B

System A			System B		
$2\theta^{o}$	d(A^{o})	I/I_o	$2\ \theta^{o}$	d(A^{o})	I/I_o
3.259	27.0926	5.1	3.783	23.3405	41.4
7.494	11.11334	80.9	8.502	10.39141	95.7
11.666	7.57982	100	12.251	7.21866	100
19.253	4.60631	55.9	19.616	4.52205	40
24.467	3.63533	63.2	20.72	4.2834	47.1
			24.101	3.68964	42.9
			27.582	3.23135	30

Table.2 — Thermogravimetric data of polymer aggregates obtained for systems A and B.

Temperature (℃)	Weight%	
	System A	System B
40	100.0	100.0
100	95.0	97.0
200	86.5	90.5
300	75.9	79.5
400	66.5	70.0
500	59.8	64.0
600	53.0	56.0
700	46.0	48.5

Nicolet, Avatar 370 from STIC Cochin. ESR (X- band) study of polythiophene copper composite was carried out at room temperature using Mn as a reference material. Spectrum was taken from IIT Bombay. SEM- EDS studies of the composite were carried out using EDS model 5- ADD0048 (ZEISS) at the resolution 5.9 KeV from Central Instrument Facility IIT BHU, Varanasi. SEM images of electropolymerized aggregates were taken using a Scanning Electron Microscope (Model JSM – 7600 F). TEM images of electropolymerized aggregates were taken from IIT Bombay using a Philips Transmission Electron Microscope (Model CM 200).

Results and Discussion

Three dimensional dendritic polymer aggregates of polythiophene and its copper composite were obtained by electropolymerization on a platinum vertical anode. Platinum circular cathode was used to provide a uniform electric field around the anode. Typical three dimensional growth patterns of systems A and B are shown in Fig. 1. Height (h) of three dimensional dendritic polymer aggregates were measured at different time (t) and results are shown in Fig. 2 (a). Linear plots between log h and log t (Fig. 2b) were obtained obeying an empirical equation $h = ct^{m}$ where m and log c are slope and intercept respectively. Two dimensional views of polythiophene (i-v) and its copper composites (vi-x) at different field intensities were taken from the upper side as shown in Fig. 3 (a). A critical field intensity (4.8 V/cm) is observed beyond which weight of the system A and B were decreased as shown in Fig. 3 (b). At high anodic potential large current flows through the system may lead to loss of π- conjugation and degradation of polymer [20]. Weight of polythiophene copper composite was measured at different time (5-60 min), keeping other parameters fixed. It is found to increase non – linearly with time as shown in Fig. 4.

However the weight of polythiophene copper composite is also measured at different cupric chloride, thiophene and perchloric acid concentrations keeping other parameter fixed. The weight of the polythiophene copper composite is decreases non- linearly with time with increased the concentration of cupric chloride as shown in Fig. 5 (a). The critical concentrations were also observed for thiophene and perchloric acid, which found to be 1.5 and 0.087 M respectively beyond which weight of the composite decreased as shown in Fig. 5 (b) and (c) . This indicated that entire process involved the process of polymerization and degradation after a critical value.

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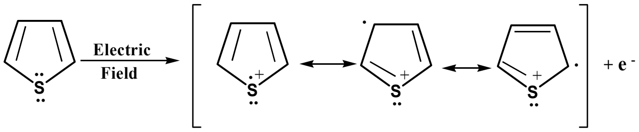
In the presence of electric field, oxidation of monomer takes place at the surface of the electrode to form the radical cation. The radical cation obtained is further stabilized by resonance:

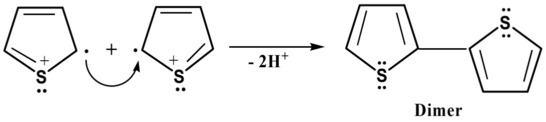


The electron thus released is associated with the H^+ ions at the cathode as follows:

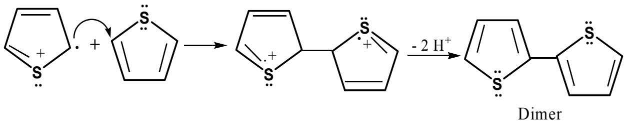
$$H^+ + e^- \longrightarrow \tfrac{1}{2} H_2\uparrow \text{ (cathode)}$$

The next step involves, radical cation – radical cation coupling/ radical cation – monomer coupling to form the dimer.

(1) Radical cation –radical cation coupling.



(2) Radical cation – monomer coupling.



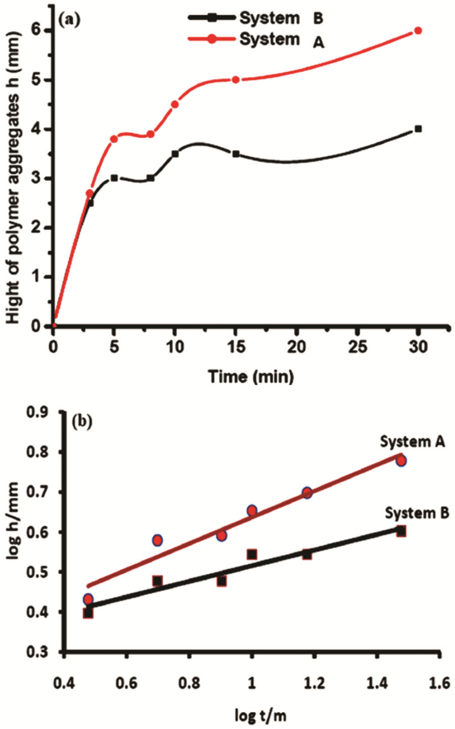


Fig. 2 — (a) Plots showing height (*h*) of polymer aggregates obtained during electropolymerization of systems (A) and (B) as a function of time (*t*). Conditions: [Thiophene] = 1.5 M, [$HClO_4$] = 0.1 M, [$CuCl_2.2H_2O$] = 0.0008 M, field intensity = 4.8 *V*/cm, time of polymerization = 30 min. (b) Plots of log (*h*) *vs.* log (*t*) for the data recorded in Fig. 2 (a).

In addition to $\alpha - \alpha^I$ in the polythiophene some $\alpha - \beta^I$ linkage can also takes place. This can lead to greater random motion of radical cation, leading to complex pattern growth and dendritic structure. The

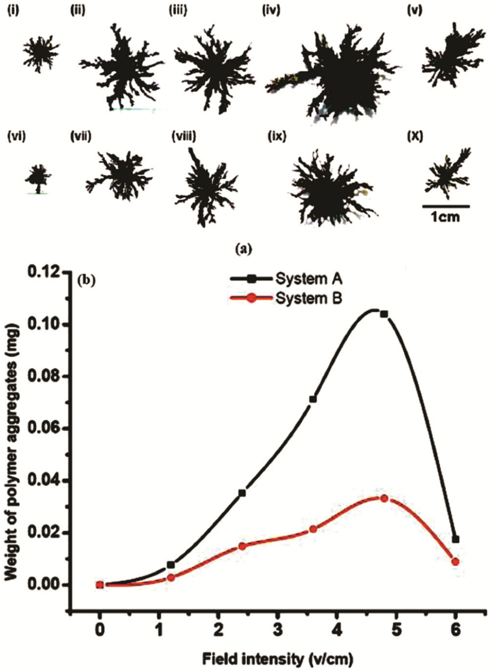


Fig. 3 — (a) Microphotographs showing two dimensional views obtained during electropolymerization in systems A (i- v) and B (vi- x) taken at different field intensities (1.2, 2.4, 3.6, 4.8, 6.0 *V*/cm) Conditions: [Thiophene] = 1.5 M, [$HClO_4$] = 0.1 M, [$CuCl_2.2H_2O$] = 0.0008 M, field intensity = 4.8 *V*/cm, time of polymerization = 30 min. (b) Corresponding weight (*w*) of system A and B obtained at different field intensities (*V/cm*).

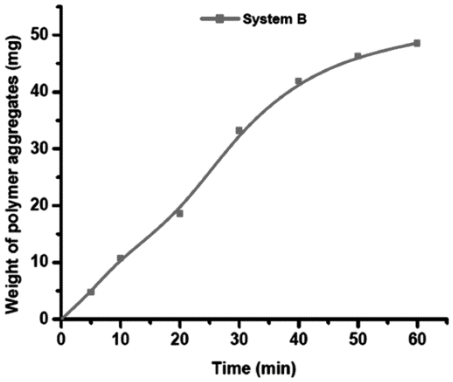


Fig. 4 — Weight of polythiophene copper composite (system B) at different time of electropolymerization. Conditions: [Thiophene] = 1.5 M, [$HClO_4$] = 0.1 M, [$CuCl_2.2H_2O$] = 0.0008 M, field intensity = 4.8 *V*/cm, time of polymerization = 30 min.

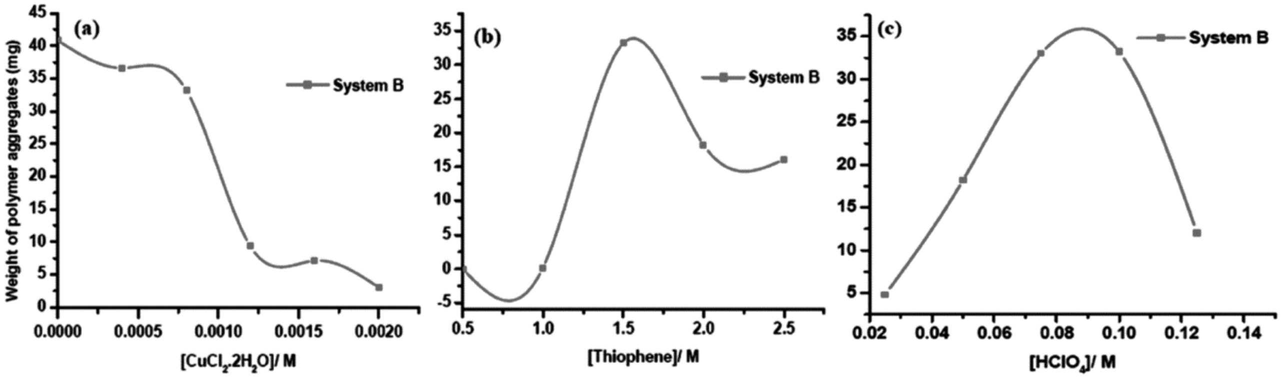
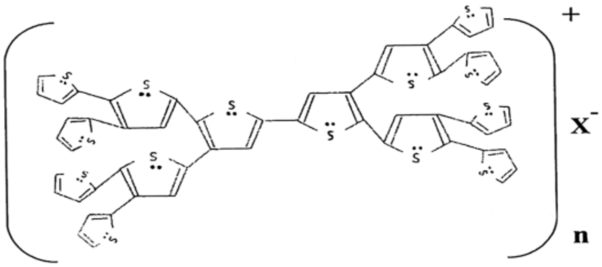
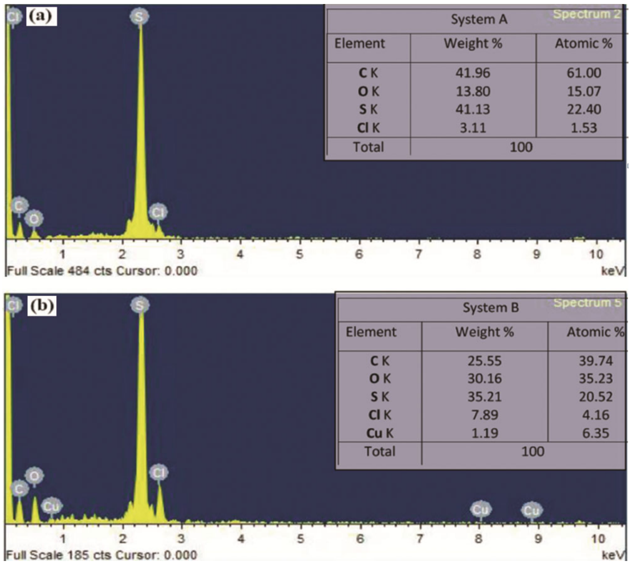


Fig. 5 — Weight of polythiophene copper composites (system B) obtained at different concentrations of (a) cupric chloride, (b) thiophene and (c) perchloric acid, field intensity = 4.8 *V*/cm, time of polymerization= 30 min.

dimer obtained during electropolymerization was further oxidized to the free radical. Here the electron is localized at the β position of the thiophene moieties. So chances of attack of another thiophene radical cation with greater electron density at α position are favored. This process would be repeated again and again with the attack at α and β position of the growing polymer chain resulting into a dendritic polythiophene in its oxidized conducting form which get neutralized by the counter ions ClO_4^- from $HClO_4$ as a dopant and Cl^- from the cupric chloride as a codopant.



$X^- = ClO_4^-, Cl^-$



System A		
Element	Weight %	Atomic %
C K	41.96	61.00
O K	13.80	15.07
S K	41.13	22.40
Cl K	3.11	1.53
Total	100	

System B		
Element	Weight %	Atomic %
C K	25.55	39.74
O K	30.16	35.23
S K	35.21	20.52
Cl K	7.89	4.16
Cu K	1.19	6.35
Total	100	

Fig. 6 — SEM- EDS spectra of (a) polythiophene and (b) its copper composite . Conditions: [Thiophene] = 1.5 M, [$HClO_4$] = 0.1 M, [$CuCl_{2.}2H_2O$] = 0.0008 M, field intensity = 4.8 *V*/cm, time of polymerization = 30 min.

Polythiophene copper composite was electrodeposited from a solution containing thiophene, cupric chloride as the source of metal ion. During this process the copper metal ion is encapsulated in polythiophene matrix as reported for encapsulation of other metal ions in the dendrimer [15]. The presence of copper in the composite is evident by ESR and SEM- EDS (Fig. 6) studies. The ESR spectrum shows a single peak at g value approximately 2.017 corresponding to Cu (II).

Electrical conductivity was measured in the solid state and found to increase linearly with concentration of Cu II (Fig. 7), obeying an empirical equation $\sigma = m[\mathrm{Cu}^{2+}] + c$ where m and c are slope and intercept respectively. The correlation coefficient value was found to be 0.992 as reported for conducting polymetallorotaxanes [24] and electrochemical inclusion of Cu^{2+} ions [25].

The powder X-ray diffraction data for system A and B are recorded in Table 1. It indicates that both the samples are different.

Thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) of polymer samples were studied. Thermograms for systems A and B are recorded in Table 2. Weight loss of 59.8% and 64% at 500ºC were observed for the samples obtained from systems A and B respectively. It was observed that polymer obtained with cupric chloride alone had higher stability as compared to that obtained in absence of cupric chloride.

The FT-IR spectrum of system B showed the (C-H) stretching vibration band at 2980 cm^{-1}; (C=C) stretching band at 1521 cm^{-1}; (C-H) in plane bending band at 1200 $\text{cm}^{-1}$and (C-S) bending band at 789 cm^{-1} The doping induced band at 1035 cm^{-1} was originating from the changes in the conjugated back bone due to the electron withdrawing and electron doping dopants on the polymer chain and the counter ion balancing appeared at 1196, 1321 and 1488.cm^{-1}. The large descending base line in the spectral region of 4000-2000 cm^{-1} was attributed due to free – electron conduction in the doped polymer. The increasing conjugation shifted the absorption frequencies of the polymer. These results supported to the polymerization. There was no remarkable difference in the spectrum of system A.

SEM and TEM images of polythiophene and its copper composite are shown in Figs. 8 and 9 respectively. SEM results revealed the formation of globular aggregate with difference in morphology (Fig. 8 (a) and (b). TEM studies (Fig. 9 a) indicated the formation of nanosized spherical particle of size 20-50 nm for system A while it increased in case of polythiophene copper composite (Fig. 9 b).

The mechanical properties and surface smoothness of the polythiophene copper composite prepared from the solution with the addition of the cupric chloride (system B) were greatly improved in comparison with those of the polythiophene from the solution in the absence of cupric chloride (system A). Accordingly the application of polythiophene modified electrode made with the addition of cupric chloride was used for developing solid-state ion-selective electrode. Potassium ion selective electrode has been constructed based on dibenzo-18-crown-6 impregnated PVC matrix membrane over as synthesized polymer modified electrode. The electrode showed Nernstian behavior with a slope of 56 mV revealing the potential application of synthesized material in designing solid state ion-selective electrode. A number of experiments were performed in different number of days in order to examine the variation in base line recovery during subsequent measurements. The open circuit potential was found to the order of 218 ± 5 mV even after prolong operation of solid-state neutral carrier based ion-selective electrode. This justifies the potential application of polythiophene film for the construction of solid-state ion-sensor suitable for practical applications. The typical potentiometric response of the solid-state ion-sensor on the addition of varying concentrations of K$^+$ is shown in Fig. 10. The response is very fast with an improved detection limit. The response of the ion-sensor is highly selective to K$^+$.

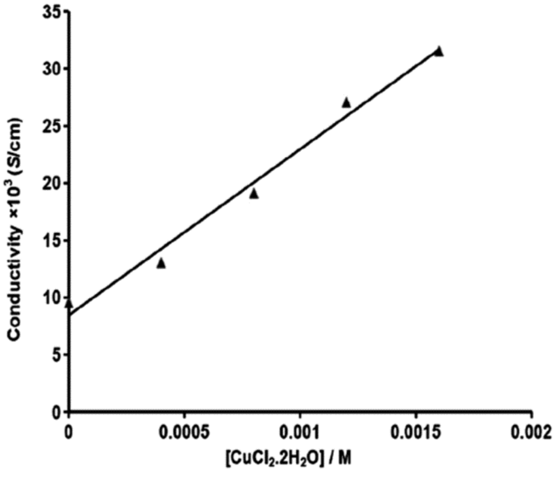


Fig. 7 — Plot of electrical conductivity of polythiophene copper composites (system B) at different concentrations of cupric chloride (0, 0.4, 0.8, 1.2, 1.6 mM) at 30.0± 0.1°C.

In addition to K$^+$ ion-sensor, polythiophene copper composite also facilitates the catalytic reduction of

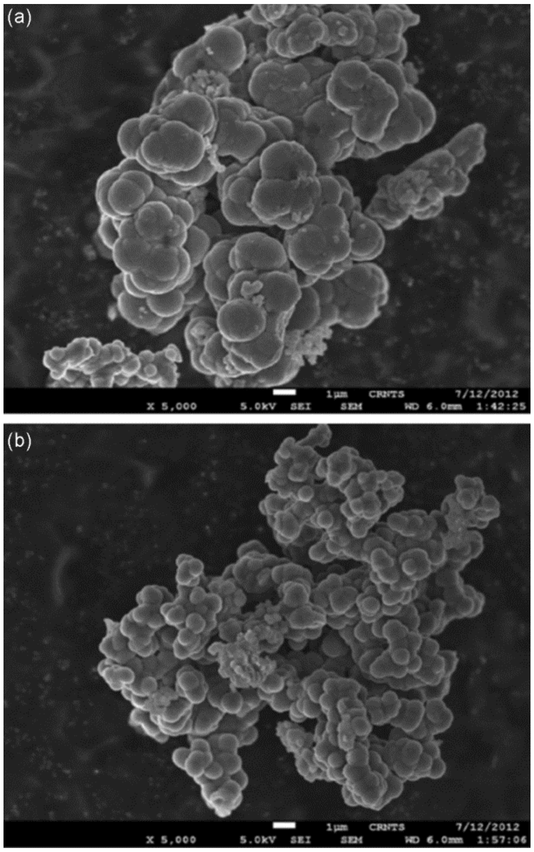


Fig. 8 — SEM images of electropolymerized aggregates obtained from systems (A) and (B).

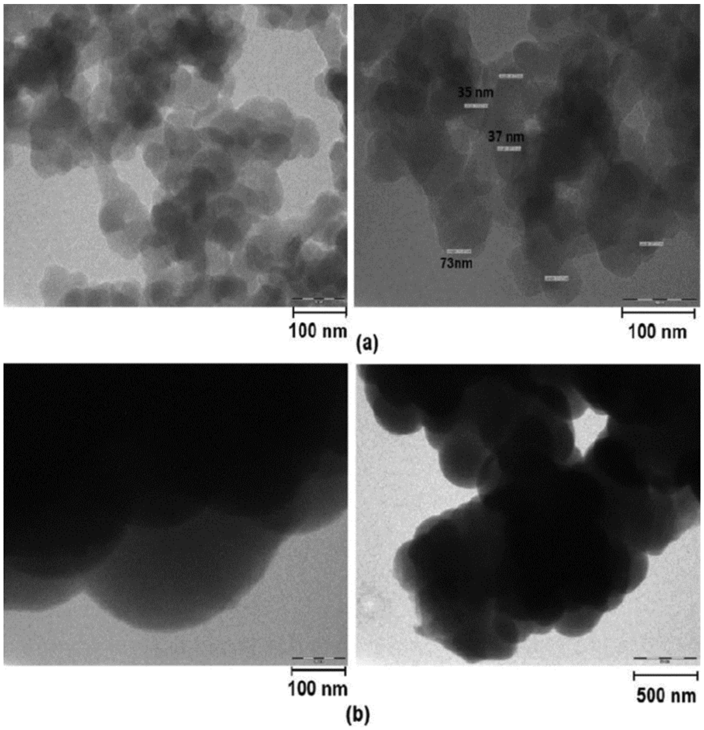


Fig. 9 — TEM images of electropolymerized aggregates obtained from systems (A) and (B).

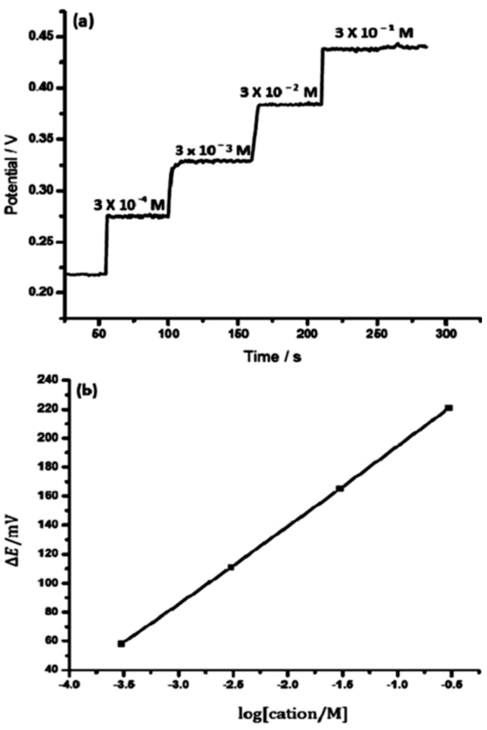


Fig. 10 — (a) Typical Potentiometric response of a solid- state ion sensor made from polythiophene copper composite modified electrode. (b) Response curve for ion sensor to K^+ in 0.1 M Tris-HCl buffer (*p*H 7.0) potential difference is plotted against logarithm of cation concentration.

H_2O_2. The polymer allows the formation of composite with Prussian blue nanoparticles. The nanocomposite modified graphite paste electrode. The bare GPE normally requires a relatively large negative potential for the determination of H_2O_2 with a required sensitivity; therefore its use is limited for practical utility, the electrocatalytic reduction of H_2O_2 with a PB system has been extensively studied in many cases due to the analogous behavior of PB as artificial peroxidase. However precise cathodic character in mixed polythiophene copper composite plays a crucial role that enables the selective detection of desired analyses in many practical applications. In the present investigation, with addition of 1.0 mM $H_2O_{2,}$ the reduction currents for both GPE of polythiophene copper composite and PBNPs. However, the polythiophene copper composite shows a higher reduction current, indicating better electrocatalytic activity toward H_2O_2 sensing. Such finding provided valuable information on the use of polythiophene copper composite as an electrode modifier as shown in Fig. 11.

In order to study the quantitative determination of $H_2O_{2,}$ the amperometric responses for these system were recorded on the addition of varying concentration (0.01 mM to 1.0 mM) of H_2O_2 in 0.1 M phosphate buffer (*p*H 7.0) at a working potential of 0.05 *V* vs. Ag/AgCl (Fig. 12). it is clear from the

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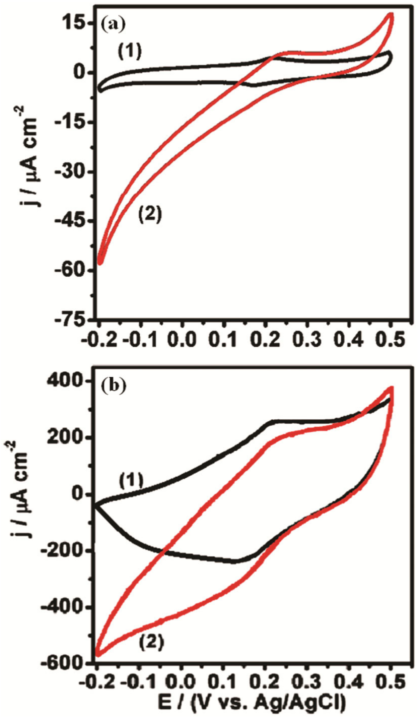

Fig. 11 — Cylic voltammograms of (a) PBNPs and (b) polythiophene copper composite modified electrode. Curves (1) and (2) represent the results obtained in the absence and presence of 1.0 mM H_2O_2 respectivly in 0.1 M phosphate buffer *p*H 7.0 containing 0.05 M KCl.

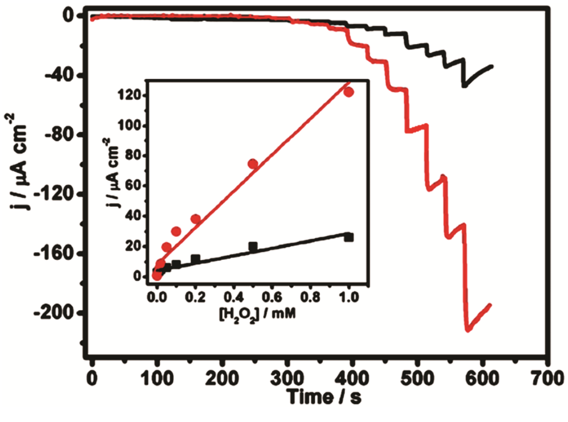

Fig. 12 — Amperometric response of PBNPs (1) and polythiophene copper composite (2) modified electrode on the addition of increasing H_2O_2 concentrations in the range 0.01 mM to 1.0 mM; operating potential, 0.05 V ; 0.1 M phosphate buffer, pH 7.0; 0.05 M KCl as supporting electrolyte. The inset shows calibration plots for PBNPs (1) and polythiophene copper composite (2) systems respectively.

Fig. 12 that the response was enhanced in the case of polythiophene copper composite, (Fig. 12), again suggesting the good electrocatalytic behavior of composite material towards the reduction of H_2O_2. The calibration curve for H_2O_2 analysis by amperometry, at a modified electrode were constructed using average currents recorded for each concentration point. The inset of Fig. 12 depicts the calibration curve for H_2O_2 at the polythiophene copper composite and PB modified electrode. The sensitivity of the mixed PB and mixed polythiophene copper composite system toward H_2O_2 was calculated to be 23 and 120 μA mM^{-1} cm^{-2} respectively. The inset of the Fig. 12 also shows the liner dependence of cathodic current on H_2O_2 concentration at range 0.01 mM to 1.0 mM.

The stability of mixed polythiophene copper composite modified electrode was investigated by storing the electrode in air at room temperature for one month and then measuring the current response of 2 mM in 0.1 M phosphate buffer (*p*H 7.0) solution. A current response of its electrocatalytic activity in the buffer solution was also examined. The relative standard deviation (RSD) of the current responses to 1 mM H_2O_2 (at 0.05 *V*) were found to be 3.9% for 15 successive measurements. On the other hand, the reproducibility of the modified electrode was also investigated by measuring the CVS after twenty repetitions cycles at 10 m*V*s^{-1} The RDS was found to be 1.7% (n= 20).

Conclusion

Three dimensional dendritic conductive polythiophene and its copper composite in acetonitrile medium have been electrochemically synthesized. Height (*h*) of three dimensional polymer aggregates varied with time (*t*) of polymerization, obeying an empirical equation $h = ct^m$. Growth kinetics studies are carried out by weighing the weight of polymer aggregates as a function of time, field intensity and the reactant concentration. Polymer aggregates are characterized by XRD, SEM, TEM, SEM-EDS, ESR, FT-IR, TG/DTG and electrical conductivity measurements. ESR and SEM-EDS studies confirmed the presence of metal ion in the composite. Electrical conductivity of polythiophene copper composite is found to be increased linearly with the concentration of cupric chloride. SEM results reveal the formation of globular aggregate with difference in morphology for system A and B. TEM studies reveal the formation of nanosized particles for system A while the particle size increased in system B. Thermal stability of composite is higher than that obtained for polythiophene. The bidirectional applications of polythiophene copper composite are described. It is used in the construction of a K^+ selective electrode which is highly selective to K^+ with extended linearity over almost six decades. It also display excellent electrocatalytic ability for H_2O_2 sensing at lower operating potential.

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