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Exploring the electrical and complex optical properties of as-synthesized thiophene-indole conducting copolymers

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Abstract

In this contest, a novel series of random thiophene-indole (Th-In) conducting copolymers have been synthesized through oxidative copolymerization of their monomers in aqueous medium at room temperature using anhydrous ferric chloride ($FeCl_3$) as an oxidant. The structure of as-studied samples have been confirmed through X-ray diffraction (XRD) technique. Field emission-scanning electron microscopy (FE-SEM) ensured the morphology of as-prepared copolymers. The complex optical parameters of the samples have been estimated through ultraviolet-visible (UV-Vis) spectroscopy. The temperature dependence of dc electrical conductivity of the samples have been obtained over a temperature range $303-393$ K, which found to be in the range $10^{-6}-10^{-4}$ Scm^{-1} followed Arrhenius relation. The degradation behaviour has been studied through thermogravimetry (TG) and differential thermal analysis (DTA) techniques.

Keywords: Materials science, Materials chemistry, Chemical engineering

1. Introduction

During recent years, investigations on organic conjugated polymeric materials have been very much intensified in the areas of material science. The increasing interest in these vibrant materials is stimulated by their wide applications in solid-state device technology likely photovoltaic, organic solar cells, sensors, light emitting diodes, Schottky diode, field effect transistors, electrochemical batteries etc. [1, 2, 3, 4, 5, 6, 7, 8]. The conjugated conducting polymers and their copolymers exhibit sufficiently high optoelectronic properties, generally used in low-cost electronic and optical devices [9]. For the effective performance, most of the above said solid-state devices have been based on the conjugated conducting polymers such as polythiophene (PTh) and polyindole (PIn) due to their excellent electrical characteristics, thermal and environmental stability and solubility [10, 11, 12].

Polymers containing thiophene monomers have been the valid issue of extensive research for more than three decades. PTh, polymers are most promisingly used in polymeric research field not only due to their electrical properties but also others, like, thermal, magnetic, electrophysical, optical properties [13, 14]. PIn is one of the conjugated conducting polymers containing the benzene ring linked with the pyrrolitic ring. Also PIn contains the heterocyclic of nitrogen atom like polypyrrole (PPy) and polyaniline (PANi). This aromatic nitrogenous polymers is more attractive because of its fairly good thermal stability, high redox activity and slow degradation rate in comparison with PPy and PANi [15, 16].

Sarac et al. [17] have reported the synthesis of 5,2 In-Th comonomer onto carbon fibers by using electrochemical polymerization produced conductive copolymer fibers with different surface morphologies. The copolymerization of aniline in the presence of alkylaniline as comonomers to synthesize the conducting copolymers of poly(aniline-co-alkylaniline) type through chemical oxidative polymerization route have been reported [18]. Lere-Porte et al [19] have been reported the synthesis of thienylene-dialkoxyphenylene copolymer by using an organometallic condensation reaction between a bis(stannyl)thiophene reagent and a substituted dibromobenzene derivative in the presence of a palladium catalyst. The copolymer with enhanced optical properties compares quite favorably to PTh and has good potential for the elaboration of optical devices. Zhao et al. [20] have been successfully designed and synthesized three series of cis/transisomers of benzidiimidazole-thiophene copolymers (PBDIT) with different length of n-alkyl chains and illuminated the relationship between the configurational isomerism and the optical and electrical properties.

There are some reports concerning the copolymerization of thiophene and indole [21], but no report on the chemically oxidative copolymerization of thiophene and indole is found in aqueous solution. In this article, we report on the novel one pot

chemical synthesis of these oligomers in aqueous solution using $FeCl_3$ as an oxidant at room temperature. The as-synthesized (Th-In) conducting copolymers have been characterized through FE-SEM, TG-DTA, UV-Vis techniques, and dc conductivity measurements.

The high oxidation potential of thiophene (1.47 V versus $FeCl_3$) compared to the PTh. This causes some degradation of the polymeric film. Addition of indole monomer into the polymer structure will result in a decrease in the oxidation potential. Hence, the formation of thiophene-indole copolymerization improved their properties such as thermal and electrical conductivity as compared to individual one.

In initiation step, the oxidation of thiophene and indole monomer yields a cation radicals and dimeric species. The chemical polymerization mechanism of monomer is alleged to proceed through a radical cation which reacts with a second radical cation to give a dimer. This dimer reacts with another cation radical of the monomer which results in build up of polymer chain. In copolymerization a chain might be built up by formation through conjugation of radicals of two different monomers succeeded by propagation. Fig. 1 is speculated for the mechanism of copolymerization from the reacted solution containing same feed ratio of both the monomers i.e. thiophene and indole.

2. Experimental

In experimental part of this research work, thiophene, indole monomers, anhydrous iron (III) chloride ($FeCl_3$), and other AR grade chemicals and reagents were purchased from commercial sources SD Fine, India and used without any further purification. The synthesis of copolymers were done through in-situ chemical oxidative route. The stoichiometric ratios of thiophene, indole and $FeCl_3$ were varied as 40:40:20; 30:30:40; 25:25:50; 20:20:60 and 10:10:80 wt. % respectively for synthesis of random (Th-In) conducting copolymer system, here in after define as a, b, c, d, and e, respectively.

In the typical reaction, a proper stoichiometry of thiophene and indole monomers were mixed in a 20 ml distilled water in a beaker. The process of copolymerization was initiated by the addition of anhydrous $FeCl_3$ with corresponding stoichiometry in that solution. The resultant mixture was continuously stirred over a magnetic stirrer and maintained at 30 °C throughout the course of reaction for 6 h. H_2O_2 (0.1 M) was used to enhance the rate of reaction and conjointly yield. The precipitate was collected by filtration and washed with triply distilled water to remove unreacted chlorine so that the washings was clear. The obtained copolymeric powder was dried in a desiccators for 12 h. After that, the powder was placed in a oven at 40 °C for 2−3 h. This synthesis approach leads to the formation of random type of copolymer system.

2.1. Material characterizations

The as-studied samples were characterized through XRD, FE-SEM, TG-DTA and UV-Vis techniques to confirmed the structural, thermal and optical properties. The XRD profile of powder samples were recorded on Rigaku miniflex-II X-ray diffraction using CuKα radiation (λ = 1.54 Å) in the 2θ range of 10−70°. The morphology of the samples were reported from FE-SEM (JEOL JSM-6360). The TG-DTA was carried out on Shimadzu DTG-60h thermal analyzer under nitrogen flow at the heating rate of 10 °C/min. The temperature of the sample was varied from room temperature to 1000 K. For the electrical measurements, the samples were polished and
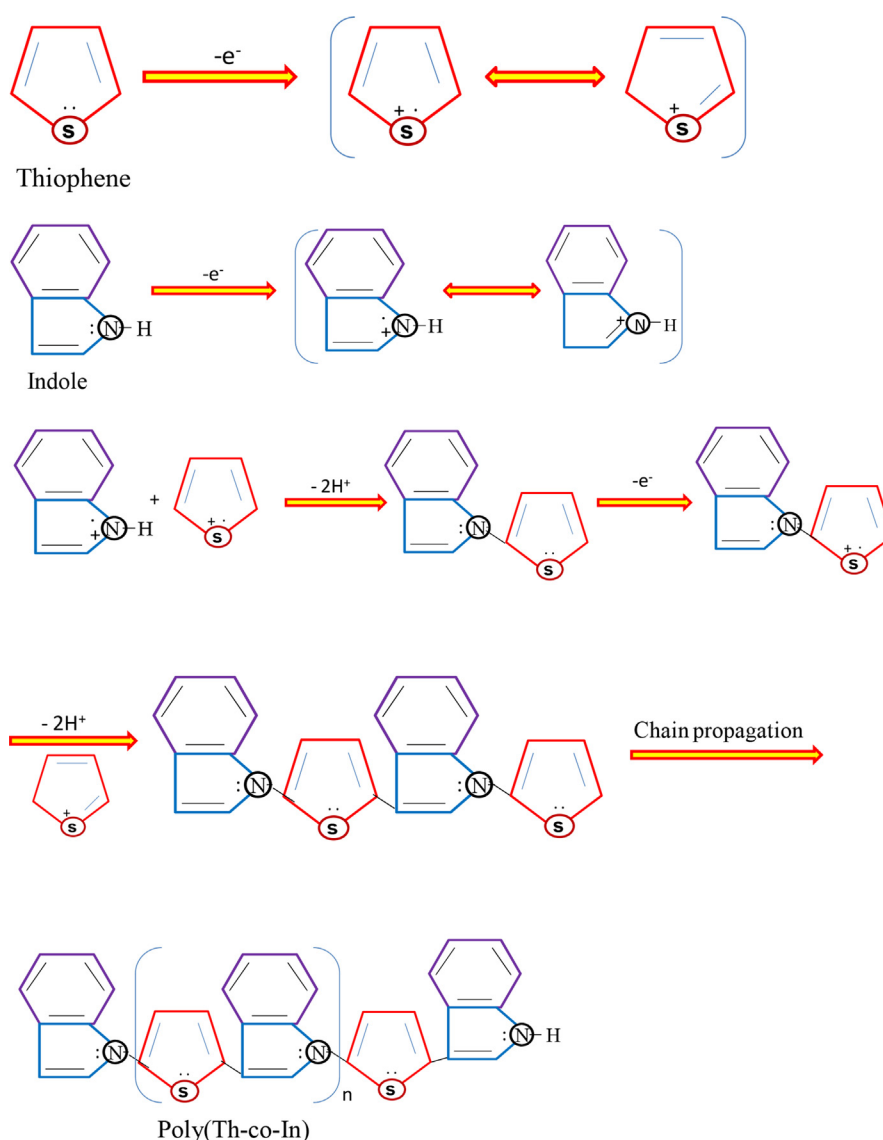
Fig. 1. Mechanism for the formation reaction of thiophene-indole conducting copolymer.

conducting silver paste was deposited on both sides. The sample area was taken to be the area exposed to the electrode surface. A firm contact was confirmed at the boundaries of the sample/electrode interfaces. Measurements of dc electrical conductivity as a function of temperature for all the samples were made by two-probe technique in the temperature range of 303−393 K. The transference numbers, both ionic (t_{ion}) and electronic (t_{ele}) for different as-synthesized samples were evaluated using Wagner's polarization technique. The Characteristic UV-Vis analysis of as-synthesized samples were recorded on Perkin Elmer UV spectrophotometer in the range 200−800 nm.

## 3. Results and discussion

3.1. XRD analysis

X-ray diffraction studies were carried out to examine the structure of as-prepared copolymeric samples. The patterns were recorded on Rigaku miniflex-II X-ray diffraction using CuKα radiation (λ = 1.54 Å) in the 2θ range of 10−70°. Fig. 2 depicts the XRD profile of as-synthesized (Th-In) conducting copolymer samples with different stoichiometry ratios of monomers to oxidant. The entire 2θ patterns does not shows any sharp peak, which is the characteristics of crystalline nature. Besides that patterns contains the broad humps between 20-30°, which attributes to amorphous nature of as-synthesized copolymers [11].

3.2. Morphology

The structure and morphology have a significant influence on physio-chemical properties of materials. Conducting copolymers properties are correlated well with the morphology and structure. Thus, in order to analyze morphology of as-prepared samples, FE-SEM studies were carried out. Fig. 3 displays FE-SEM micrographs of (Th-In) conducting copolymer samples with different stoichiometry ratios of monomers to oxidant. All the micrographs of (Th-In) conducting copolymer system exhibits very rough, micro-globular porous structure and all particles on the surface are inhomogeneous in nature which leads to non uniformity in structure [22]. FE-SEM pictures clearly indicate the agglomeration of particles in the as-studied samples of copolymer.

3.3. Thermal characterization

Fig. 4 shows the TG-DTA curve of optimized (Th-In) conducting copolymer with stoichiometry of thiophene, indole and $FeCl_3$ as (25:25:50) wt. %. The weight loss curve shows prominent weight loss up to 500 K. The entire weight loss curve broadly divided into three steps, first step of curve up to 376 K comprises physical removal of water molecules for the surface. The second step associated with
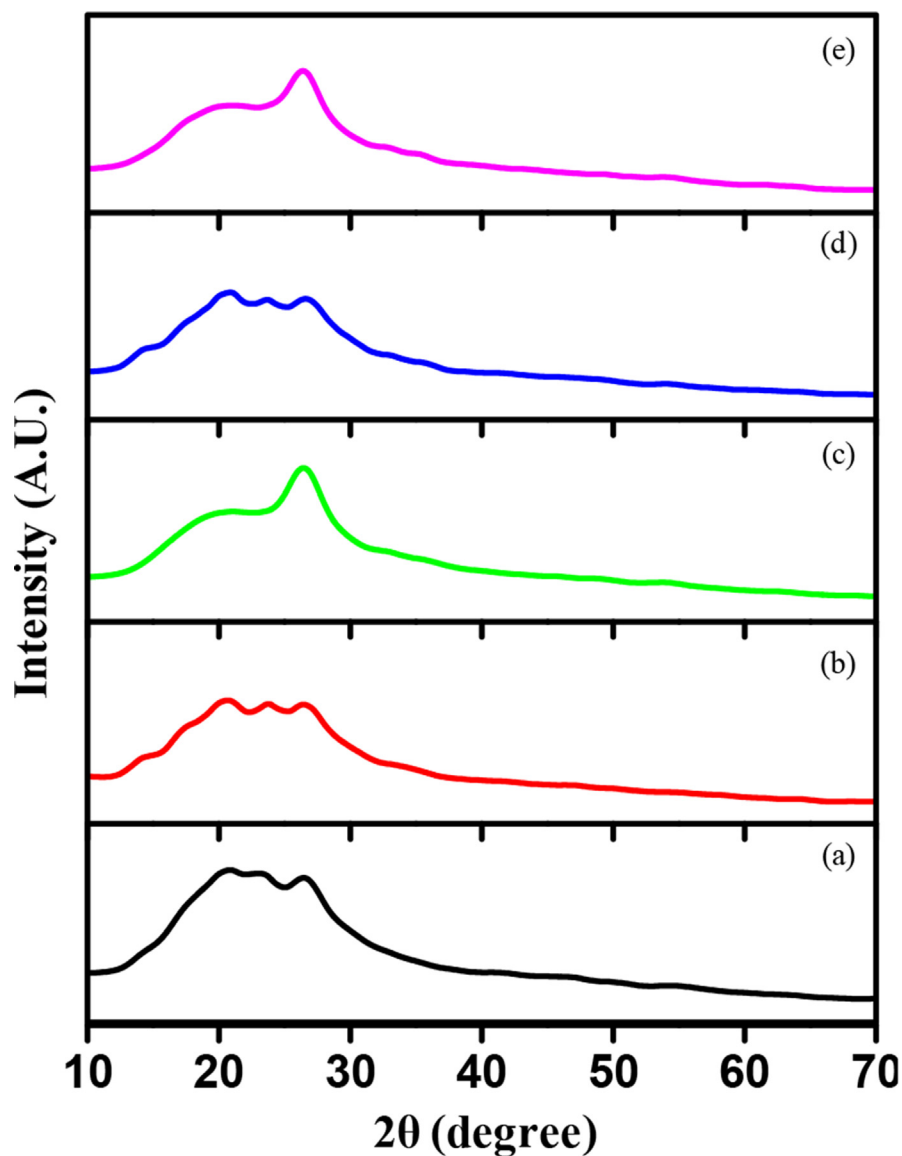
Fig. 2. XRD pattern of (Th-In) conducting copolymers with different stoichiometry of thiophene, indole and $FeCl_3$ as (a) 40:40:20, (b) 30:30:40 (c) 25:25:50 (d) 20:20:60 and (e) 10:10:80 wt. %.

rupturing of basic back bone of both polymers that PTh and PIn in copolymeric state [23]. This rupturing of basic back bone results in significant weight loss of sample. On the heat flow curve strong deep is observed, which is associated with phase change in sample [24]. During this phase, copolymeric materials was loss its chemical structure. Subsequent weight loss that is third step up to 1000 K, attributed to generation of carbonaceous gases and oxidation of sample. So, such optimized sample is suitable for optical device applications [25].
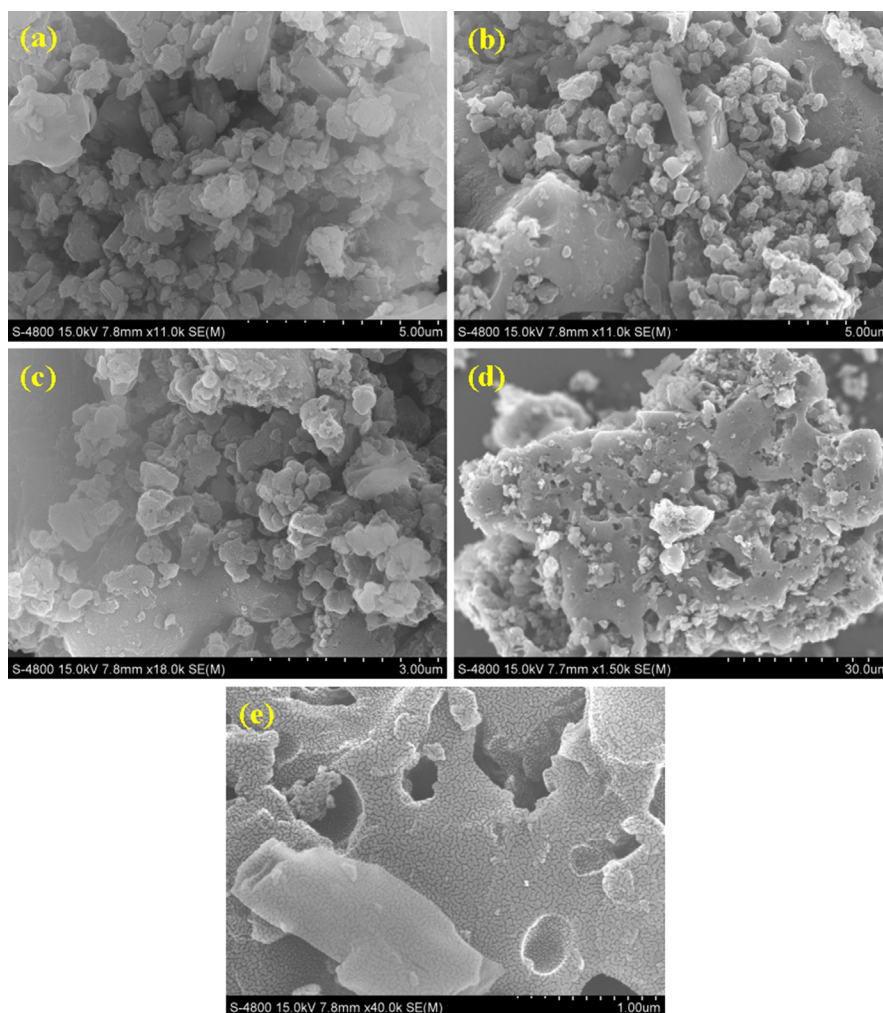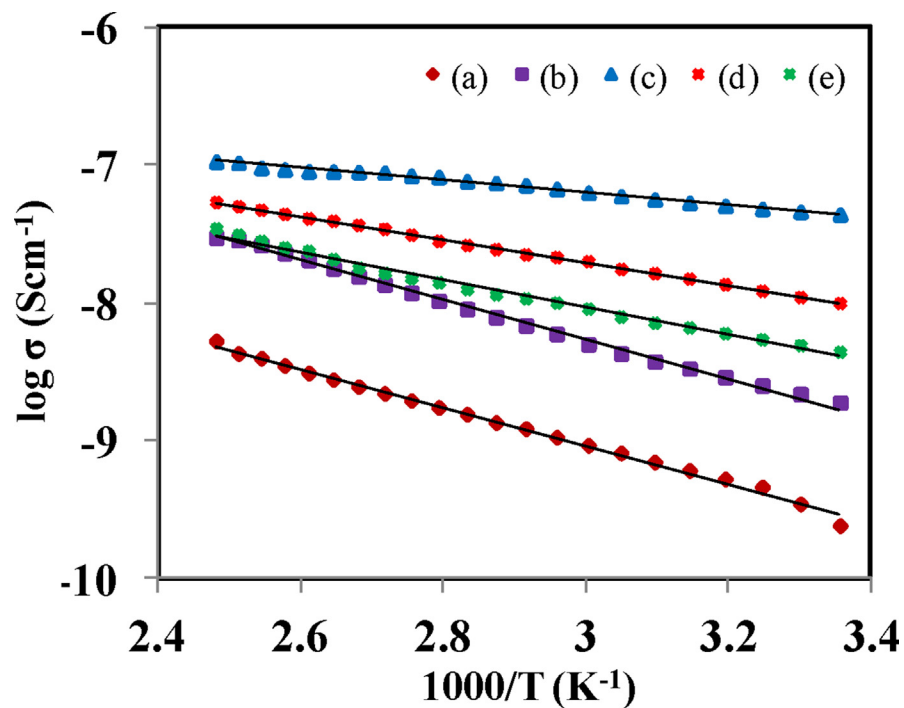
Fig. 3. FE-SEM pictures of (Th-In) conducting copolymers with different stoichiometry of thiophene, indole and FeCl$_3$ as (a) 40:40:20, (b) 30:30:40 (c) 25:25:50 (d) 20:20:60 and (e) 10:10:80 wt. %.

3.4. Temperature dependent conductivity

Fig. 5 represents the variation of log σ with inverse absolute temperature for all the samples of (Th-In) conducting copolymer system with different stoichiometry of thiophene, indole and FeCl$_3$ as (a) 40:40:20, (b) 30:30:40, (c) 25:25:50, (d) 20:20:60, and (e) 10:10:80 wt. % in the temperature range 303–393 K. From the plot, it is clear that as the temperature increases, dc conductivity of all the copolymeric samples also increases which can be in accordance with the theory explained by Armand et al. [26]. The variation of dc conductivity with temperature could be rationalized by free volume model [27]. As temperature increases, the vibrational energy of the segment is enough to push against the imposed hydrostatic pressure through its neighboring atoms and create a little space surrounding to its own volume in which vibrational motion can takes place [28]. Hence, the mobility of ions and
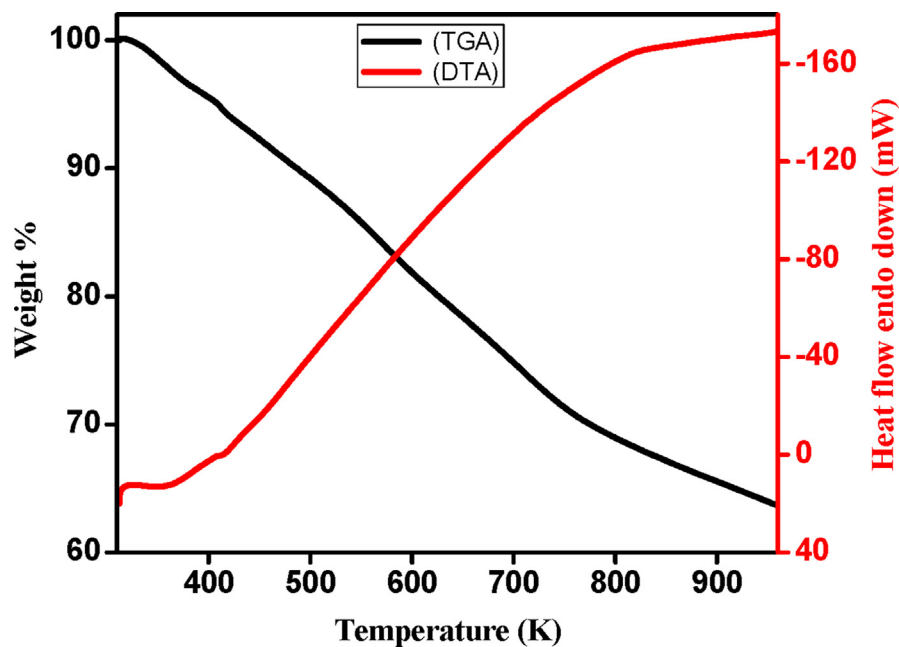
Fig. 4. TG-DTA curve of (Th-In) conducting copolymer with stoichiometry of thiophene, indole and FeCl$_3$ as (25:25:50) wt. %.

Fig. 5. Arrhenius plot for (Th-In) conducting copolymers with different stoichiometry of thiophene, indole and FeCl$_3$ as (a) 40:40:20, (b) 30:30:40 (c) 25:25:50 (d) 20:20:60 and (e) 10:10:80 Wt. %.

segments of polymer are due to the free volume around the polymer chains, results in conductivity. Thus, increase in temperature, increases the free volume of polymer segment which results in raise for conductivity. From Fig. 5, it is evident that the conductivity of studied samples varies smoothly with temperature. This indicates that the studied copolymeric materials have completely amorphous structure [29], which also reflects from the XRD patterns. The temperature dependent conductivity data of studied conducting copolymers have been fitted to the Arrhenius equation of conductivity (equation 1) [30].

$$\sigma_{dc} = \sigma_0 \exp\left(-\frac{E_{dc}}{KT}\right) \tag{1}$$

where, E_{dc} is activation energy which was calculated from the least square straight line fitting of plots and σ_0 be the pre-exponential factor.

The conductivity increases with increase in temperature, with range $10^{-4}-10^{-5}$ Scm^{-1} within measured temperature range. The increased in the conductivity is attributed to an increase in mobile ions and segment concentration. The copolymeric sample with stoichiometry of thiophene, indole and FeCl$_3$ as (25:25:50) wt. % has the highest value of σ_{dc}, which is estimated to be 8.96×10^{-4} Scm^{-1} at 393 K. This may happened due to the fact that, extent of copolymerization is maximum for copolymeric sample with stoichiometry of thiophene, indole and FeCl$_3$ as (25:25:50) wt. %, since during chemical reaction, yield of product was found to be more for this sample. The activation energy (E_{dc}) is found to be 0.061 eV which is the lowest value among all. The activation energy is the minimum energy required to overcome potential barrier in conduction mechanism. In this case, activation energy can be calculated from slope of the line multiplied by the Boltzmann constant, gives the activation energy. The activation energy of samples are varying with oxidant concentration. From Table 1, it very clear that conductivity inversely proportional to activation energy of samples.

Table 1. dc Conductivity, activation energy of the samples of (Th-In) conducting copolymers.

Samples (Stoichiometry ratios)	Conductivity (Scm^{-1}) at 303 K	Conductivity (Scm^{-1}) at 393 K	Activation energy (eV)
(40:40:20)	7.84×10^{-5}	2.24×10^{-4}	0.192
(30:30:40)	1.72×10^{-4}	5.10×10^{-4}	0.115
(25:25:50)	6.51×10^{-4}	8.96×10^{-4}	0.061
(20:20:60)	3.51×10^{-4}	6.57×10^{-4}	0.136
(10:10:80)	2.47×10^{-4}	5.25×10^{-4}	0.197
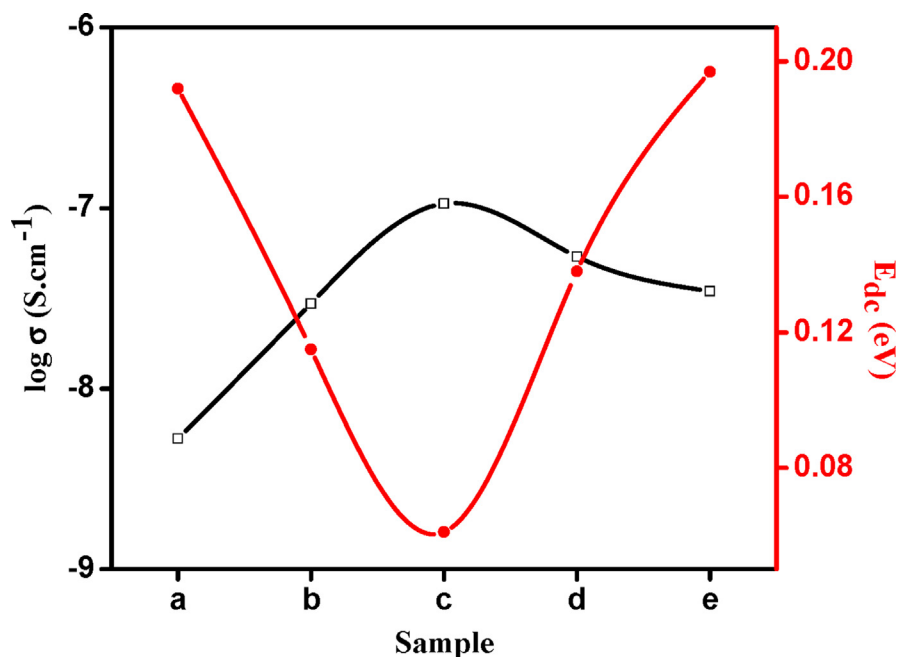
Fig. 6. Variation of σ_{dc} and E_{dc} for (Th-In) conducting copolymers with different stoichiometry of thiophene, indole and $FeCl_3$ as (a) 40:40:20, (b) 30:30:40 (c) 25:25:50 (d) 20:20:60 and (e) 10:10:80 Wt. %.

The variation of σ_{dc} and E_{dc} as a function of (Th-In) conducting copolymer system as-synthesized with different stoichiometry of thiophene, indole and $FeCl_3$ as (40:40:20−10:10:80) wt. % depicts in Fig. 6. It reveals that, the conductivity of as-synthesized samples shows the random nature. It is optimum for copolymer with stoichiometry of thiophene, indole and $FeCl_3$ as (25:25:50) wt. % and decreases continuously from copolymer sample (20:20:60) wt. %. The value of activation energy ranges between 0.061 - 0.197 eV. The maximum in conductivity corresponds with minimum of activation energy. This may be due to a maximum density of free electron and mobile ion concentration. Beyond a certain concentration of oxidant, σ_{dc} starts to decrease and E_{dc} increase. It may be due to the hindrance in "mixed anion effect" [31]. The values of dc conductivity, activation energy and transference numbers of the samples of (Th-In) conducting copolymers are as represented in Table 1.

3.5. Transference numbers

The transference numbers measurement provides the evidence of ionic and electronic contributions to total conductivity. Ionic transference number is one of promisingly studied parameters for the characterization of polymer electrolyte materials. The ionic contribution to the total conductivity was evaluated using Wagner's dc polarisation technique [32]. The as-studied samples were polarized at 303 K by a

constant dc potential of 5 V. It was observed that initial polarization current on appli-
cation of the electric field was directly proportional to the applied potential but
consequently it starts decreasing with time. This causes due to the migration of
ions because of applied electric field is balanced by diffusion. The polarization cur-
rent is generally carried by electrons or holes. The transference numbers (t_{ion}, t_{ele})
were determined using Eqs. (2) and (3) [33, 34]:

$$t_{ion} = \frac{I_i - I_f}{I_i} \qquad (2)$$

$$t_{ele} = 100 - t_{ion} \qquad (3)$$

where, I_i is the initial value of the current at the start; and I_f is the current on reach-
ing saturation.

Fig. 7 (a, b, c, d, e) represents polarization current versus time plots for samples of
(Th-In) conducting copolymer with different stoichiometry of thiophene, indole and
$FeCl_3$ as (40:40:20−10:10:80) wt. %. From Table 1, the values of t_{ion} are found to be
in the range from 0.77 to 0.84. This shows that the charge transport in all as-studied
samples is predominately due to ions. The contribution of electrons to the current is
negligible in all the samples. This suggested that the conduction mechanism in pre-
sent copolymeric samples had dominated by the ions and is close to unity. Hence
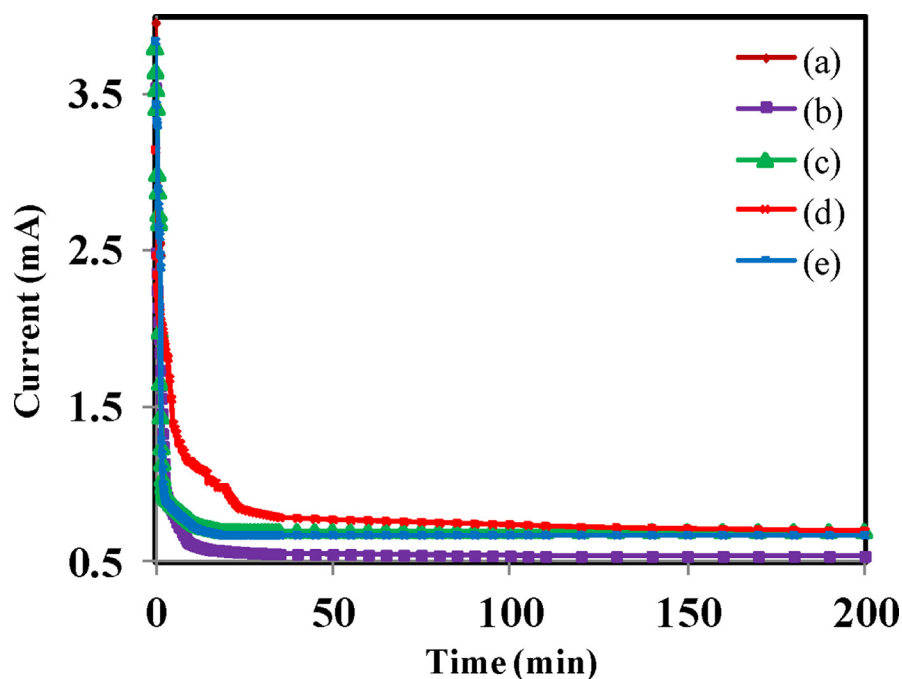
Fig. 7. Plots of polarization current versus time for (Th-In) conducting copolymers with different stoi-
chiometry of thiophene, indole and $FeCl_3$ as (a) 40:40:20, (b) 30:30:40 (c) 25:25:50 (d) 20:20:60 and
(e) 10:10:80 wt. %.
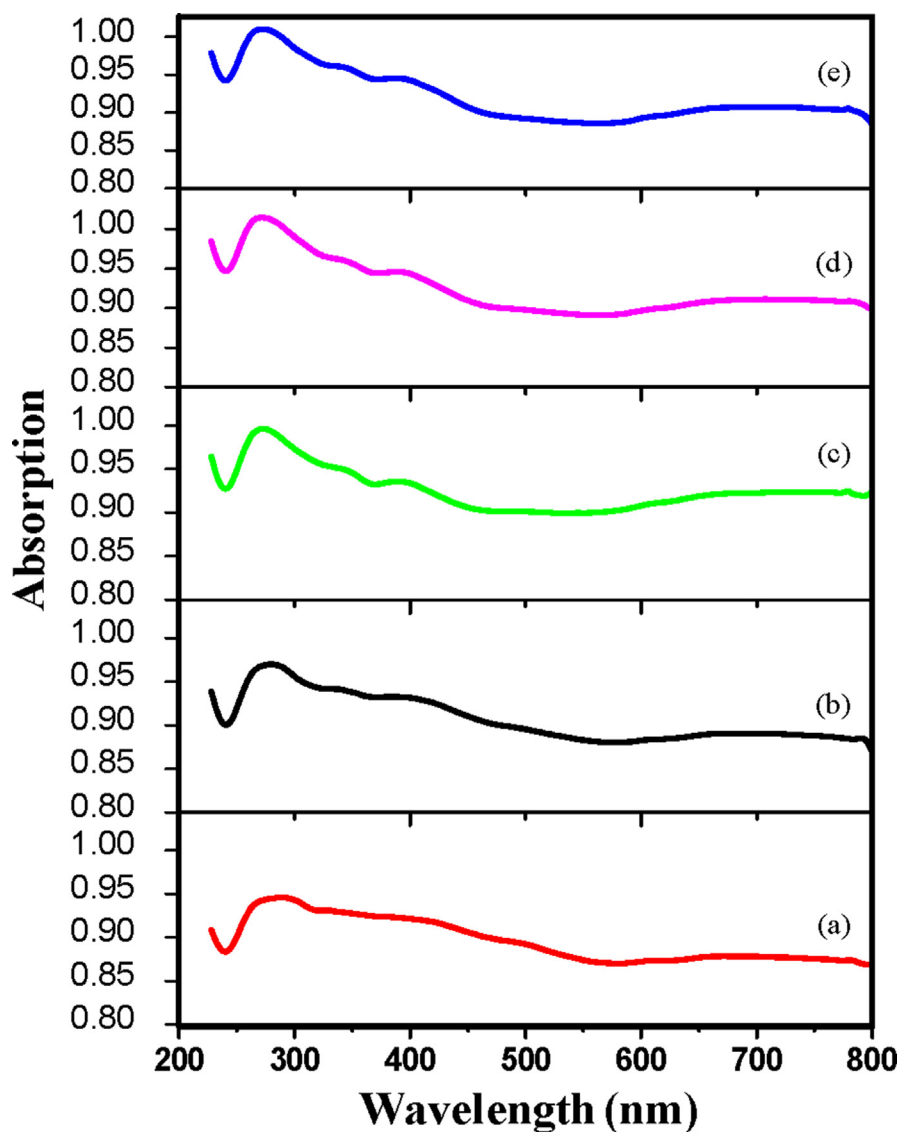
Fig. 8. UV-Vis spectra of (Th-In) conducting copolymers with different stoichiometry of thiophene, indole and $FeCl_3$ as (a) 40:40:20, (b) 30:30:40 (c) 25:25:50 (d) 20:20:60 and (e) 10:10:80 wt. %.

these copolymer electrolytes have potential applications for solid-state electrochemical cells.

Fig. 8 depicts the UV-Vis absorption spectra for the as-synthesized (Th-In) conducting copolymer with different stoichiometry of thiophene, indole and $FeCl_3$ of all the samples in the range 200 nm−800 nm. The absorption spectra is one of the frequently used tool to examine the linear absorption properties of as-studied materials. The spectra provide the knowledge regarding the electronic transitions that exist in the molecules of the materials. In case of organic molecules of studied materials, the electronic transitions normally takes place between bonding and non-

bonding orbitals towards the non-occupied antibonding orbitals [35]. The highly intense absorption peak of the as-synthesized samples was observed at 275 nm, frequently present in donor and acceptor in copolymer [36]. Peak ranging between 200 - 400 nm may attributed due to the $\pi-\pi^*$ electronic transitions of the conjugated polymer backbones [37]. Enhance photovoltaic properties like efficiency is attributed to increase in the absorption ability of materials.

Fig. 9 shows the optical band gap curve for (Th-In) conducting copolymer with different stoichiometry of thiophene, indole and $FeCl_3$. The relationship of linear absorption coefficient (α) of material and incident photon energy (hν) is given by the well-known Tauc relation (Eq. (4)) [38]:

$$\alpha h\nu = C \, (h\nu - E_g)^n \tag{4}$$

where, E_g is the optical band gap energy of material, C is a proportionality constant and n is 0.5 for direct allowed transition and equal 2 for indirect allowed transition, respectively. The optical band gap values for the samples were found to be in the range of 3.37$-$3.71 eV. The optical band gap energy values obviously concluded that, this material has potential application in optoelectronics devices.

Fig. 10 (a, b, c, d, e) represents the extinction coefficient as a function of wavelength (λ) for the samples of (Th-In) conducting copolymers with different stoichiometry of
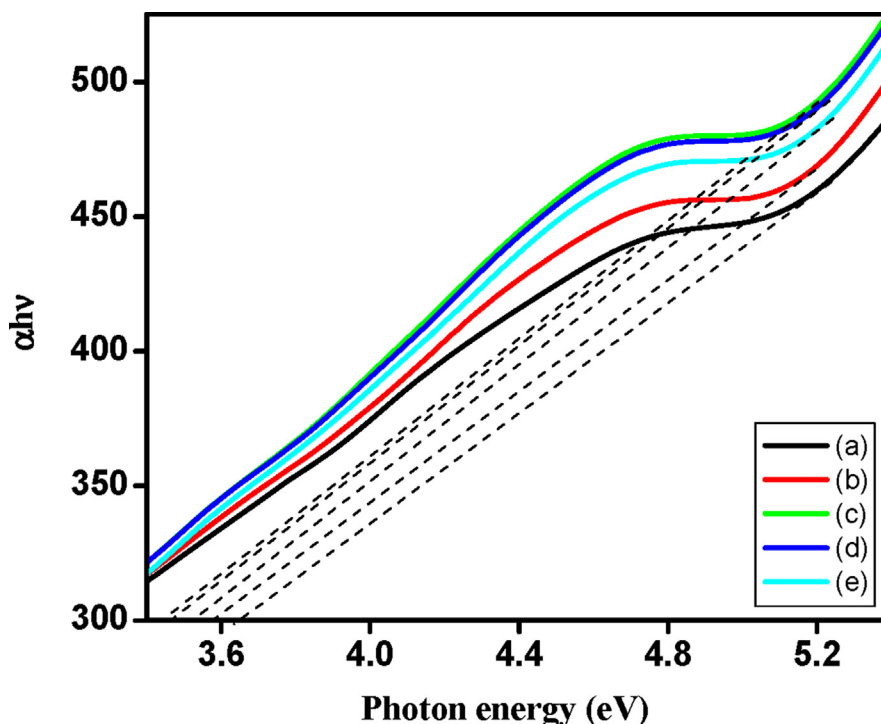

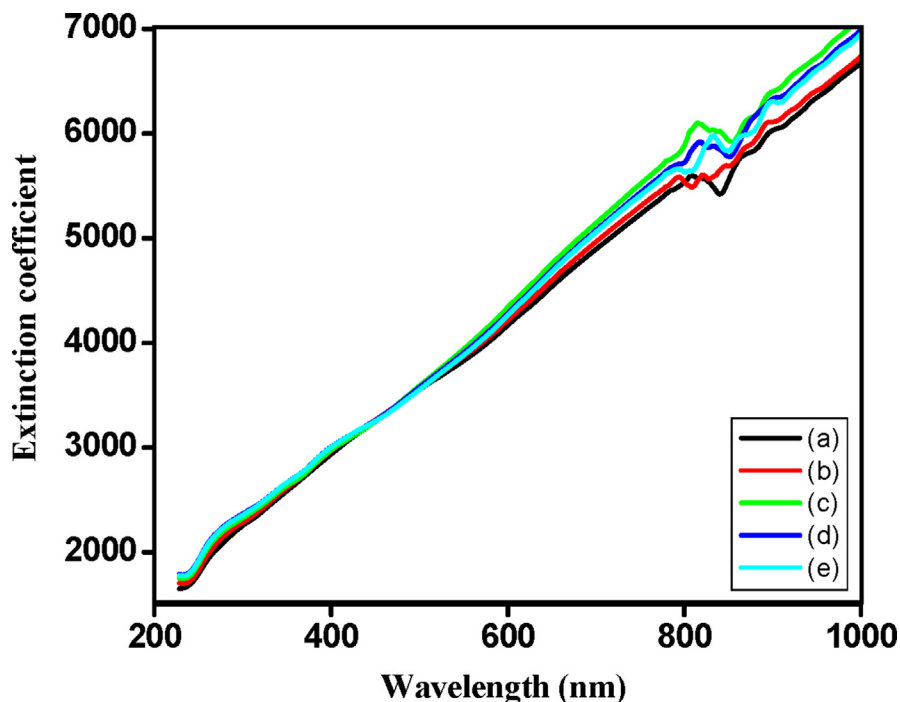
Fig. 9. Plot of αhν versus photon energy (hν) for (Th-In) conducting copolymers with different stoichiometry of thiophene, indole and $FeCl_3$ as (a) 40:40:20, (b) 30:30:40 (c) 25:25:50 (d) 20:20:60 and (e) 10:10:80 wt. %.

Fig. 10. Plot of extinction coefficient (K) versus wavelength (λ) for (Th-In) conducting copolymers with different stoichiometry of thiophene, indole and FeCl$_3$ as (a) 40:40:20, (b) 30:30:40 (c) 25:25:50 (d) 20:20:60 and (e) 10:10:80 wt. %.
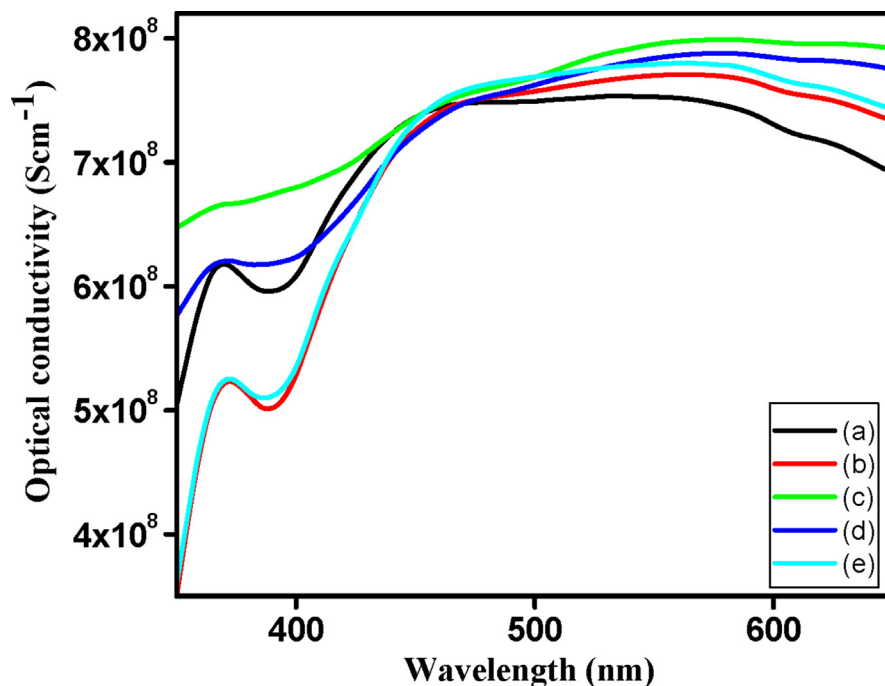
thiophene, indole and FeCl$_3$ as 40:40:20, 30:30:40, 25:25:50, 20:20:60, and 10:10:80 wt. %. The extinction coefficient pointed out the amount of absorption loss occurred when electromagnetic wave propagates through a materials. The extinction coefficient measures the fraction of light lost owing to scattering and absorption per unit distance of penetration materials medium. The extinction coefficient is related with the absorption of material and hence it depends upon absorption coefficient [39]. The extinction coefficient can be estimated by using Eq. (5) [40]:

$$K = \frac{\alpha \lambda}{4\pi} \tag{5}$$

where, K is extinction coefficient, α is % absorption coefficient and λ is wavelength.

Fig. 10 depicts that, extinction coefficient curve increases linearly with incident photon wavelength, but in the region from 800 to 850 nm the presence of a valley may be due to reflection of light from the surface of the as-synthesized samples of (Th-In) conducting copolymers. The extinction coefficient is a measure of trapping of light [41].

The optical response of material is generally calculated in terms of optical conductivity (σ) as shown in Eq. (6) [42]:

Fig. 11. Plot of optical conductivity (σ) versus wavelength (λ) for (Th-In) conducting copolymers with different stoichiometry of thiophene, indole and FeCl$_3$ as (a) 40:40:20, (b) 30:30:40 (c) 25:25:50 (d) 20:20:60 and (e) 10:10:80 wt. %.

$$\sigma = \frac{\alpha n c}{4\pi} \tag{6}$$

where, c is the speed of light, α is the absorption coefficient, n is the refractive index.

Fig. 11 (a, b, c, d, e) represents the plot of optical conductivity versus wavelength for samples with different stoichiometry of thiophene, indole and FeCl$_3$ as 40:40:20, 30:30:40, 25:25:50, 20:20:60, 10:10:80 wt. %. The plot illustrated that, the optical conductivity increases with increase in concentration of oxidant upto 25:25:50 wt. % of monomer to oxidant proportion. Further, increase in concentration of oxidant results in decrease of the optical conductivity. The highest value of optical conductivity is acquired by the sample with stoichiometry of thiophene, indole and FeCl$_3$ as 25:25:50 wt. %, whereas the lowest value by the sample with stoichiometry as

Table 2. Optical parameters of the samples of (Th-In) conducting copolymers.

Samples (Stoichiometry ratios)	E_g (eV)	$\sigma \times 10^8$ (Scm^{-1}) at (550 nm)
(40:40:20)	3.71	7.282
(30:30:40)	3.58	7.413
(25:25:50)	3.37	7.813
(20:20:60)	3.44	7.674
(10:10:80)	3.49	7.534

30:30:40 wt. %. The different optical parameters of the samples of (Th-In) conducting copolymers are given in Table 2.

4. Conclusions

A novel one-pot chemical oxidative copolymerization technique has been used in the synthesis of (Th-In) conducting copolymer system in aqueous solution. The structure and morphology of as-synthesized copolymers were confirmed through XRD and FE-SEM analysis respectively. The thermal study confirmed that, the optimized copolymeric sample had fairly good thermal stability. The temperature dependence of dc electrical conductivity of the copolymeric samples were obtained over a temperature range from 303 - 393 K found to be in the range of $10^{-6}-10^{-4}$ Scm^{-1} followed Arrhenius relation. The ionic transport number data indicates that the conduction is predominantly due to ions rather than electrons. The absorption spectrum of as-synthesized samples were analysed ranges over $200-800$ nm for the determination of optical parameters. The optical band gap values for the samples were found to be in the range of $3.37-3.71$ eV. The critical analysis of results shows that all complex optical parameters vary with the concentration of oxidant. The estimated optical band gap energy has accepted value for photovoltaic activities and has potential for application in solar cells and optical devices.

Declarations

Author contribution statement

N.S. Wadatkar: Conceived and designed the experiment; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

S.A. Waghuley: Conceived and designed the experiment; Analyzed and interpreted the data.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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