

Surfactant modulated structural modification of hybrid poly(*p*-phenylenediamine)/titanium dioxide composites and investigation of their functional behaviour

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Abstract. Hybrid polymer materials obtained by combining functional polymers with metal oxides are important functional materials having significant technological implications. Herein, we have described surfactant modulated structural manipulation of hybrid poly(*p*-phenylenediamine)/TiO₂ composites using oleic acid as the surfactant molecule and investigated functional utility of the polymer composites. Hybrid polymer composites were synthesized by an oxidative polymerization technique using H₂O₂ as the oxidant and chloroglycinato(1,10-phenanthroline) copper(II) monohydrate as the catalyst. Structural characterization was performed by using conventional techniques like Fourier-transform infrared, ultraviolet–visible spectroscopy, photoluminescence, X-ray diffraction and thermogravimetric analysis. The effect of structural modification on the functional behaviour of the hybrid polymer composites was investigated and important observations were noted. Structural modification of the hybrid polymer composites significantly improved the mechanical and thermal characteristics. Conductivity values obtained from *I*–*V* measurement and band gap calculation indicate that there is scope for using such materials as wide band gap semiconductor materials and also as insulator materials.

Keywords. Poly(*p*-phenylenediamine); hybrid polymer; oleic acid; surfactant; optoelectronics.

1. Introduction

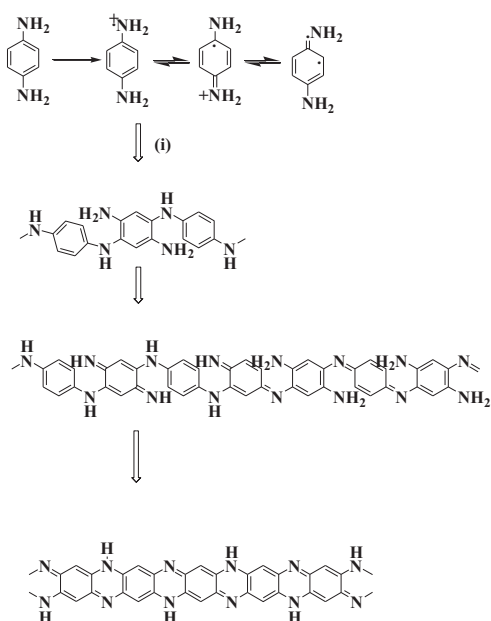
Aryldiamines are preferentially employed for the synthesis of new functional conjugated polymers [1]. Among polyaryldiamines, polyphenylenediamines are most frequently studied due to their ease of preparation through oxidative polymerization of phenylenediamine. Oxidation of the end amino groups results in the formation of different functional polymers such as linear azopolymers, polyaminoanilines, ladder polyphenazines and so on [2,3]. Composite materials derived from diaminobenzene polymers attract importance for various electronic applications. For example, highly conducting composites of polymeric *p*-phenylenediamine (PpPDA) with silver nitrate are reported in the literature [4]. It is possible to significantly modify the material and conducting properties of polymer composites by designing new polymeric composites from diaminobenzene polymers with suitable constituents. In these composites the polymeric structure retains its original structural characteristics, but on the other hand collectively they exhibit improved mechanical and thermal characteristics. Due to oligomeric nature of polyphenylenediamines, they have specific structural characteristics and therefore, finding diverse applications in various fields such as sensors, electrocatalysis, etc. Growing scientific focus is noticed on the investigation of conductive behaviour of the aromatic polymer family such as polyaniline,

its derivative copolymers, polyaminopyridine, polyaminoquinoline, polymethylquinoline, polypyrrole, polythiophene, etc. [5]. In recent years, the polymeric materials have been gaining popularity in the field of organic electronics as organic conductive materials, because of their good environmental stability [6], possibility of tuning its conductivity by doping with suitable dopants [7] and relatively better gas separation efficiencies [8]. Furthermore, the polymers exhibit wide scope of applications in various fields, for example, in rechargeable batteries [9], electrochromic displays [10], electro catalysts [11], antistatic and anticorrosive materials [12], electrode materials [13], sensors [14], detectors [15] and gas separation membranes [16]. Transition metal oxide like TiO₂ possesses interesting characteristics like cost economic, nontoxic nature, ease of handling and resistance towards photochemical and chemical erosion [17]. Because of these characteristics, such metal oxides are extensively used for the production of solar cells, chemical sensors, for hydrogen gas evolution, as pigments, self-cleaning surfaces and environmental purification application materials [18].

Composite materials usually possess superior mechanical and thermal characteristics. For tuning their thermal and chemical stability and hence to make them fit for various applications, it is important to control the size and shape of constituent polymer particles which can be performed many times by using suitable surfactant molecules. Emulsion

Table 1. Stoichiometric ratio of reactants for the synthesis of hybrid polymer composites.

Number (<i>N</i>)	1,4-Diamino benzene	TiO ₂ wt%	Oleic acid (mmol)	Chloro(glycinato) (1,10-phenanthroline) copper(II) monohydrate	30% H ₂ O ₂
Composite 1	6.0 mmol	10	1.0	30 mg (0.08 mmol)	1.5 ml
Composite 2		12	1.5		
Composite 3		10	1.5		
Composite 4		12	1.0		
Composite 5		10	0.0		
Composite 6		12	0.0		

(i) Chloro (glycinato) 1,10 – Phenanthroline) Copper(II) monohydrate, 30 % H₂O₂**Figure 1.** Oxidative oligomerization of 1,4-diaminobenzene.

polymerization of the vinyl monomer can be cited as an example where the use of the surfactant molecule allows the reduction of interfacial tension which promotes emulsification of the reactive vinyl monomer to form stable colloidal dispersion of polymeric particles [19]. For emulsion polymerization of monomers inside the micelles surfactant acid molecules are usually employed. The purpose of using these surfactant molecules is to stabilize the polymeric particles during nucleation which further promotes the stabilization of the resulting latex [20]. In some cases, factors like dipolar interactions also play a pivotal role during the stabilization of polymer molecules. In such cases, long hydrophobic chains of the amphiphilic molecules also allow structural manipulation of the polymeric unit through interdigitation of the alkyl chain in between the polymer chains [21]. Oleic acid (OA) is a popular surfactant used for the synthesis of composites in

non-aqueous fluids [22]. Over the last decade, a combination of OA with oleylamine was used for the composite synthesis of various materials because it affects the synthesis of composites [23].

Study presented here constitutes synthesis, characterization and investigation of the properties of PpPDA composites with TiO₂ particles which are structurally modified using the surfactant molecule OA during synthesis. Structural changes achieved in these cases will be correlated with the concomitant change in physical characteristics like electrical conductivity, mechanical strength and other stability parameters of the polymeric composites.

2. Experimental

2.1 Materials

Titanium dioxide (TiO₂), 1,4-diaminobenzene, OA and hydrogen peroxide were procured from TCI, Japan and Sigma Aldrich and were used as such. The mixed ligand copper(II) complex was synthesized by using a literature procedure [24].

2.2 Material characterization

Characterization of products was performed by using Fourier-transform infrared (FT-IR), X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), atomic force microscopy (AFM), ultraviolet–visible (UV–VIS) spectroscopy and thermogravimetric analysis (TGA). FT-IR spectra of the composites were recorded at room temperature on a Carry 630 FT-IR within the range of 400–4000 cm^{−1}. For morphological characterization Carl Zeiss Sigma VP Field Emission Scanning Electron Microscopes was used. AFM spectra were recorded on a MFP-3D Infinity AFM. For recording XRD data RIGAKU Ultima IV X-ray diffractometer was used.

For the X-ray CuKα source with an incident radiation of 1.54 Å was used. UV–visible spectra were recorded on a Carry 100 UV–VIS spectrophotometer within the specified wavelength range of 200–800 nm. Similarly photoluminescence

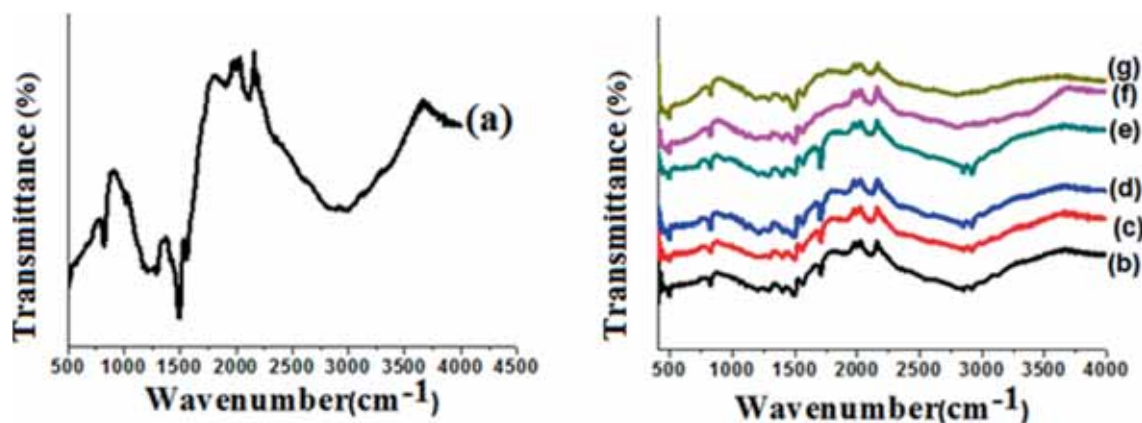


Figure 2. FT-IR spectra of (a) PpPDA, (b) composite 1, (c) composite 2, (d) composite 3, (e) composite 4, (f) composite 5 and (g) composite 6.

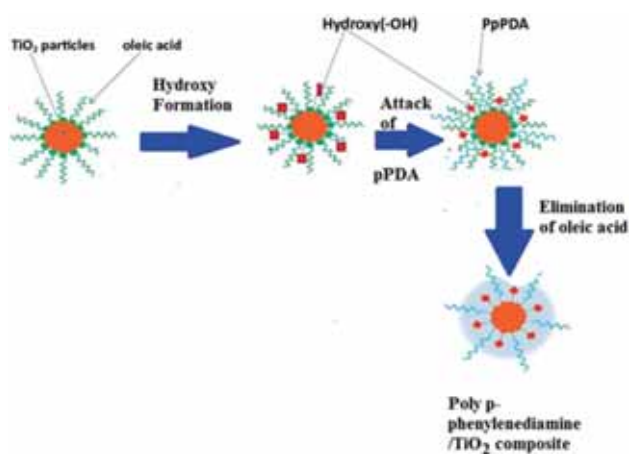


Figure 3. Surfactant modulated polymeric aggregation pattern.

(PL) measurements were carried out with a Cary Eclipse Fluorescence Spectrometer.

2.3 Procedure for the synthesis of composites

A simple synthetic procedure was employed for the synthesis of the polymer composites. A total of 0.6488 g (6.0 mmol) of *p*-phenylenediamine was dissolved in 2.0 ml 1 N HCl solution. To this solution 30 mg (0.08 mmol) of chloro(glycinato)-(1,10-phenanthroline) copper(II) monohydrate was added followed by addition of a specific amount of TiO₂ as mentioned in table 1. The solution was mixed properly. This was followed by addition of OA to the resulting solution in a definite proportion as mentioned in table 1. The solution was then shaken vigorously for thorough mixing of all the constituents. Finally, 1.5 ml of 30% H₂O₂ was added to it which results in an instantaneous exothermic reaction. The reaction mixture was then heated to 60°C for 1 h. Initially a dark brown material was produced which was

then purified with methanol and dried in an oven at 80°C for 1 h.

3. Results and discussion

Polymeric materials have better ease of processability and are convenient to assemble [25]. The cost economic nature of such materials is another important characteristic that has attracted the attention of the scientific community. These can even be considered as effective replacement in diverse field of science [26]. In recent years, widespread application of inorganic/organic polymer composites have been observed in industry and many other fields of science. The beauty of such composite materials is that they simultaneously possess the properties of the polymeric materials and the inorganic constituents [27]. We have employed the reported polymerization technique for the synthesis of polymer composites, which involves oxidation of *p*-phenylenediamine in the presence of hydrogen peroxide as the oxidizing agent, but with simultaneous dispersion of the calculated amount of TiO₂ particles in the reaction mixture [28]. Thus an *in-situ* polymerization technique was employed for the synthesis. The polymerization reaction of 1,4-diaminobenzene is represented in figure 1.

In general, composites synthesized from diaminobenzene compounds possess many interesting properties and they have the capacity to coordinate with metal centres. Such type of coordination has also been observed in the case of the hybrid polymer composites reported in this work, as is evident from spectroscopic data. FT-IR spectra of the polymer and polymer composites are represented in figure 2. Characteristic peaks for PpPDA were observed at 515 cm⁻¹ (due to the C–N bond of the aromatic ring), 592 and 700 cm⁻¹ (C–C and C–H bonding of the aromatic ring), 1302 and 1503 cm⁻¹ (C–N stretching of the benzenoid ring) and 1572.52 cm⁻¹ (CQN stretching of the quinoid ring). Similar characteristic peaks have also been observed for *p*-phenylenediamine–TiO₂ nanocomposites [29]. However, in this case, there is a

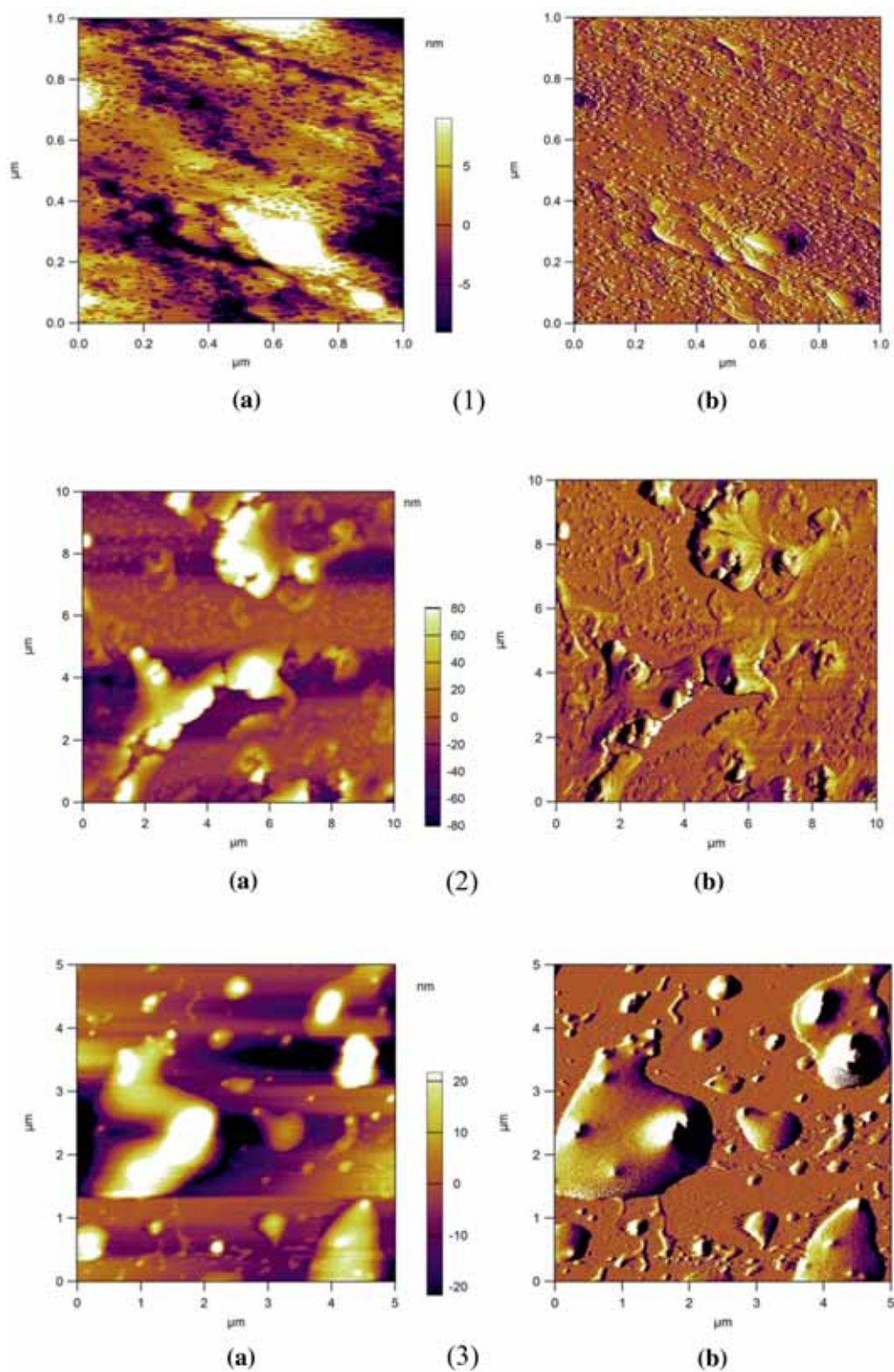


Figure 4. AFM image of (1) composite 1, (2) composite 3 and (3) composite 5. (a) Topography map. (b) Amplitude retrace.

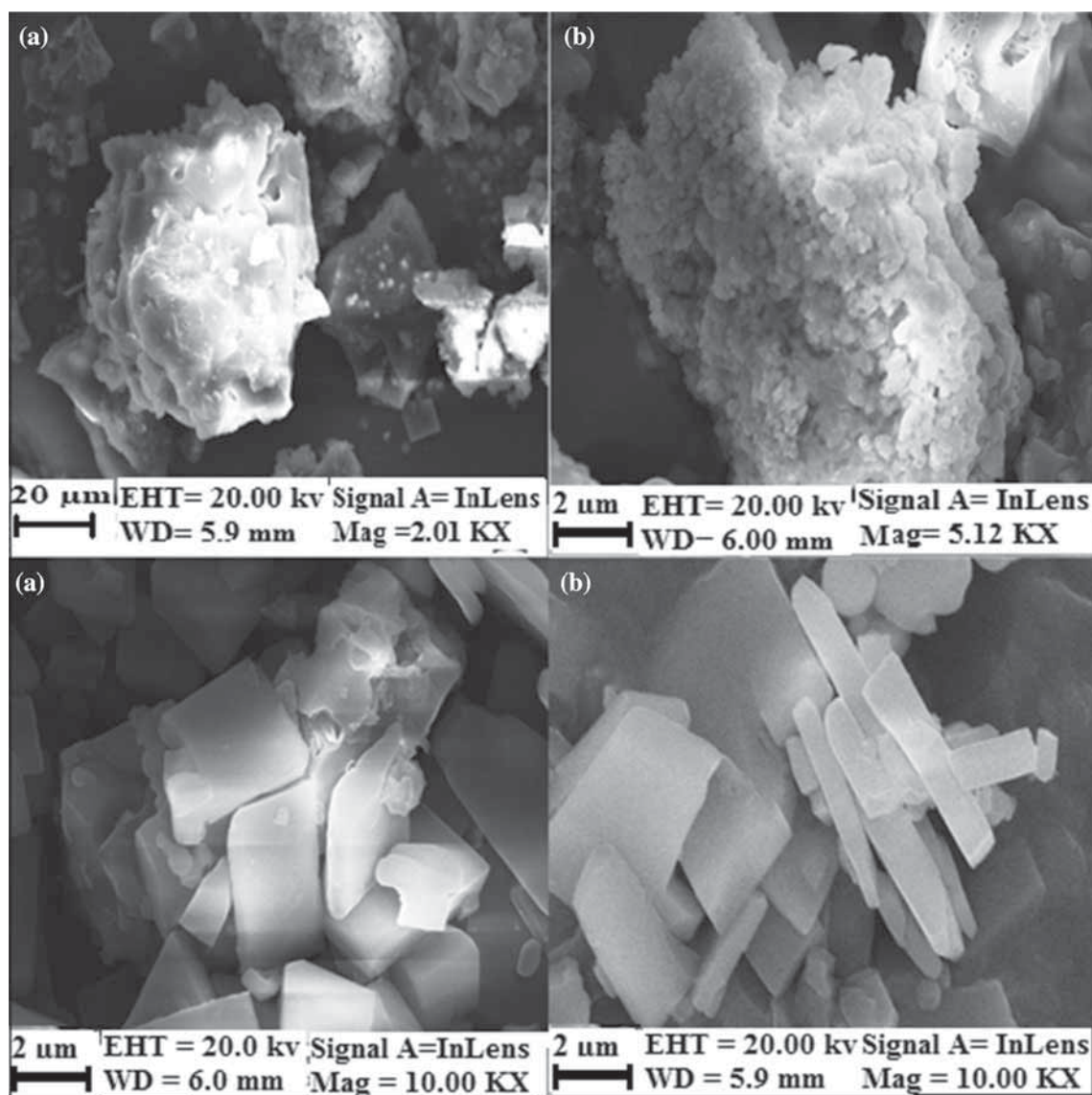


Figure 5. FESEM image of composites: (a) polyphenylenediamine/TiO₂ with OA and (b) polyphenylenediamine/TiO₂.

displacement of the peak caused by addition of TiO₂ particles to the polymeric framework during synthesis that is clearly observed, indicating coordination of the TiO₂ moiety with the polymer framework.

The absorption peak for the -NH₂ group of the parent oligomer observed at 3333 cm⁻¹ has been shifted for the hybrid polymer composites. We observed the same at 3125, 3153, 3113, 3118, 3115 and 3116 cm⁻¹ respectively, for the six PpPDA composites. Shifting of these vibrations indicates the association of the polymer with the 'Ti' metal centre of TiO₂. The characteristic peak for Ti-O stretching vibration in the composite materials was observed at 510 cm⁻¹. The OA molecule initially interacts with the TiO₂ particle leading to OH group formation at the surface of TiO₂. The formation of the

hydroxyl group strongly influences the polymeric aggregation pattern with simultaneous elimination of the OA moiety from the surface as shown in figure 3. This apparently results in an agglomerated structure of the hybrid polymer composite.

The presence of the OA moiety in the agglomerated structure is clearly indicated by the sharp and strong absorption peak observed at 1710 cm⁻¹. This can be attributed to the absorption by the C=O group of carboxylic acid. The appearance of the broad peak at 3156 cm⁻¹ supports the presence of the -OH group. Strong absorption due to C-N, C-N and CQC bonds of the hybrid polymer composites is shifted to the higher wavenumbers, while absorption due to stretching of N-H has been shifted to the lower wavenumber.

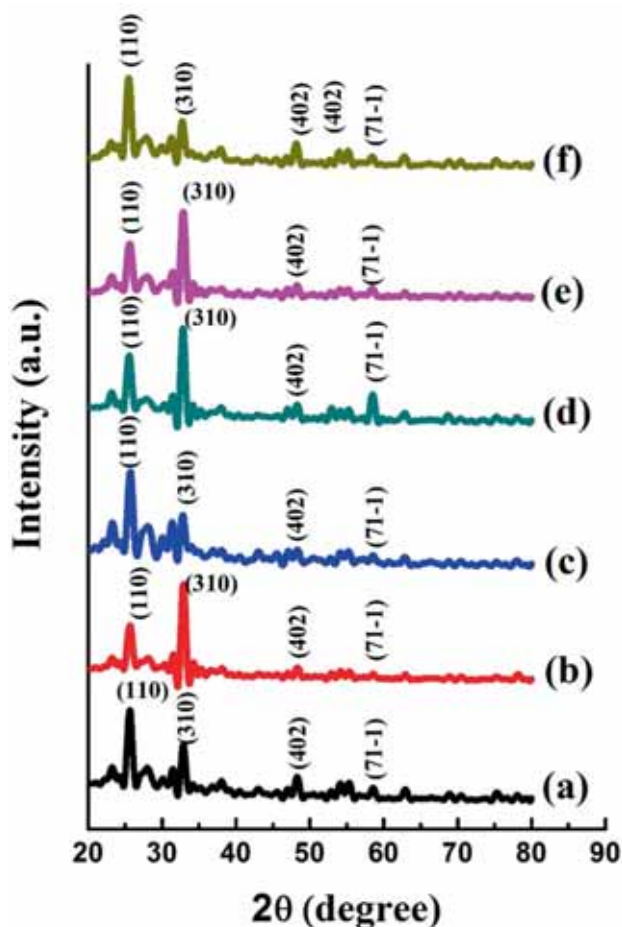


Figure 6. XRD spectra of the composites: (a) composite 1, (b) composite 2, (c) composite 3, (d) composite 4, (e) composite 5 and (f) composite 6.

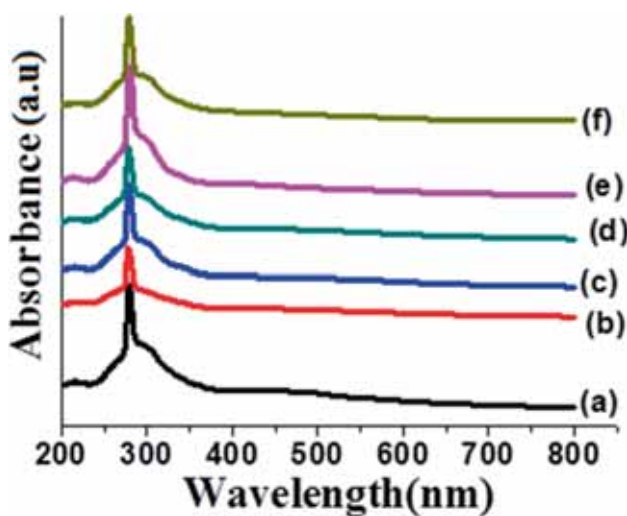


Figure 7. UV-VIS spectra of composites: (a) composite 1, (b) composite 2, (c) composite 3, (d) composite 4, (e) composite 5 and (f) composite 6.

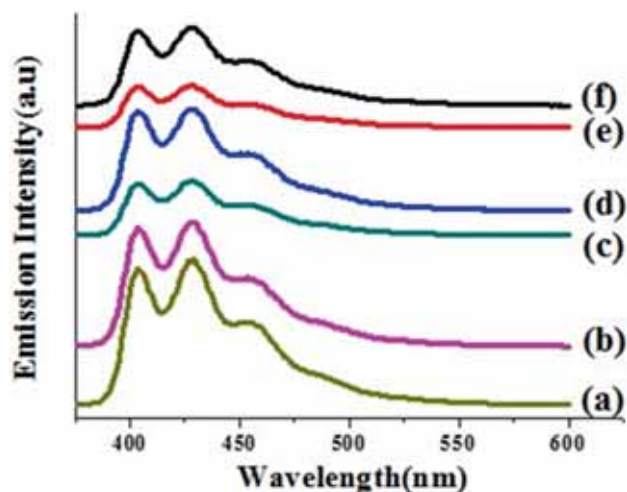


Figure 8. PL spectra of the composites: (a) composite 1, (b) composite 2, (c) composite 3, (d) composite 4, (e) composite 5 and (f) composite 6.

According to the patterns, absorption intensity is increased due to the addition of TiO_2 particles to polymer composites, due to the homogeneous distribution of TiO_2 in the composite matrix and the formation of the agglomerated structure. In order to study the morphological changes induced in the polymer composite, AFM images were recorded for the hybrid polymer composite 1, composite 3 and composite 5 and the same is represented in figure 4. AFM was recorded by using a platinum tip coated on silica in tapping mode.

The topographic map and amplitude retrace of the AFM image of the composites give an approximate idea about polymeric aggregation in the composite. It is evident from the AFM record that polymer composites are accompanied by much micrometric roughness. In fact, the presence of TiO_2 particles during the synthesis results in generation of such structures. The presence of surfactant molecules during the synthesis attributes specific structural features to TiO_2 molecules as depicted in figure 3 and thereby modulating the growth of polymer composites. It is anticipated that the polymer composites have a large surface area. Surface characteristics strongly regulate the properties and performance of a broad range of materials. The rough surface is a clear indication of the occurrence of the phenomena of polymer self-organization which can promote ordered structure formation in the polymer. Indeed, we can mention that the rough surface is an indication of higher degree of ordering in the polymeric material. Higher surface ordering again can be correlated with increased hole mobility that results in a balanced carrier transport in the active layer. Overall, the topographic contrast observed in the topography mapping is ascribed due to the amphiphilic OA moiety present in the composite. A marked phase variation is also visible in the phase retrace of the sample indicating association

of amphiphilic surfactant molecules in the composite. However, comment on surface roughness of the composite can only be made through three-dimensional projection of the image.

Field emission scanning electron microscope (FESEM) was used further for better understanding of the morphological changes occurred due to the incorporation of the surfactant molecule and the same is represented in figure 5. The FESEM image shows that the morphology of the polymer composite synthesized by using the surfactant molecule possesses a highly agglomerated structure and TiO_2 particles are evenly dispersed into the polymer matrix. This may change the properties of PpPDA, while such agglomerated structural motifs are not observed in the polymer composite synthesized without using the surfactant molecule. From the image we can ascertain that the TiO_2 particles are embedded within the structure built by PpPDA chains and generate the porous PpPDA/ TiO_2 composites. There is a large number of clews present in the polymer. The irregular shapes and the porous nature of the compacted powders are evidenced in the FESEM image presented here. Porous polymeric materials are prospecting materials because they have large specific surfaces. Such polymeric materials are usually lighter in weight and possess thermal and electrical insulating properties.

Therefore, these materials possess diverse application prospects. These can find use as catalytic supports, adsorbents, light weight structural materials, insulators and so on. For example, a porous carbon nanotube–polymer nanocomposite film can be used as the transparent electrode and light weight EMI shielding material [30,31]. The XRD spectrum of the polymer composites show a series of sharp lines in the region of $20^\circ < 2\theta < 65^\circ$ which depicts that the polymer composites have a crystalline structure with long range ordering. The XRD patterns of the composites are shown in figure 6.

The absence of the broad peak in the XRD spectra further indicates the absence of amorphous components. The peaks of the hybrid polymer composites were identified by comparison with JCPDS-84-1286. A comparison of 2θ angles confirms a brookite structure for TiO_2 particles with $2\theta = 25.4^\circ$ which corresponds to the (110) plane of TiO_2 . The other diffraction peaks at 33.78° , 47.88° and 58.50° can be attributed to (310), (402) and (71-1) crystal planes of the brookite phase respectively.

UV–VIS spectra of the hybrid polymer composites are represented in figure 7. From the spectra, it has been observed that a strong absorption peak appears at 285 nm which is due to the TiO_2 particle and corresponds to the band gap energy of 3.77 eV. The band gap energy is calculated from the formula

$$E = h \cdot c / \lambda,$$

where E corresponds to the band gap energy, λ corresponds to the cut off wavelength, h is the Planck's constant and c corresponds to the velocity of light.

The values obtained for these synthesized composite materials are indicative of the fact that these materials also have the scope of being used as wide band gap semiconductors (WBGSs). The advantage of this fact is that WBGSs are comfortably used in devices that operate at higher voltages, frequencies and temperatures which are sometimes difficult with conventional semiconductors. The strong absorption at 285 nm can be ascertained to π – π^* transition in the TiO_2 molecule [32]. Another peak at 300 nm further indicates the presence of quinoid imine units ($-\text{C}=\text{N}$) [33].

The PL study helps one to assess the efficiency of charge carrier trapping, make an understanding of recombination of electron–hole pairs in semiconductors, charge transfer phenomena and like. When the photogenerated electron recombines with the hole, energy is released in the form of fluorescence [34]. PL spectra of the polymer composite materials are represented in figure 8. The spectra exhibit a strong blue/near UV emission with significant bands at 408 and 428 nm. It has been noted that the emission band features of the hybrid polymer composites are similar to those of the plain TiO_2 particles. The strong emission band at 455 nm is due to the defects on the surfaces of composites. It is reported that the green emission of the TiO_2 composites results from the surface defects formed by oxygen vacancies or the Ti interstitials on the composite surface [35].

Thermal stability of the composite materials was studied using TGA. The thermograms of the composites are shown in figure 9. For all the six composites initial weight loss was observed up to a temperature of 100°C . This can be attributed to the loss of moisture content of the composites. The composites are thermally stable up to a temperature of 180°C beyond which the composites start decaying slowly and continuously in two steps. Weight loss of 30–40% was recorded for all the hybrid polymer composites up to a temperature of 260°C . This indicates the degradation of the polymeric structure.

The current–voltage (I – V) characteristic of the hybrid polymer composites was studied to determine the resistivity (ρ) of the composites and is shown in figure 10. From the parameters like resistance (R), area of pellet (A) and thickness of the pellet (l) used during I – V measurement, the resistivity for the six different composites is calculated from the relation:

$$\rho = (A/l)R_b$$

where ρ is the resistivity and R_b is the bulk resistance of the pellet. The resistivity values in turn help to calculate the conductivity (σ) of the composites. The resistivity and conductivity values calculated for the composites are tabulated in table 2.

The results show that incorporation of TiO_2 into the polymer matrix increases the value of conductivity as compared

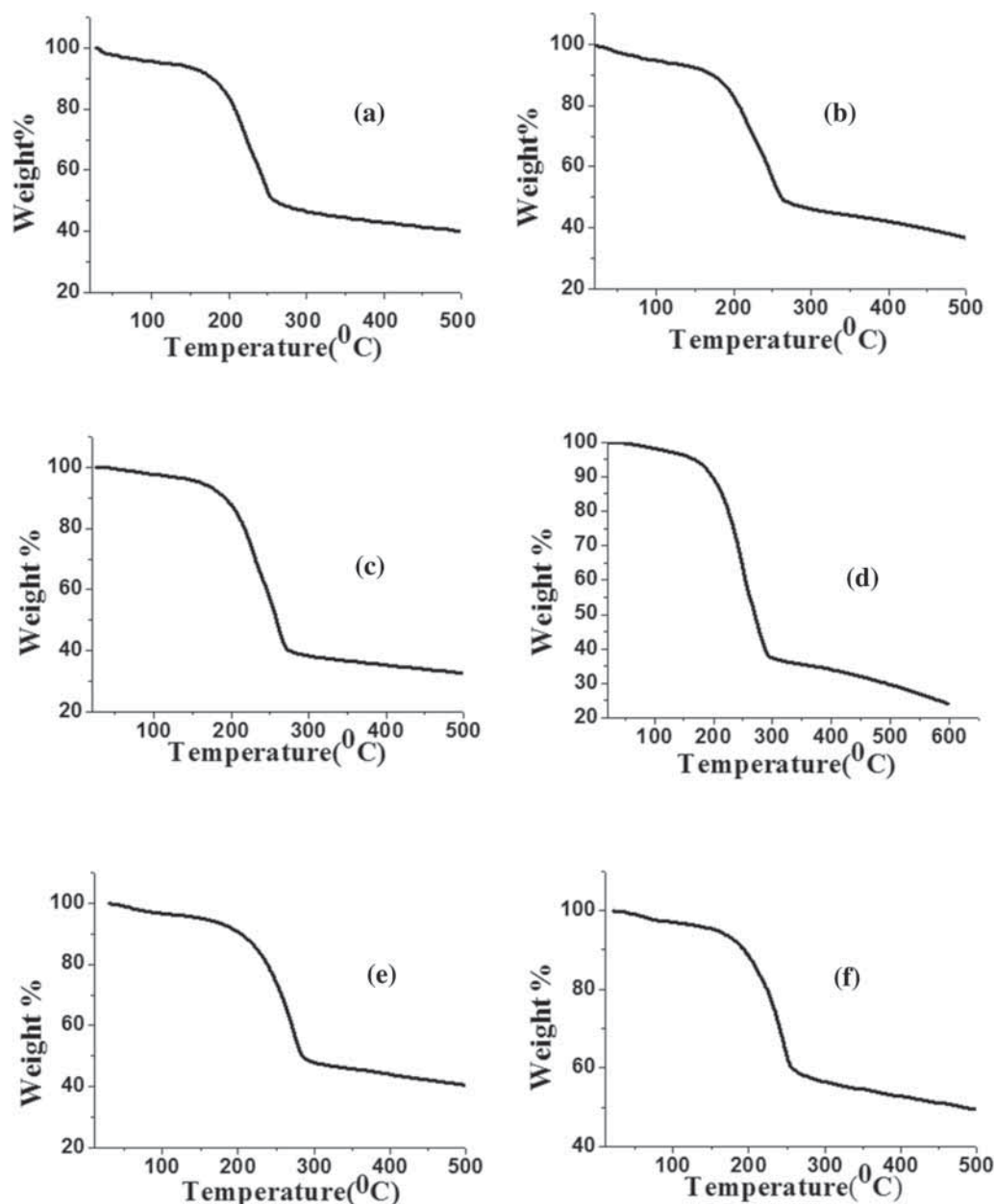


Figure 9. TGA graph of the composites: (a) composite 1, (b) composite 2, (c) composite 3, (d) composite 4, (e) composite 5 and (f) composite 6.

to the parent polymer. The reported conductivity for PpPDA is $2.4 \times 10^{-10} \text{ S cm}^{-1}$ [36]. Most interestingly, for composite 2 where increased amounts of OA (1.5 mmol) and TiO_2 (12%) were used, we have noted significant improvement in conductivity which falls well within the semiconducting range. This fact indicates that composite 2 can be used as the WBGs. Similarly, for composite 1 and composite 5, the same proportion of TiO_2 was used but composite 5 does not contain surfactant component. Although the conductivity values are of the same order, but composite 1 has relatively

higher values of conductivity. This can be attributed to the presence of the surfactant molecule in compound 1. In the case, of composite 6, which also does not contain the surfactant molecule, an increase in the proportion of TiO_2 did not help to increase the conductivity. Rather, the conductivity value decreases further. In such case, the composite is suitable to use as an insulator. Thus tuning the ratio of the surfactant molecule and TiO_2 , it is possible to obtain important hybrid polymer composites suitable for optoelectronic application.

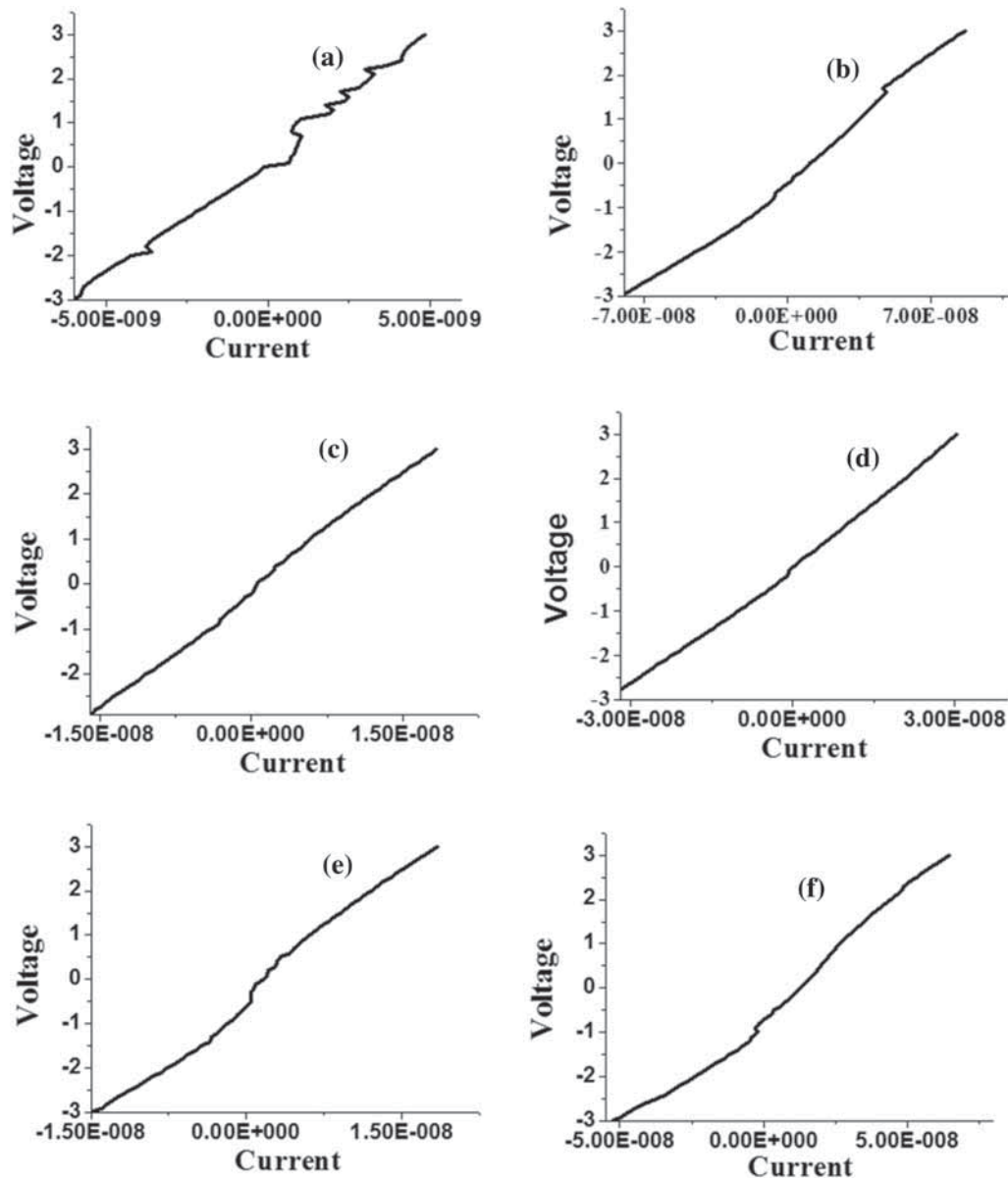


Figure 10. Current vs. voltage curve of the composites: (a) composite 1, (b) composite 2, (c) composite 3, (d) composite 4, (e) composite 5 and (f) composite 6.

Table 2. Conductivity of the hybrid polymer composites.

Number (<i>N</i>)	Resistance (ohm)	Resistivity (ohm cm)	Conductivity (S cm^{-1})
Composite 1	6.45×10^6	2.4832×10^7	4.02×10^{-8}
Composite 2	1.4896×10^6	5.734×10^6	$1.746.45 \times 10^{-7}$
Composite 3	143.8882×10^6	5.53945×10^8	1.805×10^{-9}
Composite 4	96.6311×10^6	3.72629×10^8	3.72629×10^{-9}
Composite 5	18.8280×10^6	7.24878×10^7	1.379×10^{-8}
Composite 6	49.2877×10^6	1.89757×10^8	5.269×10^{-9}

4. Conclusion

We have demonstrated that surfactant molecules can be successfully used to tune the morphology and physical properties of PpPDA polymeric composites with TiO₂ particles, to obtain materials with tailor-made properties. Discussion presented in the work reveals that the polymeric composites are expected to find utility as the WBGs and as the insulator in the electronic industry. Further the hybrid polymeric composites can be obtained through a simple synthetic method and have good mechanical and thermal stability. These can be considered as potential materials for the electronics industry.

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