Mechanism of photoinduced charge transfer at MEH-PPV and titanium dioxide nanoparticle interface

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In this study, we investigated mechanisms of photoinduced electron transfer from a conjugated polymer (poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV) to titanium dioxide (TiO\textsubscript{2}) nanoparticles (acceptor) through steady-state photoluminescence (PL) spectroscopy. Since mixed phase TiO\textsubscript{2} has better photocatalytic compared to single phase, it is an efficient charge separation process during photoexcitation of polymer nanocomposites by incorporating the mixed phase TiO\textsubscript{2} nanoparticles into the MEH-PPV polymer matrix through in situ polymerization. Structural characterization revealed only physical interaction between the polymer matrix and dispersed nanoparticles. The absorbance spectra of nanocomposites also indicated the absence of ground state complex formation. Luminescence quenching of polymer nanocomposites compared to pristine MEH-PPV signifies the charge transfer taking place at the MEH-PPV/TiO\textsubscript{2} interfaces. Thus, the MEH-PPV/mixed phase TiO\textsubscript{2} nanocomposite serves as an active layer for photovoltaic application.

Keywords: Charge transfer, Conjugated polymer, Hybrid polymer nanocomposite (HPNC), Photoluminescence quenching, Photovoltaics

Hybrid polymer nanocomposites (HPNCs) are prepared by combining organic conjugate polymer with inorganic semiconductor nanoparticles. These have been an object of great attention in the field of optoelectronic devices. This combines the processability of organic material with the superior electrical conductivity and stability of inorganic nanoparticles\textsuperscript{1}. The basic requirement of a photovoltaic material is to generate free charge carriers under photoexcitation. But the major drawbacks of using conjugated polymers in photovoltaics is short exciton diffusion length (5-20 nm)\textsuperscript{2} and the trap limit electron transfer caused by single oxygen radical scavenger, water molecules, halogens and defects in the polymeric chain due to photo oxidation\textsuperscript{3}. Hence, the limitations are overcome by inclusion of high electron affinity substance, such as fullerene derivative phenyl-C61 butyric acid methyl ester (PCBM)\textsuperscript{4} or nanoparticle (ZnO, TiO\textsubscript{2})\textsuperscript{5,6}. Among them, nanoparticles are considered to be more attractive owing to their large surface-to-bulk ratio, giving an extension of interfacial area for electron transfer, and higher stability. Nanoparticles contained in the polymer layer acts as dopants and increases the charge carriers and conductivity, thereby influence the optoelectronic properties of final device application\textsuperscript{7} for different uses\textsuperscript{8,9}.

In the case of photovoltaics, the charge separation process must be fast compared to radiative or non-radiative decays of the singlet exciton\textsuperscript{8}. However, electron transport in the polymer/nanoparticle interface is usually limited by poorly formed conduction path. Hence, in bulk heterojunction, the morphology and the domain sizes of the polymer phase should be comparable to the diffusion length of the excitons for effective charge transfer at the interface. Both polymer and nanoparticle phases have to be continuous for effective charge transport\textsuperscript{6}. Therefore, the present study proposes the in situ polymerization of \(\alpha,\alpha'\)-dibromo-2-methoxy-5-(2-ethylhexyloxy) benzene into poly (2-methoxy,5-(2'-ethyl-hexyloxy)-p-phenylenevinylene) — MEH-PPV in the presence of titanium dioxide (TiO\textsubscript{2}) nanoparticles to form HPNCs. The uniqueness of this work lies in the fact of utilizing the mixed phase TiO\textsubscript{2} nanoparticles to prepare HPNCs. Generally, in case of formulating a HPNCs using TiO\textsubscript{2} nanoparticles, anatase phase TiO\textsubscript{2} is preferred compared to rutile or...
brookite\(^{10}\) owing to its wider band gap (3.2 eV), lower rates of recombination (10 fold higher hole trap compared to rutile) and higher surface adsorptive capacity\(^{11}\). But in the mixed phase TiO\(_2\), the migration of electrons and holes, because of the difference valance band and conduction band, makes it superior than the anatase TiO\(_2\). The enhanced activity of mixed phase TiO\(_2\) relative to pure phases was due the transfer of electrons from lower energy rutile to anatase which acts as electron trapping site leading efficient electron-hole separation making it a suitable candidate for photovoltaics\(^{12}\).

Usually the nanoparticles tend to agglomerate and phase separate during the formation of bulk heterojunction leading to poor device performance\(^1\). To resolve the agglomeration problem and enhance the interaction between MEH-PPV and TiO\(_2\), the prepared TiO\(_2\) nanoparticles were ultrasonicated with \(\alpha,\alpha'\)-dibromo-2-methoxy-5-(2-ethylhexyloxy) benzene (monomer of MEH-PPV) followed by polymerization. Thus, incorporation of nanoparticles into the polymer matrix introduce new energy states which can mediate the electron transport from LUMO of MEH-PPV to the conduction band of TiO\(_2\) nanoparticles under photoexcitation. Consequently, the two major drawbacks of short exciton diffusion length of MEH-PPV (~14 nm) and low electron mobility were supposed to overcome by intermixing of materials with high electron affinity in MEH-PPV using in situ polymerization. \((\chi\) of TiO\(_2\) = 4eV; \(\chi\) of MEH-PPV = 3eV).

### Materials and Methods

#### Synthesis of TiO\(_2\) nanoparticles

TiO\(_2\) nanoparticles were prepared by sol-gel method as described. 1.0 mL of titanium tetrachloride (TiCl\(_4\)) was slowly added to the 10% diluted sulfuric acid solution at 0\(^\circ\)C under constant stirring for about 30 min. During this process, white fume of HCl was released as a consequence of the reaction between TiCl\(_4\) and H\(_2\)SO\(_4\) resulting in the formation of a grey coloured solution. This grey solution was heated at 60\(^\circ\)C until a clear solution was obtained which was left undisturbed for 12 h for cooling. Later NaOH was added dropwise to the above solution until pH = 7 was attained (neutralization process) where the solution transformed to a yellow colour solution followed by gelation period of 12 h. The precipitate formed was filtered and washed twice with distilled water. Later the filtrate was calcined at 600\(^\circ\)C for two hours to acquire TiO\(_2\) nanopowder. The product obtained was grinded into a fine powder using mortar and stored in a desiccators until further usage.

#### Synthesis of MEH-PPV

Poly 2-methoxy-5-(2’-ethylhexyloxy-p-phenylene vinylene) (MEH-PPV) was prepared by the well known glicht route process\(^{13}\) through solution polymerization technique in a course of three stages of reactions. First step involves the preparation of 1-methoxy-4-(2-ethylhexyloxy) benzene (MEHB – labeled as Monomer-1) from the base materials P-methoxyphenol (PMP) and 2-ethylhexyl bromide. Then \(\alpha,\alpha'\)-dibromo-2-methoxy-5-(2-ethylhexyloxy) benzene (MEH-DBMB – labeled as Monomer-2) was prepared through bromination of MEHB. Finally, polymerization of MEHDBMBD yields Poly 2-methoxy-5-(2’-ethylhexyloxy-p-phenylene vinylene) (MEH-PPV). The synthesis procedure was reported elsewhere\(^{14}\) and the schematic diagram of the reaction is given in Scheme 1.

#### Preparation of MEH-PPV/TiO\(_2\) nanocomposite

The TiO\(_2\) incorporated polymer nanocomposites were synthesized through in situ polymerization represent in flow diagram (Scheme 2). The \(\alpha,\alpha'\)-dibromo-2-methoxy-5-(2-ethylhexyloxy) benzene – MEHDBMB (monomer of MEH-PPV) was dissolved in Tetrahydrofuran (THF). The TiO\(_2\) nanoparticles were dispersed in the MEHDBMB solution with different loading concentrations of 1, 3 and 5 wt.\% with respect to weight of MEHDBMD.

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**Scheme 1 — Reaction Scheme of MEH-PPV preparation**
Polymerization of 300 g MEHDBMB (monomer-2) with TiO$_2$ content was carried out in 30 mL THF solution with 2 g potassium tert butoxide (t-BuOK) as the catalyst. To this reaction mixture, 60 mg of benzyl bromide (chain stopper) was added to prevent gelation. The reaction mixture was refluxed in N$_2$ atmosphere at 68°C for 3 h. The reaction product was precipitated by adding 40 mL methanol and filtered after reaching room temperature. The filtrate was washed with distilled water until pH 7 was attained, followed by 3 times washing with 20 methanol. The precipitate was dried in vacuum oven for 12 h.

Deep red MEH-PPV/TiO$_2$ hybrid nanocomposites were obtained and subjected to structural and photophysical characterization to analyze the effect of nanoparticle interaction with conjugated polymer.

**Characterization of hybrid nanocomposite**

Fourier transformed infrared (FTIR) spectra were recorded using Nicolet iS5-6700 under ATR condition at wavenumber ranging from 4000 cm$^{-1}$ to 500 cm$^{-1}$. X-ray diffraction (XRD) pattern were obtained using Rigaku Mini Flex X-ray diffractometer model using a monochromatic copper radiation (CuK$_\alpha$) of wavelength $\lambda = 1.54$ Å in the range of 20-80° with the step size of 0.02°. TiO$_2$ nanoparticles were dispersed in 5 mL distilled water through ultrasonication for 30 min and the particle size distribution was measured using MALVERN particle size analyzer under ambient condition with a count rate of 172 kcps. SEM micrographs were obtained from Field Emission Scanning Electron Microscopy (FESEM) - FEI Quanta 200 Model SEM. The photophysical characterization of all the materials was studied through UV-visible absorption spectra recorded using Cary 500 Scan model made by VARIAN, with wavelength ranging from 200 to 700 nm and Photoluminescence (PL) emission spectra in the wavelength ranging from 200 to 1100 nm recorded on a Cary Eclipse mode made by VARIAN using xenon pulse lamp as the source in ambient condition.

**Results and Discussion**

**Characteristics of TiO$_2$ nanoparticles**

**Structural characterization**

Fig. 1 displays XRD patterns of synthesized TiO$_2$ nanoparticles. The prepared TiO$_2$ constitutes of mixed phase of tetragonal anatase (represented by A) and rutile (represented by R) along with traces of orthorhombic brookite (represented by B) which was in agreement with the data reported in the databases cards JCPDS no. 00-021-1272, JCPDS no.00-021-1276 and JCPDS no.00-029-1360, respectively. The diffraction peaks at 25.3°, 37.9°, 48.2°, 55.1°, 62.7° reveals the anatase phase of TiO$_2$ nanoparticles. The diffraction peaks at 27.5°, 45.5°, 53.9°, 66.3° and 69° indicating the rutile phase of TiO$_2$.

In the phase composition of TiO$_2$, an additional peak at 30.8˚ confirms the fraction of brookite phase arises due to decrease in pH during synthesis. Addition of NaOH had favoured the formation of rutile. Generally, the higher surface energy has contributions to non-equilibrium transition from anatase to rutile which was facilitated by calcining at 600°C. But it was observed that the incorporation of sulfate ion during the synthesis stabilized the anatase phase, inhibiting the prominent formation of the rutile phase. The proposition of anatase/rutile phase composition can be estimated using the Spurr and Myers equation:

$$f = \frac{1}{1+1.26\frac{T_R}{T_A}}$$
Where, \( I_R \) and \( I_A \) are the peak area of diffraction peaks of rutile (110) and anatase (101), respectively. From the above equation the anatase to rutile proportion was estimated as ~83%. The XRD studies revealed the formation of mixed phase TiO\(_2\) with predominant orientation in anatase phase.

**Morphological studies: SEM and particle size analysis of TiO\(_2\) nanoparticles**

The SEM micrographs of TiO\(_2\) nanoparticles at 25 kX magnification (Fig. 2A) show that the particles are spherical with an average diameter of 140 nm; and crystalline in nature with defined grain boundaries. The particles are agglomerated owing to the high surface energy of TiO\(_2\) nanoparticles which is observed from the SEM images. Fig. 2B displays the size distribution of TiO\(_2\) nanoparticle which covers the range from 150 to 250 nm with the average size of 189 nm. A small hump around 280 nm denotes the agglomerates.

**Characteristics of MEH-PPV/TiO\(_2\) hybrid nanocomposite**

**Structural characterization**

Fig. 3 shows the FTIR spectra of MEH-PPV, TiO\(_2\) and MEH-PPV/TiO\(_2\) nanocomposites. The FTIR spectrum of MEH-PPV [Fig. 3(i)] denotes the main characteristic absorption bands at 2957, 2856 and 2924 cm\(^{-1}\) band of CH\(_3\), CH\(_2\) asymmetrical and C-H stretching vibrations, respectively. Three semicircular stretch bands associated with the phenyl ring are observed at 1408, 1501 and 1606 cm\(^{-1}\). The other vibration at 863 and 965 cm\(^{-1}\) indicates out of plane phenyl CH wag and trans double bond C-H wag. Symmetrical and asymmetrical C-O-C stretching vibration modes are located at 1032 and 1202 cm\(^{-1}\), respectively corresponds to alkyl oxygen stretch and phenyl oxygen stretch. The small band at 1736 cm\(^{-1}\) could be attributed due to the carbonyl absorption. The 1460 and 794 cm\(^{-1}\) shows band of CH\(_3\) asymmetrical C-H bending and mono substituted aromatic ring C-H bending \(^{14}\). The band at 1447 cm\(^{-1}\) corresponds to O-H bending vibration of water. Ti-O-Ti vibration bonds were found at 875 cm\(^{-1}\). The peak observed at 1102 cm\(^{-1}\) corresponds to the C-O vibration. The band at 609 and 635 cm\(^{-1}\) could be attributed to the stretching mode of Ti-O bonds,
which are characteristic of titanium oxide. The FTIR spectra of hybrid nanocomposite were similar to that of MEH-PPV. Since TiO$_2$ was incorporated in a very low quantity, there is no significant change in the FTIR spectra was observed in the nanocomposites. The presence of additional bands at 1650-1700 cm$^{-1}$ denotes the Ti-OH bond. The band around 856 cm$^{-1}$ signifies the presence of TiO$_2$ nanoparticles. Thus, the presence of the nanoparticles in the composites was confirmed.

The XRD studies of the nanocomposite were carried out in order to examine the influence of TiO$_2$ nanoparticles into the MEH-PPV polymer. Fig. 4 shows the XRD pattern of MEH-PPV/TiO$_2$ nanocomposite. It is evident from Fig. 4(i) that the pristine MEH-PPV polymer with a broad peak at $2\theta = 22^\circ$, is highly amorphous in nature. Similarly, the diffraction peak of polymer nanocomposites displayed the broad peak at $\sim 22^\circ$ with a slight peak shift due to the internal stress induced by the addition of TiO$_2$ nanoparticles into the polymer matrix. Due to trace amount of TiO$_2$ dispersion the diffraction peaks of the nanoparticles were not distinct in XRD of polymer nanocomposites. But in Fig. 4(iii), a low intensity peak at $26.8^\circ$ denotes TiO$_2$. This might be due the improper dispersion of TiO$_2$ nanoparticles in the polymer nanocomposites which tends to agglomerate and became visible during analysis.

**Photophysical characterization**

HPNC thin films were obtained by dissolving HPNCs in toluene at a concentration of 10 mg/mL. This solution was spin coated on to a cleaned glass substrate at a speed of 1500 rpm for 5 times at 35$^\circ$C to obtain approximately 1 μm thick film for PL studies.

The absorbance and emission spectra of MEH-PPV and MEH-PPV/TiO$_2$ nanocomposites are given in Fig. 5 A & B. Both MEH-PPV and the nanocomposite exhibit a broad absorbance peak centered at $\sim 490$ nm is attributed to the $\pi-\pi^*$ transition of the conjugated polymers. No evidence of any additional peak in the measured spectral region denotes the absence of ground state complex which implies that there is no formation of any new complex species with the addition of TiO$_2$ in MEH-PPV. When the thin films of MEH-PPV and hybrid nanocomposite were excited at 480 nm, the emission spectra of hybrid nanocomposite films were similar to that of the pristine MEH-PPV. However, the decrease in PL intensity was observed as the TiO$_2$ content increases since the film was coated in same condition and at the same concentration of solution. The decreased intensity could be due to the quantity of TiO$_2$. On examining the emission spectra, it can be seen that the luminescence primarily results from the excitons

![Fig. 4 — XRD patterns of MEH-PPV and MEH-PPV/TiO$_2$ nanocomposites](image)

![Fig. 5 — (A) Absorbance and (B) emission spectra of MEH-PPV and MEH-PPV/TiO$_2$ nanocomposites](image)
which radiatively recombine in MEH-PPV. A predominant peak at 630 nm is attributed to the interchain excitons of MEH-PPV, since the thin films were obtained from the solution of higher concentration. A small hump at 590 nm in the case of 1% TiO$_2$, HPNC film signified the presence of intrachain excitons of MEH-PPV in a minimal quantity. This was owing to the fragmentation of few polymer chains through addition of nanoparticles. Nevertheless, the intensity of the PL emission (630 nm) in the composites decreasing substantially with increasing TiO$_2$ nanoparticle content denotes the charge separation occurring at the interface of the luminescent polymer and nanoparticle which is responsible for the photoluminescence quenching.$^{18}$

The charge separation at the interface is on the basis of relative energy levels of MEH-PPV and TiO$_2$ nanoparticles where the disassociation of the excitons is energetically allowed. Due to better PL quenching and enhanced charge transfer these hybrid nanocomposites are expected to be useful in photovoltaic applications.$^4$

**Charge Transfer Process from MEH-PPV to mixed phase TiO$_2$**

An electron and hole that is coulombically bound is termed as an exciton. A charge separation can take place only when the binding energy is overcome which is done by photoexcitation of the conjugated polymer. Such a charge separation can be made efficient with a material with higher electron affinity and only if the LUMO level of polymer is lower than Conduction band of the semiconductor metal oxide where the polymer acts as donor and metal oxide as an electron accepting material. Additionally, there should not be much potential difference between both donor and acceptor. A short range interaction brings about spatial overlap of wavefunction of donor and acceptor; as a result disassociation of exciton takes place significantly at the polymer/nanoparticle interface. Moreover, the interface between the polymer and the nanoparticle plays a crucial role in determining the performance of the device. Hence intermixing with the polymer at the nanometer scale for efficient charge transfer is achieved in this case. anatase phase has more electron affinity, hence mixed phase TiO$_2$ which was predominantly in anatase phase had facilitated efficient separation of photogenerated electrons from MEH-PPV. In this process, the rutile phase has lower conduction band compared to anatase supported in initial extraction of electrons from MEH-PPV. The electron in rutile is transferred to anatase phase which facilitates movement of electrons further away from MEH-PPV which inhibits the recombination process. Hence, the mixed phase TiO$_2$ acts as an efficient quencher for MEH-PPV and therefore, the MEH-PPV/TiO$_2$ can be a suitable active layer in photovoltaics. The process of charge transfer from MEH-PPV to mixed phase TiO$_2$ is represented in the Fig. 6.

**Conclusions**

The results of the analysis of photoinduced charge transfer from MEH-PPV to the mixed phase TiO$_2$, particularly the steady state PL measurements, reveal remarkable quenching of luminescence with increased TiO$_2$ content. The luminescence quenching was due to the transfer of photogenerated electrons from the polymer to TiO$_2$. Structural analysis indicates that the chemical structure of the polymer remains unaffected by the incorporation of TiO$_2$ nanoparticles. In summary, the new approach of incorporation of mixed phase TiO$_2$ nanoparticles through in situ polymerization in the conjugated polymer matrix has resulted in efficient charge separation. Hence, this type of polymer nanocomposites is a suitable candidate for photovoltaic applications as active layer.

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**Conflict of interest**

The authors declare no conflict of interests in this study.
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