

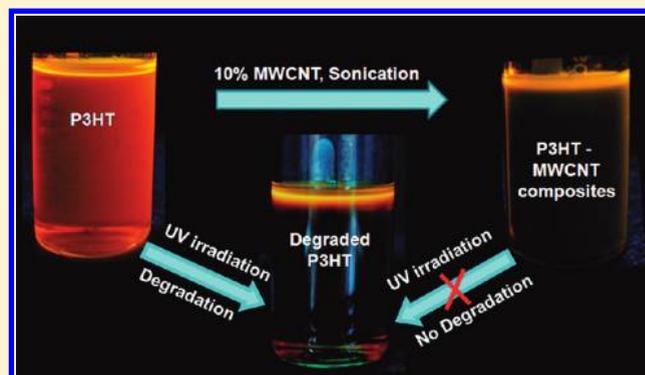
Enhancing the Photostability of Poly(3-hexylthiophene) by Preparing Composites with Multiwalled Carbon Nanotubes

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S Supporting Information

ABSTRACT: Poly(3-hexylthiophene) (P3HT) degrades in organic solvents containing dissolved molecular oxygen when irradiated with ultraviolet light. Hence, it is important to develop strategies that can enhance the photostability of P3HT and enhance the device performance. In this work, we report that preparing composites of P3HT with appropriate amounts of multiwalled carbon nanotube (MWCNT) results in superior photostability of P3HT. UV–visible and fluorescence spectroscopy have been used as primary tools to study the photostability of P3HT and its composites. Scanning electron microscopy (SEM) images of the composites display dispersed CNTs being well coated by P3HT. Transmission electron microscopy (TEM) micrographs along with SAED patterns reveal that P3HT coats the CNTs, which is the reason for superior dispersion of the composite. ESR spectroscopy was also performed to pursue and follow the degradation of P3HT. Ten weight percent of MWCNTs in P3HT was found to be the optimum loading amount that results in maximum photostability of the P3HT as compared to the other ratios. This enhanced photostability of P3HT on preparing composites with MWCNT in addition to its easy processability directly from solution makes these composites immensely important for optoelectronic applications.



1. INTRODUCTION

Studies on electroactive polymers has been an area of intense interest for fundamental reasons as well as for technological applications.¹ Polythiophenes are important and well-explored representative class of conjugated polymers that find wide applications in polymer LEDs, organic transistors, solar cells, photoresists, antistatic coatings, and optical and electrochemical sensors.^{2–4} The chemical stability of conducting polymers has attracted enormous debate, because lithography processes used during submicrometer device fabrication involves exposure to intense UV light or electron beam irradiation.⁵ This usually causes the photodegradation/bleaching of the organic materials. Various methods have been used to improve the thermal, mechanical, electrical, and optical properties of conducting polymers, such as introducing alkyl groups into the main chain, synthesis of soluble precursors, preparation of conducting polymer composites, blending with metal salts/nanoparticles, and copolymerization.^{4,6} Yet meager or practically no efforts have been made to prevent the photodegradation of conjugated polymers.

Carbon nanotubes (CNTs) are also an important class of organic materials that have fascinating properties like large elastic modulus and electric conductivity along the tube axis, while being flexible and nonconductive in the perpendicular direction which makes them fit for applications in nanoelectronics⁷ and

biochemical sensors.⁸ Boosted by the promising properties of both carbon nanotube and conducting polymers, various reports on the polymer/CNTs dispersions based hybrid materials have been studied extensively.^{9–12} Moreover, due to the enhanced conductivity and mechanical properties of P3HT in easily processable P3HT–MWCNT nanocomposites, they are projected as good candidates for possible device fabrication and optoelectronic applications.¹³

Despite possessing promising properties, the stability of conjugated polymers such as P3HT in optoelectronic devices has been a challenge due to the degradation it undergoes in the presence of light during fabrication and operation. The prime reason for this degradation is the effect of organic/nonaqueous solvents while processing and the presence of dissolved molecular oxygen in addition to the exposure or irradiation of UV or visible light.^{14,15} This has resulted in device malfunction or inferior quality devices in several cases that requires stabilizing the P3HT or any other conjugated polymeric material. In the scope of this work, we present a systematic study on enhancing the photostability of P3HT by preparing nanocomposites with

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MWCNT and proving that irradiation of UV light on this nanocomposite causes no photodegradation to P3HT. We have used UV–visible absorption spectroscopy, photoluminescence spectroscopy, and ESR spectroscopy to understand the photodegradation behavior of the P3HT and have optimized the percentage of MWCNTs doping required for enhanced photostability of as synthesized P3HT.

2. EXPERIMENTAL SECTION

2.1. Chemicals and Solvents. MWCNT (Shenzhen Nanotech, China) and anhydrous CaSO_4 (Merck) were used as received. All solvents including chloroform and methanol (Merck) were used after purification by standard purification techniques.¹⁶

2.2. Instrumentation. UV–visible spectra were recorded on a Perkin-Elmer Lambda 25 UV–vis spectrophotometer at room temperature. Photoluminescence studies were done using a Varian photoluminescence spectrophotometer. Scanning electron microscopy images were recorded in a LEO VP 1430 scanning electron microscope. Transmission electron microscopic studies were done using a JEOL 2100 transmission electron microscope. UV degradation experiments were performed in a Delta Scientific variable intensity UV chamber. ESR spectroscopy was done on JEOL JES-FA200 electron spin resonance (ESR) spectrometer. Ultrasonications were done in a JAC Ultrasonic 1505 ultrasonicator. Degradation chamber which was used contains three Hg discharge lamps (Philips, G6 T5, TUV 6W). We measured the spectral power density at the place where the samples were kept for degradation studies. Emission from Hg vapor lamps primarily consists of three lines 365.4 I-line, 404.7 H-line, and 435.8 G-line. The relative intensities of these lines bear a constant ratio at a particular temperature. Optical power meter (ThorLabs Inc.) set at 404.7 nm (H-line of Hg vapor) shows radiant power 4.5 mW.

2.3. Synthesis of Poly(3-hexylthiophene). The synthesis and characterization of P3HT was reported earlier.^{17,18}

2.4. Preparation of MWCNT–P3HT Nanocomposite. The MWCNT–P3HT nanocomposite solutions were prepared by ultrasonication technique and had a deep brown color. Three different ratios of MWCNT (5%, 10%, and 15%) with P3HT were prepared and their photostability was studied and compared with the stability of the pure P3HT. While preparing the composites, a solution of 10 mg of P3HT in 5 mL of chloroform and the required amount of MWCNT were added in each case and the solutions were ultrasonicated for 30 min at room temperature.

2.5. UV–Visible and Photoluminescence Studies. Stock solutions for UV–visible and photoluminescence studies were prepared by dissolving 10 mg of P3HT in 5 mL of dry chloroform. Similar concentration of P3HT was maintained in the composites and in the pure polymer solutions. Necessary equivalent dilutions of both pristine P3HT solution and composite solutions were made using micropipettes to record the spectra. While studying the UV degradation properties, the solutions were irradiated in the UV chamber in steps of 1 min exposure time and the spectra were recorded after every exposure (Figure 1).

3. RESULTS AND DISCUSSION

SEM images were recorded on dried samples coated with gold. Figure 2a–d shows SEM images of as-synthesized, pristine P3HT films, 5% MWCNT–P3HT composite films, 10% MWCNT–P3HT composite films, and 15% MWCNT–P3HT composite

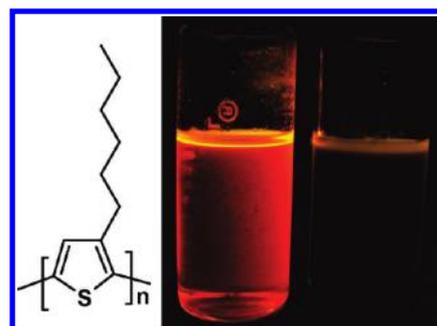


Figure 1. Poly(3-hexylthiophene) (P3HT) structure, chloroform solution of pristine P3HT (orange-red solution), and P3HT–MWCNT nanocomposite (10%) (brown solution) illuminated under UV light.

films. They reveal the presence of a random network of interconnected bundles of MWCNT dispersed in the polymer matrix. In the 5% MWCNT-loaded composite, the amount of CNT is found to be insufficient to interact with all the P3HT present and a major part of P3HT remains exposed as observed clearly in Figure 2b. In the case of the 10% MWCNT-loaded composite, the carbon nanotubes are well coated and neither P3HT nor the MWCNT is found to be excess, but are distinguished as a well-dispersed homogeneous composite film in Figure 2c. On increasing the quantity of MWCNT to 15% in the composite, plenty of uncoated CNT are observed lying apart from the composite indicating excess loading of carbon nanotubes. The thickness of the P3HT coating on the MWCNT surface also reduces when the ratio of MWCNT is enhanced from 10% to 15% in the solution of P3HT. A better understanding of the polymer coating on the CNT surfaces was observed from the TEM micrographs. TEM images of pristine P3HT films and 10% MWCNT-loaded composites were recorded and are represented along with their respective SAED patterns in inset (Figure 2e,f). A lighter contrast on the tubular dark MWCNT demonstrates the P3HT coatings as seen in the 10% MWCNT-loaded composite. Further, comparison of SAED pattern of this light contrast part with the SAED pattern of pure P3HT confirms this. Additional figures (Figures S1–S7) are included in the Supporting Information. The dispersion of MWCNTs in conjugated polymers has been a problem in processing it.¹⁹ It is likely that the interaction between P3HT and MWCNTs via π – π and CH– π forces overcomes the van der Waals interaction between MWCNTs, resulting in uniform dispersion within the solution that stays stable for several weeks.²⁰

In conjugated polymers, the extent of conjugation directly affects the observed energy of the π – π^* transition which appears as the maximum absorption.²¹ The broad absorption spectra of pristine P3HT with absorption maxima at 443 nm is indicative of extensive π -conjugation throughout the polymer backbone (Figure 3a). All the composites showed absorption maxima with minor blue shifts. In case of the 5% MWCNT-loaded composite, the absorption maxima was observed at 437 nm with a blue shift of 6 nm from the absorption peak of P3HT (Figure 3b). The 10% MWCNT-loaded composite showed absorption maxima at 432 nm with blue shift of 11 nm (Figure 3c). The 15% MWCNT-loaded composite also showed absorption maxima at 432 nm (Figure 3d) identical to that with the 10% composite, indicating that increasing the loading of CNT beyond a certain extent does not alter the absorption behavior of P3HT. Appearance of the absorption maxima at the same position for both 10% and 15% MWCNT-loaded composites implies that 10% is the optimum

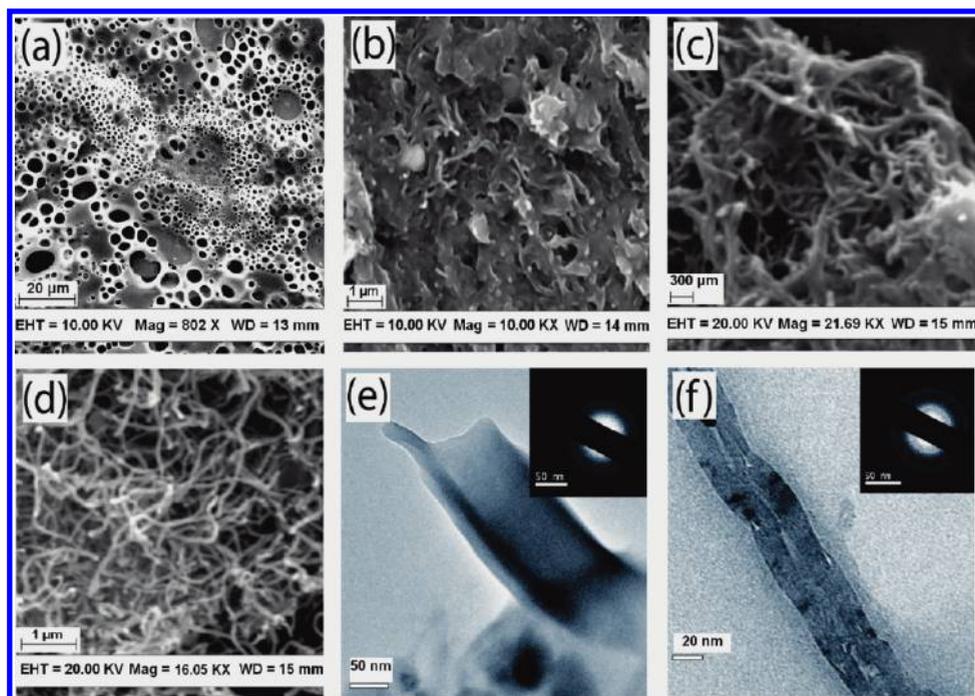


Figure 2. SEM micrographs of (a) as synthesized P3HT, (b) P3HT mixed with 5 wt % MWCNTs, (c) P3HT mixed with 10 wt % MWCNTs, (d) P3HT mixed with 15 wt % MWCNTs, and (e) TEM image of as-synthesized P3HT. SAED pattern shown in inset indicates amorphous nature of polymer (f) TEM image of P3HT mixed with 10 wt % MWCNTs. Inset show SAED pattern of the polymer coated MWCNTs.

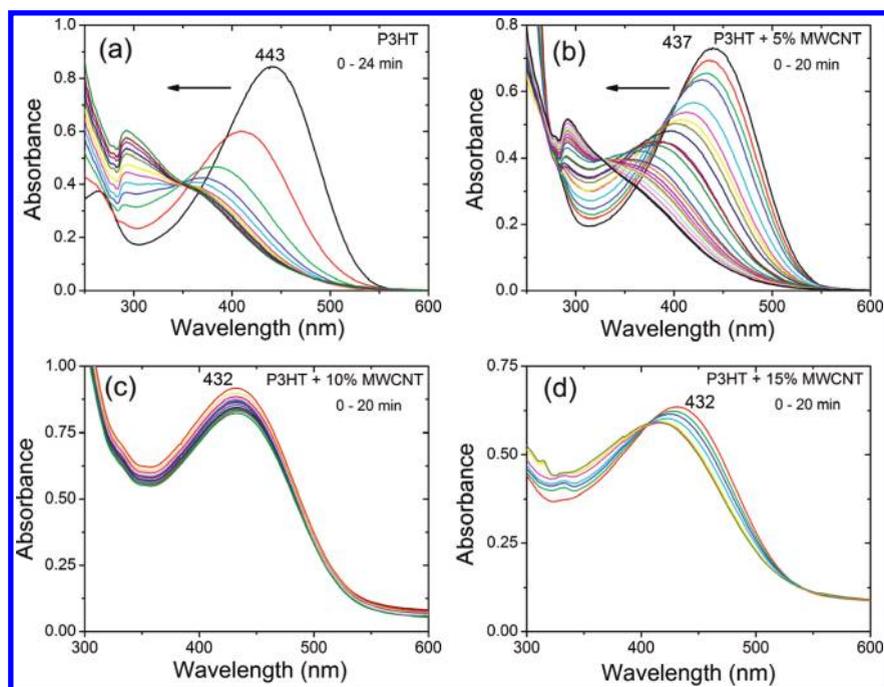


Figure 3. UV—visible spectra of P3HT and various composite percentages of MWCNT on UV irradiation: (a) pristine P3HT solution (0–24 min), (b) P3HT composite with 5% MWCNT solution (0–20 min), (c) P3HT composite with 10% MWCNT solution (0–20 min), and (d) P3HT composite with 15% MWCNT solution irradiated with UV light different intervals of time (0–20 min).

loading percentage. Excess amount of MWCNT, as observed in SEM micrograph for 15% MWCNT-loaded composite, remains uncoated by the polymer, and therefore has no significant role on the absorption maxima compared to the 10% addition. The minor blue shifts observed for the absorption maxima of the

composites are common and are in agreement with earlier reports in the literature for composites with P3HT.^{22,23}

To study the photodegradation behavior, the three CNT composites with P3HT (5%, 10%, and 15% MWCNT loaded) were exposed to UV radiation in chloroform solution in steps of

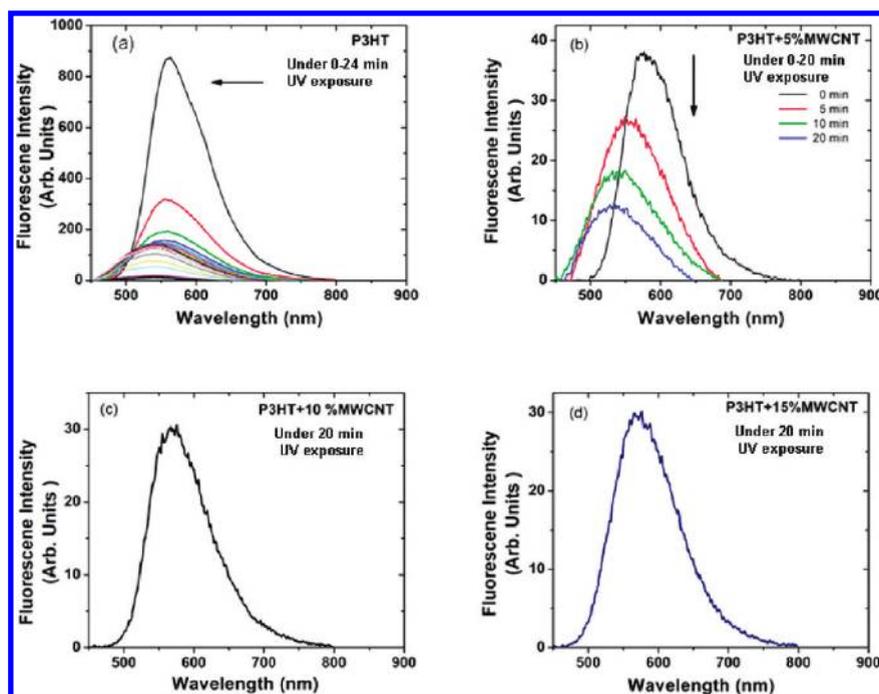


Figure 4. Photoluminescence spectra of P3HT and various composite percentages of MWCNT on UV irradiation: (a) pristine P3HT solution (0–24 min), (b) P3HT composite with 5% MWCNT solution (0–20 min), (c) P3HT composite with 10% MWCNT solution irradiated with UV light for 20 min, and (d) P3HT composite with 15% MWCNT solution irradiated with UV light for 20 min.

1 min exposure time each. Gradual UV irradiation on the chloroform solution of pristine P3HT caused a rapid decrease in absorption intensity and significant blue shifts (Figure 3a) up to a level of 20 min irradiation time during which the entire polymer degraded (absorption spectra recorded until 24 min irradiation). This notable change is attributed to the disruption of the π -conjugation and shortening of the conjugated backbone followed by complete degradation of the polymer. Gradual decrease in the absorption intensity of the original P3HT peak is a clear indication that photodegradation of P3HT occurs on exposure to UV irradiation. (The plots presented are for 2 min irradiation time increment.) In the case of 5% MWCNT-loaded composite, the original absorption maxima (437 nm) is blue-shifted steadily along with regular reduction in the intensity up to complete degradation of polymer, resulting in rapid disappearance of the peak within 20 min of UV-irradiation time (Figure 3b). (Every plot recorded for 1 min irradiation is presented.) However, the presence of 5% MWCNT in the P3HT solution slows down the photodegradation initially compared to pristine P3HT. The 10% MWCNT-loaded composite does not show any change in absorption maxima (432 nm) even after prolonged irradiation time of 20 min (Figure 3c). Again, in the case of 15% MWCNT-loaded composite (absorption maxima at 432 nm), a negligible 7 nm blue shift of absorption maxima with minor decrease in the absorption intensity was observed (Figure 3d). (Plots are presented for 0, 2, 4, 8, 12, 16, and 20 min irradiation only for clarity.) Overall, the 15% MWCNT–P3HT composite showed only minor spectral changes even on irradiation up to the 20th minute, after which the spectra were seen to be static. Observations from these UV irradiation results indicate that the 10% MWCNT-loaded composite is best stabilized under UV irradiation. The plausible reason for this is that the presence of 10% MWCNT in P3HT is the optimum amount for effective coating of all the polymers present in the solution which is also well established

and supported by SEM results. On loading of a lesser amount of CNT's, as in the case of 5% MWCNT-loaded composite, much of the P3HT remains uncoated, leaving them exposed to UV irradiation and photodegradation.

The photoluminescence (PL) spectrum of P3HT sample (Figure 4a) shows an intense emission peak at 575 nm (443 nm excitation). On exposing the P3HT solution to UV irradiation for 1 min, there is a drastic reduction in the PL intensity indicating that major part of the polymer backbone has undergone degradation. Further irradiation leads to complete quenching of the PL intensity indicating full degradation of the polymer within 20 min of exposure time to UV irradiation conforming well with the UV–visible spectra (Figure 3a). Figure 4, b, c and d, represents changes in the PL spectra of 5%, 10%, and 15% MWCNT composites with P3HT. All the data in these figures signify that the PL spectrum of the P3HT is quenched on preparing the P3HT–MWCNT composites irrespective of the ratios. The 5% MWCNT-loaded P3HT composite showed emission at 573 nm (437 nm excitation) with diminished intensity (Figure 4b) compared to the pristine P3HT. On exposing to UV irradiation for up to 20 min, a near-total quenching of PL intensity along with a blue shift of ~ 40 nm for the composite is observed. This quenching and modification in the PL intensity may be due to the π – π interaction of the P3HT with CNTs forming additional decaying paths of the excited electrons via the MWCNT.¹³ The 10% and 15% MWCNT-loaded composite also showed a similar PL peak at 573 nm (437 nm excitation) (Figure 4, c and d). Both these samples showed no further quenching or shift in PL peaks on exposing to UV irradiation for 20 min, indicating higher photostability of both these composites as compared to P3HT and 5% MWCNT–P3HT composite. The clear changes observed in the PL efficiency of P3HT in the presence of MWCNT are perhaps due to acceptance of an electron from the excited state of P3HT by MWCNT. Similar kind of photo-induced

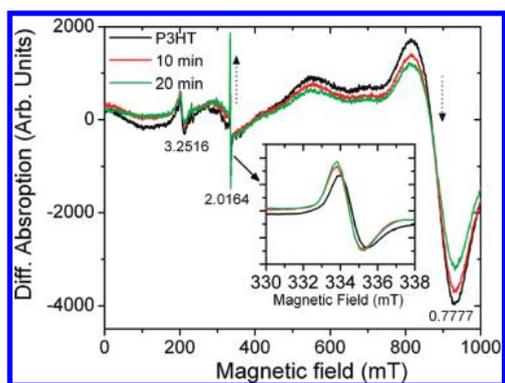


Figure 5. ESR spectra of P3HT exposed until 20 min irradiation time.

electron transfer from excited state of a conducting polymer to C_{60} is reported in the literature where π - π interactions are dominant.²⁴ In addition to the π - π interactions, the conjugated polymer-MWCNT is also known to show CH- π interactions^{13,20,21,25} which collectively are reported to be responsible for the changes in the PL spectra.

Electron spin resonance is a very sensitive probe for studying the electronic structure and defects providing vital information about the chemical environment of the unpaired electrons. Figure 5 illustrates the electron paramagnetic resonance (EPR) spectra of P3HT before and after UV irradiation. Inset of the figure shows the expanded view of sharp peak ($g = 2.0164$) close to the free electron g value ($g_{th} = 2.0023$). The deviation from the free electron g value was due to the coupling of internal molecular magnetic field (arising from unquenched angular momentum) with spin momentum. The deviation of the resonance line position is controlled by the spin-orbit coupling parameter λ , and the energy difference, ΔE , between the corresponding electronic levels belongs to the same wave vector²⁶ (eq 1).

$$g = g_{th} + \frac{\lambda}{\Delta} E \quad (1)$$

After UV irradiation, a shift in the peak position from $g = 2.0164$ to 2.0172 was observed, as shown in the inset of Figure 5. Also, the absorption intensity of this peak monotonically increases with increasing UV-irradiation time. This sharp peak observed near free electron g value indicates that electrons are delocalized on the polymer backbone. Apart from these peaks, we observed a very strong absorption peak at higher magnetic fields ($g = 0.7777$). After irradiation, this peak shifted to $g = 0.7787$. The intensity of this peak monotonically decreased with increasing irradiation time. The line shapes of these peaks were asymmetric with the asymmetry parameter $\alpha = 1.37$ and 0.42 for $g = 2.0164$ peak and $g = 0.7777$ peak, respectively. This asymmetric "Dysonian line shape" arises due to localization of conduction electrons, known as conduction electron spin resonance (CESR). If the length of the sample along the propagation direction of microwaves is larger than the skin depth, then the microwave field would have been damped within the sample. In such cases the absorption line shape is expressed as a sum of absorption and dispersive components to explain asymmetry observed experimentally.²⁷ Our studies confirm that the peak at approximately $g = 0.7777$ arises from P3HT chain, whereas peak at approximately $g = 2.0164$ arises due to the formation of paramagnetic defects. It has been reported previously that such

increase in the intensity of EPR peak was observed near free electron g value only in the presence of oxygen.²⁸ This is also in good agreement with the reported photo-oxidative pathway resulting in a P3HT radical¹⁵ that finally leads to the photodegradation of conjugated polymers. Change in the g value after irradiation indicated modification of internal molecular field due to structural modification along with change in the corresponding energy level consistent with change in the UV-vis absorption peak observed experimentally. These ESR spectra results of P3HT before and after UV exposure are strong evidence of our understanding on the oxygen-mediated photodegradation process. Further, attempts to quantitatively measure the relative photodegradation for the three composites having various percentages of MWCNTs in P3HT using ESR did not give any conclusive results. This was due to the very low concentration of P3HT and percentage of MWCNTs in the solution form, showing almost undetectable change in the concentration of paramagnetic species after UV exposure.

In an earlier report on photodegradation of P3HT, it was suggested that both reduced π -conjugation and chain scission are responsible for the degradation process.¹⁵ The reduction of conjugation, manifesting itself as photobleaching, was reported largely as the product of photosensitization and reaction of singlet oxygen. In the absence of dissolved oxygen in the solution, no photochemistry is observed. Chain scissions occur via the classical route of photooxidation where scission is initiated by residual trace amounts of transition metal salt impurities used in the preparation process of CNTs. Hence, using higher than 10% CNTs with P3HT provides lesser stability to P3HT due to higher quantities of metal impurities. Based on these studies, two plausible pathways are proposed by virtue of which enhanced photostability is achieved in the P3HT-MWCNT composite. First of all, the electron-transfer event from the P3HT to the MWCNT, as evident from the quenching of PL, greatly changes the redox potential of P3HT to oxygen and thereby enhances the oxidative stability of P3HT-MWCNT complex compared to the pristine P3HT. Second, the π - π interaction between the P3HT-CNT composite improves the stability of the π -conjugation system thereby preventing photosensitization and lesser opportunity for the reaction of singlet oxygen with P3HT. These P3HT-CNT composites are shown to possess higher photostability than pristine P3HT, and they can be processed from solution directly as films on desired substrates and yield stable and higher efficiency devices.²⁹

4. CONCLUSION

Nanocomposites of P3HT polymer and MWCNT were prepared by the ultrasonication technique, providing an alternative and easy method of preparing uniform composites from readily available polymeric materials and carbon nanotubes. We have shown that poly(3-hexylthiophene) (P3HT) degrades rapidly in organic solvents containing dissolved molecular oxygen when irradiated with UV light. The photodegradation of conjugated polymer P3HT was characterized by UV/vis, PL, and ESR spectroscopic techniques. The 10% MWCNT-P3HT composite was found to be highly stable for weeks and did not degrade on exposure to UV light. Well coating of nanotubes by polymer P3HT was confirmed by SEM and 15% TEM imaging. Modifications of the absorption maxima in the composites compared to the neat polymer along with strong photoluminescence quenching implied π - π interaction between the polymer and the

nanotubes. Photochemical stability of P3HT was confirmed to significantly enhance on preparing P3HT–MWCNT composites compared to the neat P3HT polymer. The well-documented increased electrical conductance with this enhanced photostability allows these composites for better applications in optoelectronics.

■ ASSOCIATED CONTENT

S Supporting Information. SEM images of 5%, 10%, and composites of P3HT–MWCNT at different magnifications. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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