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Photosensitized Solid-state Polymerization of Diacetylenes in Nanoporous TiO$_2$ Structures

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In situ topochemical polymerization of two diacetylene monomers within nanoporous TiO$_2$ thin films was carried out under visible light irradiation. One of the monomers used contains a carboxylic acid group, which could help to link the monomer onto the TiO$_2$ surface covalently. UV-Vis absorption and Raman studies showed that both monomers were successfully photopolymerized. These results suggest that the covalent linkage of the diacetylene to the nanoparticle through the carboxylic acid group is not needed. Since photopolymerization of diacetylene is typically induced by excitation of the monomer at $\lambda < 300$ nm, the observed red shift of the photopolymerization wavelength is attributed to the photosensitization effect of TiO$_2$. The morphological study of the polydiacetylene/TiO$_2$ nanocomposite revealed that the diacetylene monomers were polymerized in the vicinity of the TiO$_2$ nanoparticles. This is attributed to the fact that the electron-transfer process occurs at the interface of nanocrystalline TiO$_2$ (nc-TiO$_2$) and the diacetylene monomer and the polymerization is expected to be initiated near the nc-TiO$_2$ surface. Photopolymerization of the carboxylated diacetylene monomer with other oxides nanoparticles, such as ZnO and SiO$_2$ was also investigated.

Keywords: Polydiacetylene, nanocomposite, photosensitization, TiO$_2$ structures

1 Introduction

Polydiacetylene (PDA) possesses a fully conjugated backbone in the crystalline state as well as tailorable pendant side groups and functionalities (1). Polymerization of diacetylene is a lattice controlled topochemical solid-state reaction. The charge carrier mobilities of crystalline PDA at room temperature are almost 4 orders of magnitude larger than those of partially crystalline or amorphous conjugated polymers (2). PDA can be structured in the form of bulk material, mono- and multi-layered films (3), nanowires (4), and even incorporated into inorganic host matrices to form nanocomposites (5, 6). It has also been used as an active material for fabricating organic field-effect transistors (7, 8). In our prior work, *in situ* polymerized diacetylene was employed for hole transport in solid-state dye-sensitized solar cells (DSSCs) (9, 10). Moreover, researchers have explored PDA's chromogenic transitions that can be activated optically, thermally, chemically, biologically or mechanically (1, 11). These transitions at the nanometer scale have been investigated for sensor applications (12).

TiO$_2$ has been extensively studied as a photocatalyst for environmental application such as water purification (13). In addition, nanocrystalline TiO$_2$ (nc-TiO$_2$) has attracted enormous attention as a photoelectrode for electron conduction/collection in DSSCs (14, 15). It has been shown that styrene (16, 17), methyl methacrylate (18) and pyrrole (19) can be polymerized via photogenerated cationic radicals on TiO$_2$ powders. Upon photoexcitation, TiO$_2$ may undergo electron transfer and/or energy transfer to the adsorbed species, leading to chemical reactions in the heterogeneous photocatalysis process (20). Because of the high excited-state energy level of most monomeric adsorbed species, electron transfer is usually the most prevalent mechanism for polymerization. In a typical electron-transfer process as shown in Figure 1, the photoexcited TiO$_2$ may initiate an oxidation or reduction process of the adsorbed species by injecting either a hole or an electron depending upon the energy level structure of the adsorbed species.

Solid-state polymerization of diacetylene is commonly accomplished by exposure to UV irradiation ($\lambda < 300$ nm) or γ-radiation, and in some cases, thermally generated phonons are sufficient to induce the polymerization (21, 22). Each of these approaches, however, poses some limitation regarding an efficient polymerization of diacetylene for practical applications, such as photovoltaic devices. For example, the γ-ray and high-temperature treatment is not
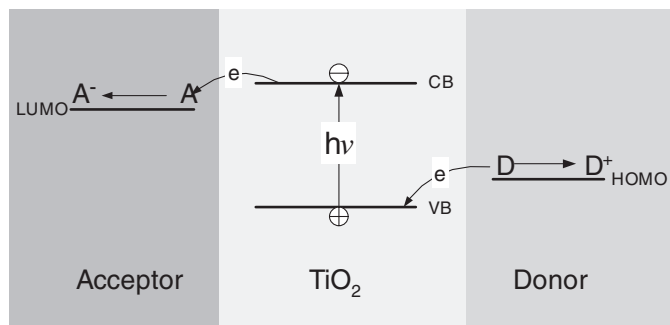
Fig. 1. Illustration of an electron transfer process with TiO$_2$.

suitable for DSSC fabrication due to potential damage of other materials in the photovoltaic device. In addition, the thermal polymerization is rather slow for realistic applicability. When the diacetylene is *in situ* polymerized under UV light in the TiO$_2$ film, due to the strong absorption of TiO$_2$ in the short UV region, only the diacetylene monomers that are close to the top surface of the nanoporous TiO$_2$ film or within the UV penetration depth can be exposed and polymerized. Wegner et al. reported that some dyes could sensitize diacetylene polymerization into the visible (23, 24). The dye molecules either form a crystal complex with diacetylene monomers or are incorporated into diacetylene Langmuir-Blodgett multilayers. For the phenazine-sensitized polymerization of amphiphilic carboxylated diacetylenes, it has been established that the reaction is induced by hole injection from the excited phenazine to the diacetylene monomer (25).

We have recently demonstrated that an amphiphilic carboxylated diacetylene can be *in situ* topochemically polymerized within nanoporous TiO$_2$ films under violet-blue light irradiation (26). The carboxylic acid groups are known to bind to titania and are in close proximity. In the present work, experimental investigation of the photopolymerization mechanism was carried out with the carboxylic acid containing diacetylene monomer and compared to similar studies with a diacetylene monomer without a carboxylic acid group. The photopolymerization was carried out within nanoporous TiO$_2$ structures using visible light. It is believed that under visible light irradiation, nc-TiO$_2$ is first excited and the polymerization is subsequently initiated through electron transfer from the diacetylene monomer to the excited TiO$_2$. Since the electron-transfer process occurs near the surfaces of nc-TiO$_2$, the photopolymerization seems to be initiated in close proximity to the nc-TiO$_2$ particles. The morphological study of the PDA/TiO$_2$ nanocomposite clearly showed that the monomers were photopolymerized over the surface of the TiO$_2$ nanoparticles. Further studies on the photopolymerization of the carboxylated diacetylene monomer with ZnO and SiO$_2$ nanoparticles were also carried out.

2 Experimental

Two diacetylene monomers were used in the present study. 10,12-Pentacosadiynoic acid (PCDA) was purchased from GFS Chemicals, and 2,4-hexadiyne-1,6-bis(carbazolyl) (DCH) was provided by Professor Sandman at the University of Massachusetts Lowell. The chemical structures of the monomers along with the illustration of the solid-state polymerization of the diacetylenes by the 1,4-addition mechanism are shown in Figure 2. PCDA is an amphiphilic diacetylene with two asymmetric side groups, consisting of a 12-C alkyl chain and a COOH-terminated 8-C chain. The carboxylic acid group is expected to attach the monomer onto the TiO$_2$ surface via covalent linkage. However, the DCH monomer does not contain the carboxylic acid group and has two symmetric carbazole side groups. TiO$_2$ (P25, average particle size of 25 nm), ZnO and SiO$_2$ nanoparticles were acquired from Degussa, Aldrich and Nanophase, respectively. Fluorine-doped tin oxide coated glass substrates (FTO; sheet resistance: 15 Ω/sq) were purchased from Hartford Glass Co. Inc.

Nanoporous TiO$_2$ films, about 3 μm thick, were made by spin-coating nc-TiO$_2$ paste onto FTO substrates. The nc-TiO$_2$ paste was prepared following the procedure described by Nazeeruddin et al. (15). The nanoporous TiO$_2$ films were sintered at 450°C for 30 min. The diacetylene monomers were then added into the TiO$_2$ films at room temperature by drop-casting from solutions of PCDA (40 mg/ml) and DCH (15 mg/ml) in tetrahydrofuran (THF), respectively. The monomer containing TiO$_2$ films were covered with glass dishes and dried under ambient conditions. The remaining solvent was further removed under vacuum at 35°C for 1 h. During the drying process, the composite films were covered with aluminum foil to avoid light exposure. Polymerization was then carried out by exposing the monomer-containing composite films to a monochromatic light beam at 415 nm. As control, diacetylene monomers
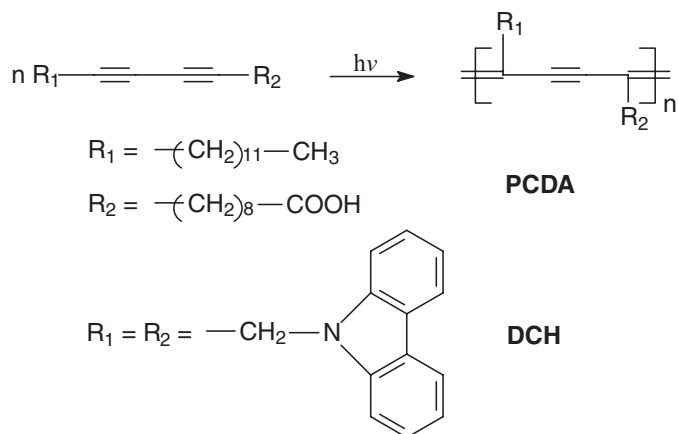

Fig. 2. Solid-state polymerization of diacetylene and chemical structures of the diacetylenes.

were drop-cast onto glass slides and then polymerized by shining with UV at 254 nm (UV-254). In addition to TiO_2, two other types of nanoparticles, ZnO and SiO_2, were used to test the photopolymerization of PCDA. TiO_2, ZnO and SiO_2 nanoparticles were first loaded into 250-μL plastic pipettes, and the PCDA monomer solution was then injected into the nano-powders. After drying under vacuum, the photoreaction was performed by visible light illumination at 423 nm.

UV-Vis absorption spectra were measured with a spectrometer (Perkin-Elmer/Lambda-9). Raman spectra for PCDA, poly(PCDA) by UV-254 exposure, and poly(PCDA)/TiO_2 nanocomposite by 415-nm exposure were collected with a Raman spectrometer (Lambda Solutions/Dimension-P2; excited at 785 nm). Raman spectrum for poly(DCH)/TiO_2 nanocomposite by 415-nm exposure was detected with a Raman system (Ocean Optics/R-3000; excited at 785 nm). Morphology of the nanocomposite was characterized by scanning electron microscopy (JEOL/JSM-7401F).

3 Results and Discussion

Figure 3 shows the UV-Vis absorption spectra of PCDA in THF, poly(PCDA) on a glass slide (UV-254 irradiated), poly(PCDA) within a nanoporous TiO_2 film (415-nm irradiated). The PCDA monomer in THF exhibits absorption below 300 nm with a peak absorption around 250 nm. Under UV-254 irradiation, the drop-cast PCDA film turned blue which is indication of the polymerization. But the monochromatic light (at 415 nm) irradiated PCDA film did not show any color change. However, when the PCDA/TiO_2 film was irradiated at 415-nm, the blue-

Fig. 4. Raman spectra of PCDA (solid line), poly(PCDA) by UV-254 exposure (dashed line), and poly(PCDA) inside a nanoporous TiO_2 film by 415-nm exposure (dotted line).

color signature of the polymerization was clearly observed. Poly(PCDA) (UV-254 irradiated) exhibits the characteristic absorption of PDA in the visible region with an absorption peak at ~645 nm and a vibronic side peak at the shorter wavelength. Similarly, the PCDA monomer irradiated by 415-nm light in the presence of nc-TiO_2 also shows the characteristic absorption of PDA.

The Raman spectra of PCDA, poly(PCDA) prepared on a glass slide by UV-254 illumination, and poly(PCDA) *in situ* prepared within a nanoporous TiO_2 film by exposure to 415-nm light are shown in Figure 4. The PCDA monomer shows a C≡C stretching vibration band at 2255 cm^{-1}. The poly(PCDA) polymer prepared on the glass slide by UV-254 irradiation exhibits the characteristic PDA Raman bands at 2074 cm^{-1} and 1450 cm^{-1}, corresponding to the C≡C and C=C stretching vibrations of the PDA polymer backbone, respectively. In comparison, the 415-nm light treated PCDA in the presence of nc-TiO_2 also shows the similar characteristic PDA Raman bands. Both the UV-Vis and Raman spectroscopic studies indicate that the PCDA monomer can be polymerized in the nanoporous TiO_2 film by visible light irradiation.

The DCH monomer was also investigated for the photopolymerization. Solid-state polymerization of thick DCH samples is usually induced by γ-ray radiation to achieve complete and uniform polymerization (27). Figure 5 shows the UV-Vis absorption spectra of DCH in THF and poly(DCH) within a nanoporous TiO_2 film (415-nm exposure). The DCH monomer in THF exhibits multiple absorption peaks below 350 nm. Among them, the three peaks between 280–340 nm are attributed to the carbazole side groups. In the presence of nc-TiO_2, the DCH film irradiated with monochromatic light at 415 nm shows the
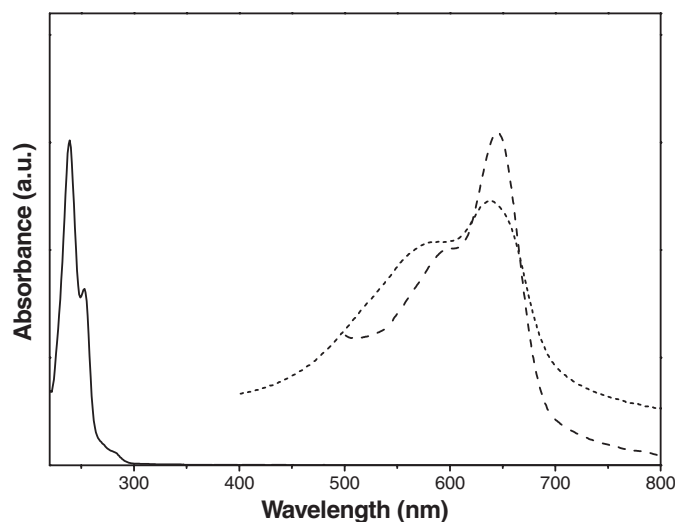
Fig. 3. UV-Vis absorption spectra of PCDA in THF (solid line), poly(PCDA) by UV-254 exposure (dashed line), and poly(PCDA) within a nanoporous TiO_2 film by 415-nm exposure (dotted line).
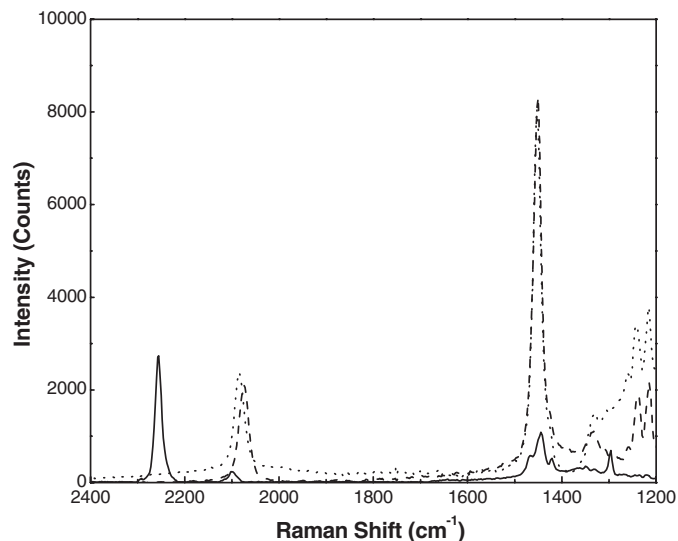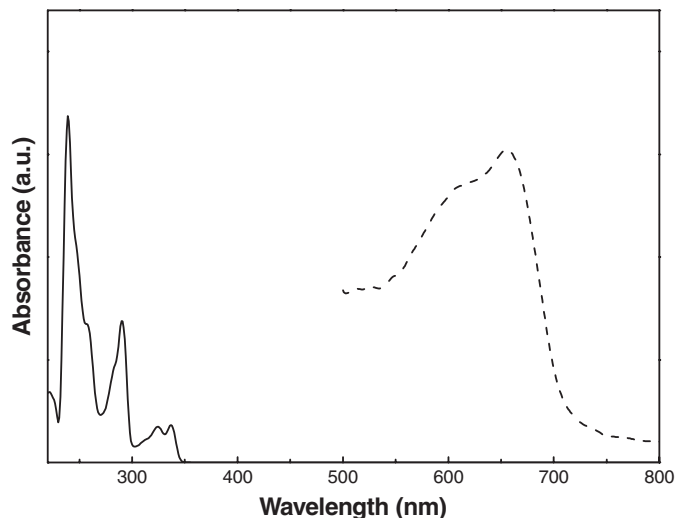
Fig. 5. UV-Vis absorption spectra of DCH in THF (solid line) and poly(DCH) within a nanoporous TiO_2 film by 415-nm exposure (dashed line).

characteristic absorption spectrum of PDA with an absorption peak around 654 nm and a broad vibronic side peak at the shorter wavelength. However, the 415-nm light irradiated drop-cast DCH film exhibits no characteristic absorption of poly(DCH).

The Raman spectrum of poly(DCH)/TiO_2 nanocomposite was also measured. The polymer/TiO_2 composite shows the characteristic Raman spectra of poly(DCH) (27). As shown in Figure 6, the Raman band assigned to the $C\equiv C$ stretch of poly(DCH) at 2094 cm^{-1} was clearly observed. The Raman shifts at 1420, 1447, and 1463 cm^{-1} are attributed to the Fermi resonance (28) that involves the
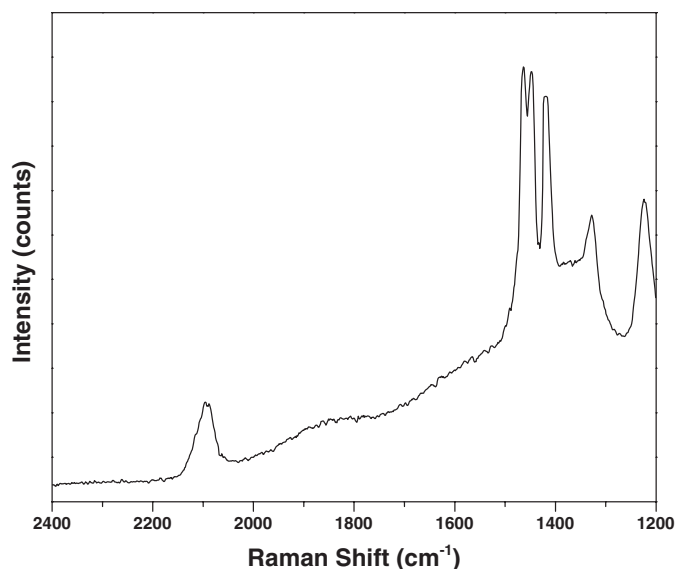
$C=C$ bond, the carbazole side group, and the methylene unit of poly(DCH). These results showed that the DCH monomer can also be polymerized within nc-TiO_2 structures by visible light, suggesting that the covalent linkage to the nanoparticle through –COOH of the monomer is not required.

It is the excitation of the monomer that initiates the reaction during the solid-state photopolymerization of diacetylene (22). Since the diacetylene monomers do not absorb in the visible region, the observed polymerization of PCDA and DCH by 415-nm irradiation can only be attributed to the photocatalytic or photosensitization effect of TiO_2. The Degussa P25 nc-TiO_2 powders consists of both anatase phase ($\sim$70%) and rutile phase ($\sim$30%) TiO_2. The bandgap excitation is approximately at 400 nm and 420 nm for anatase and rutile, respectively (29). The irradiation at 415 nm may create carriers (electrons and holes) in TiO_2 either due to interband excitation or excitation to or from defect states in the band gap (30). Based on the energy levels of TiO_2(31) and a diacetylene (32)as sketched in Figure 7, it is believed that upon photoexcitation, the hole created in TiO_2 grabs an electron from the HOMO of the diacetylene monomer and the cationic radicals thus formed, initiates the polymerization process.

The morphology of the poly(PCDA)/nc-TiO_2 nanocomposite was investigated by SEM. Figure 8 shows the SEM images of a nanoporous TiO_2 film and a THF-rinsed poly(PCDA)/nc-TiO_2 composite film. The typical morphology of the nc-TiO_2 film with an average TiO_2 particle size of $\sim$25 nm is shown in Figure 8a. Since the TiO_2-sensitized photopolymerization of diacetylene involves electron transfer at the diacetylene/TiO_2interface, it is anticipated that the polymerization occurs at the surfaces of the TiO_2 nanoparticles and propagates away from

Fig. 6. Raman spectrum of poly(DCH) within a nanoporous TiO_2 film by 415-nm exposure.
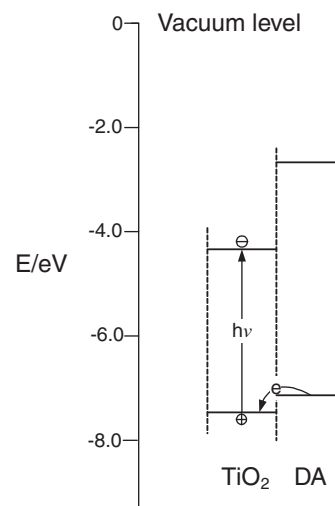

Fig. 7. Schematics of photosensitized polymerization of diacetylene with nc-TiO_2.
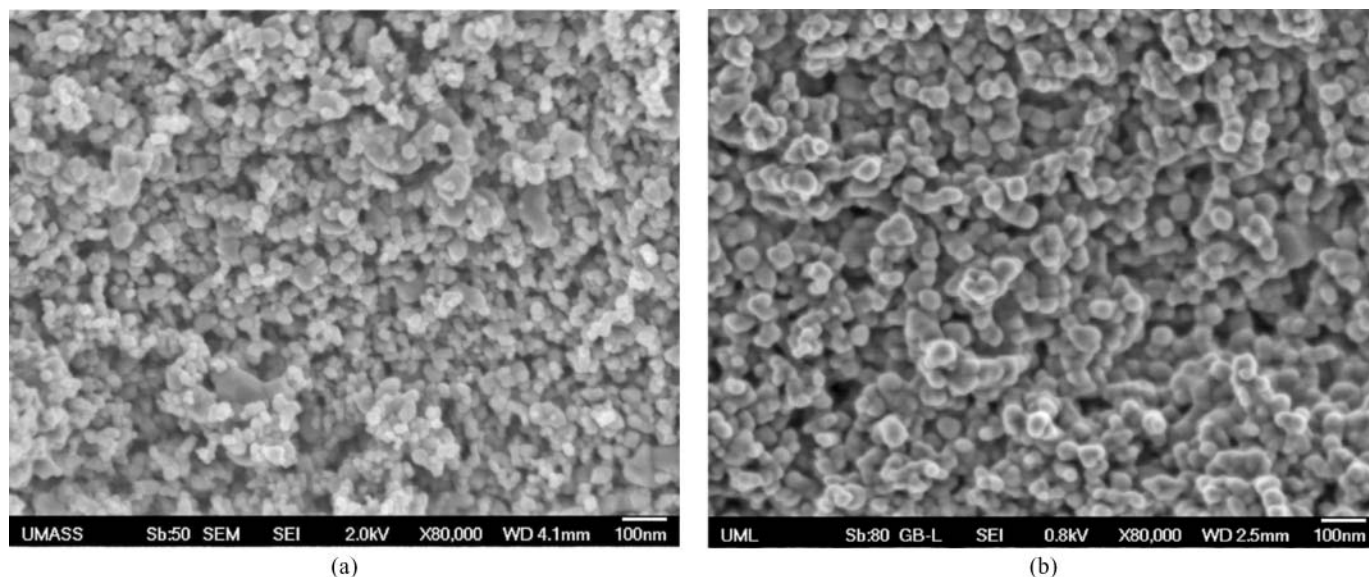
Fig. 8. SEM cross-sectional views of an nc-TiO₂ film (a) and a THF-rinsed poly(PCDA)/nc-TiO₂ composite film (b).

the TiO_2 nano-particles. The diacetylene monomers too far from the interfaces might not be polymerized under the experimental condition. The poly(PCDA) polymer is insoluble in THF, therefore, rinsing with THF removes the unpolymerized monomers and leaves the polymerized PCDA on the TiO_2 nanoparticles. Compared to the SEM image of the P25 TiO_2 nanoparticles, the feature size of the PDA/TiO_2 nanocomposite as shown in Figure 8b is about 40 nm. This 15-nm size increase can be attributed to the poly(PCDA) formed around the nc-TiO_2 particles. It is noted that the poly(PCDA)/TiO_2 composites undergoes a blue-to-red transformation upon the THF treatment. This color change is believed to result from a phase transition involving reorganization within the side groups (22).

In addition to the TiO_2 nanoparticles, two other types of nanoparticles, ZnO and SiO_2, were used to study the photosensitization effect and ensure that it is not impurities or oligomers present induce polymerization. ZnO is also commonly used as a semiconductor for fabrication of organic solar cells. Bulk ZnO is a direct gap band semiconductor with a band-gap of $\sim$3.4 eV (33), corresponding to an absorption edge at $\sim$370 nm. SiO_2 has average band-gap energy of 8.9 eV (34), corresponding to an absorption edge at $\sim$140 nm. The photoreaction was carried out in three plastic pipettes with monochromatic light at 423 nm. With the same exposure time, the blue-color signature of the polymerization was clearly observed in the TiO_2 and ZnO containing pipets. The PDA formed in the presence of TiO_2 showed darker blue color compared to that with ZnO nanoparticles. This result further indicates that the photosensitized polymerization of diacetylenes in the visible region is due to the photoexcitation of the nanoparticles. The nc-TiO_2 has stronger absorption in the violet part of visible spectrum than ZnO. Even though bulk ZnO has

an absorption edge at $\sim$370 nm, ZnO nanoparticles may have surface and bulk defects that could lead to a weak absorption tail into the violet. On the other hand, SiO_2 nano-particles could not sensitize the polymerization under the above conditions most likely due to its large band gap.

4 Conclusions

We have investigated the photosensitized solid-state polymerization of two diacetylene monomers with/without the carboxylic acid group inside TiO_2 nanostructures by visible light irradiation. The experimental results showed that both monomers can be photopolymerized in the presence of nc-TiO_2, indicating that the covalent linkage of the monomer to the nanoparticle is not required. It is believed that under visible light irradiation TiO_2 is first excited and the polymerization is then initiated through electron transfer from the diacetylene monomer to the excited TiO_2 at the interface. The morphology of the polydiacetylene/nc-TiO_2 nanocomposite clearly indicated that the polymerization is originated near the nc-TiO_2 surface. This could be attributed to the fact that the electron-transfer process occurs at the interface of nc-TiO_2 and diacetylene. Since visible light can transmit through the entire nanoporous TiO_2, it is possible to obtain uniform polymerization of diacetylene inside the TiO_2 nanopores. Photopolymerization of the carboxylated diacetylene monomer using ZnO nanoparticles was also achieved. This enhanced polymerization of diacetylenes by visible light may provide a new approach toward fabrication of polydiacetylene/TiO_2 or ZnO nanocomposites and further development of optoelectronic devices. Polymerization of conjugated polymers

in nanostructured semiconductors are of great importance as sensitizers and as hole conductors for organic solar cell applications.

Acknowledgments

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