

FORMATION OF TiO₂/POLYDIACETYLENE NANOCOMPOSITE BY PHOTSENSITIZED SOLID-STATE POLYMERIZATION

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Introduction

Polydiacetylene (PDA) possesses a fully conjugated backbone in the crystalline state and has tailorable side groups and functionalities.¹ The charge carrier mobilities of crystalline PDA are almost 4 orders of magnitude higher than those of partially crystalline or amorphous conjugated polymers.² PDA can be structured in the form of bulk material, mono- and multi-layered films³, and even incorporated into inorganic host matrices to form nanocomposites⁴. PDA has been used as an active material for fabricating organic field-effect transistors⁵ and in-situ polymerized diacetylene by UV light in nanoporous TiO₂ films has been used as a hole-transporter in solid-state dye-sensitized solar cells (DSSC).⁶

Polymerization of diacetylene is a lattice controlled topochemical solid-state reaction. It is commonly accomplished by exposure to UV irradiation ($\lambda < 300$ nm) or γ -radiation. In some cases thermally generated phonons are sufficient to induce the polymerization.^{7,8} However, these approaches pose some limitation regarding an efficient polymerization for practical applications. For example, the γ -ray and high-temperature treatments are not suitable for DSSC fabrication due to potential damage of other materials in the device. For the in-situ polymerized diacetylene with UV light at 254 nm in a TiO₂ film, due to the strong absorption of TiO₂ at 254 nm, only the monomers that are within the UV penetration depth can be exposed and polymerized.

It was reported that styrene⁹, methyl methacrylate¹⁰ and pyrrole¹¹ can be polymerized via photogenerated cationic radicals on TiO₂ powders. We have recently demonstrated that diacetylene can also be polymerized within nanoporous TiO₂ films under visible light irradiation.¹² This enhanced polymerization of diacetylenes by visible light could provide a new approach toward fabrication of TiO₂/PDA nanocomposites and further development of optoelectronic devices. We will report on the experimental investigation of the photopolymerization and the morphological study of the nanocomposite.

Experimental

An amphiphilic diacetylene, 10,12-pentacosadiynoic acid (PCDA) was purchased from GFS Chemicals. The chemical structure of the monomer along with the scheme of the solid-state photopolymerization of the diacetylenes by the 1,4-addition mechanism are shown in Fig. 1. TiO₂ nanoparticles (P25) were acquired from Degussa. Fluorine-doped tin oxide coated glass substrates (FTO) were purchased from Hartford Glass Co. Inc.

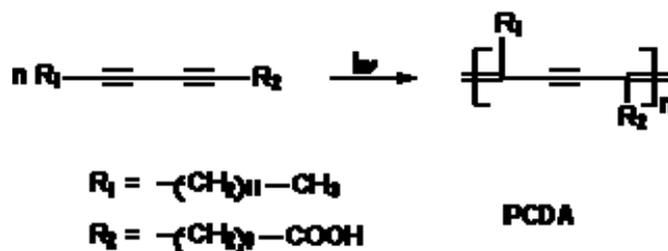


Fig. 1 Solid-state photopolymerization of diacetylene.

Nanoporous TiO₂ films about 3 μm thick were made onto FTO substrates by spin-coating TiO₂ paste which has been reported elsewhere¹³. The TiO₂ films were sintered at 450°C (30 min). The monomer was then added into the TiO₂ films at room temperature by drop-casting from PCDA solution (40 mg/ml) in tetrahydrofuran (THF). The TiO₂/PCDA films were dried under ambient conditions. The remaining solvent was removed under vacuum (35°C/1 hour). Polymerization was carried out by exposing the TiO₂/PCDA films at 415 nm. As a control, the monomer was drop-cast onto glass slides and then polymerized at 254 nm.

UV-Vis absorption spectra were measured with a spectrometer (Perkin-Elmer/Lambda-9). Raman spectra were collected with a Raman spectrometer (Lambda Solutions/Dimension-P2; excited at 785 nm). Morphology of the nanocomposite was characterized by scanning electron microscopy (JEOL/JSM-7401F).

Results and Discussion

Fig. 2 shows the UV-Vis absorption spectra of the monomer and polymers. The PCDA monomer in THF exhibits absorption below 300 nm with a peak absorption around 250 nm. When exposed to UV-254 irradiation, the PCDA film turned blue with a golden luster; but with monochromatic light at 415 nm, the irradiated PCDA film did not show any color change. However, when the TiO₂/PCDA film was irradiated at 415 nm, the blue-color which is the indication 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 TiO₂/poly(PCDA) nanocomposite by 415-nm irradiation also shows the characteristic absorption of PDA.

The Raman spectra of the monomer and polymers are shown in Fig. 3. The PCDA monomer shows a C \equiv C stretching vibration band at 2255 cm^{-1} . The poly(PCDA) polymer prepared on the glass slide by UV-254 irradiation exhibits the characteristic Raman bands at 2074 cm^{-1} and

1450 cm^{-1} , corresponding to the $\text{C}\equiv\text{C}$ and $\text{C}=\text{C}$ stretching vibrations of the PDA polymer backbone, respectively. In comparison, the 415-nm light treated PCDA in the nanoporous TiO_2 films also shows the similar characteristic Raman bands.

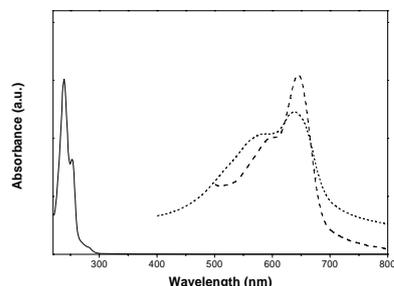


Fig. 2 UV-Vis absorption spectra of PCDA in THF (solid), poly(PCDA) by UV-254 exposure (dashed), and poly(PCDA) within a nanoporous TiO_2 film by 415-nm exposure (dotted).

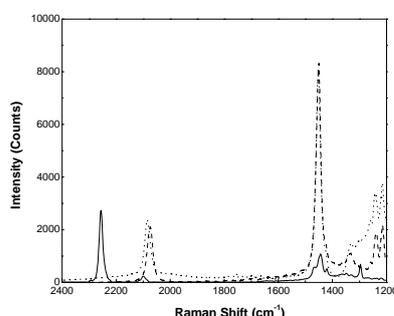


Fig. 3 Raman spectra of PCDA (solid), poly(PCDA) by UV-254 exposure (dashed), and poly(PCDA) inside a nanoporous TiO_2 film by 415-nm exposure (dotted).

It is the excitation of the monomer that initiates the reaction during the solid-state photopolymerization of diacetylene.⁸ Since the diacetylene monomer does not absorb in the visible region, the observed polymerization of PCDA by 415-nm irradiation can only be attributed to the photocatalytic or photosensitization effect of TiO_2 . 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.¹⁴ 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.

Fig. 4 shows the SEM images of a nanoporous TiO_2 film and a TiO_2 /poly(PCDA) nanocomposite film. The typical morphology of the TiO_2 film with an average particle size of ~ 25 nm is shown in Fig. 4a. Since the TiO_2 -sensitized photopolymerization of diacetylene involves electron transfer at the diacetylene/ TiO_2 interface, it is anticipated that the polymerization starts on the surfaces of the nanoparticles and propagates away from the nanoparticles. However, monomer that is too far from the interface might not be polymerized under the experimental conditions. The poly(PCDA) is insoluble in THF, therefore rinsing with THF removes the unpolymerized monomers and leaves the

PCDA polymer on the TiO_2 nanoparticles. Compared to the SEM image of the P25 TiO_2 nanoparticles, the feature size of the TiO_2 /poly(PCDA) nanocomposite as shown in Fig. 4b is about 40 nm. This 15-nm size increase can be attributed to the poly(PCDA) formed around the TiO_2 nanoparticles.

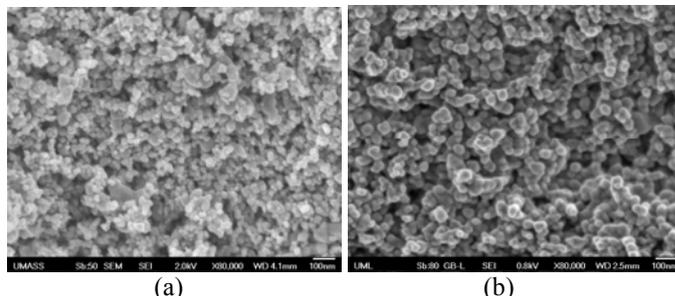


Fig. 4 SEM cross-sectional views of a TiO_2 film (a) and a TiO_2 /poly(PCDA) nanocomposite film (b).

Conclusions

Photosensitized solid-state polymerization of a diacetylene monomer within TiO_2 nanocomposite films under visible light irradiation was investigated. Both UV-vis and Raman studies confirmed the TiO_2 assisted photosensitized polymerization. The morphology of the TiO_2 /PDA nanocomposite clearly indicated that the polymerization originates near the TiO_2 surface. The TiO_2 /PDA nanocomposites would offer a new approach to the development of optoelectronics.

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