

Nanocrystalline TiO₂-Catalyzed Solid-State Polymerization of Diacetylene in the Visible Region

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Polydiacetylenes (PDAs) constitute a unique class of macromolecules that combine highly ordered and conjugated backbones with tailorable pendant side groups and terminal functionalities.¹ PDAs are prepared via topochemical solid-state polymerization. They are typically crystalline with high charge carrier mobilities that are approximately 10³ larger than those of partially crystalline or amorphous conjugated polymers.² In our prior studies, in-situ polymerized carboxylated diacetylenes were used for hole transport in dye-sensitized nanocrystalline TiO₂ solar cells (DSSCs).^{3,4} One major advantage of this method is that by being able to first add the small monomer species and then carry out in-situ solid-state polymerization, more polymer molecules can be ultimately integrated into the nanoporous TiO₂ structure.

TiO₂ is a well-known wide band gap semiconductor. In addition to working as a photoelectrode for electron collection in DSSCs,^{5,6} nanocrystalline (nc) TiO₂ has been extensively studied as a photocatalyst for environmental applications such as water purification, wastewater treatment, hazardous waste control, and air purification.⁷ TiO₂ is excited by photons with energy equal to or greater than the band gap ($E_g = 3.2$ eV for anatase and $E_g = 3.0$ eV for rutile⁸), and then undergoes electron transfer and/or energy transfer to the adsorbed species, leading to chemical reactions in the heterogeneous photocatalysis process.⁹

Solid-state polymerization of diacetylenes is commonly accomplished by irradiation with short wavelength UV or high-energy radiation with γ -ray or by thermal treatment below their melting point.¹⁰ γ -Ray and high-temperature treatment is not suitable for device fabrication because of potential damage of other integrated materials or components. At lower temperatures, the polymerization is extremely slow and can take days. In preparation of PDA/TiO₂ nanocomposites, TiO₂ absorbs strongly in the short UV region. This strong absorption limits penetration of the UV irradiation through the entire nanoporous TiO₂ film, and thus only diacetylene monomers that are close to the top surface or within the UV penetration depth can be exposed and polymerized.

To optimize the in-situ polymerization of diacetylenes in our DSSC devices, we investigated the polymerization of an amphiphilic diacetylene within nanoporous TiO₂ films under visible light irradiation. The results demonstrated a significantly enhanced polymerization of the diacetylene monomer under these conditions. This surprising enhancement is believed to be facilitated by the inherent surface photocatalytic behavior of TiO₂ when exposed to visible light.

Several 3- μ m thick nanoporous TiO₂ films (Degussa P25) were spin-coated onto fluorine-doped tin oxide coated glass substrates (FTO; only used for the purpose of device fabrication). After sintering at 450 °C for 30 min, the diacetylene monomer, 10,12-pentacosadiynoic acid (DA-3261; GFS Chemicals), was added into

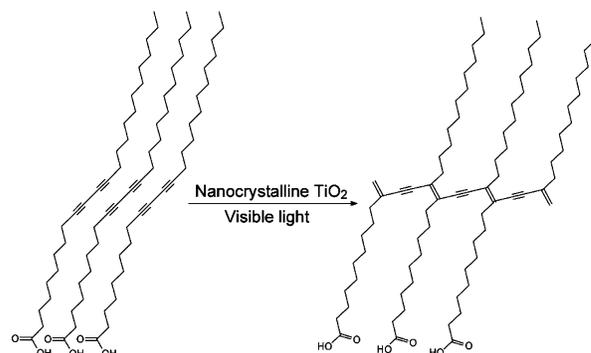


Figure 1. Solid-state polymerization of DA-3261.

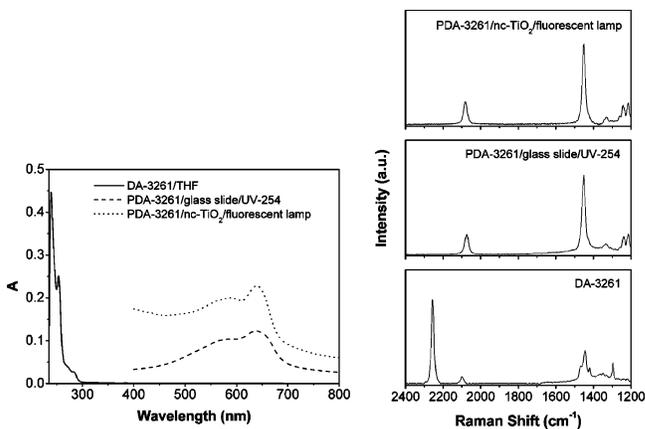


Figure 2. UV-vis absorption spectra (left) and Raman spectra (right) of DA-3261, PDA-3261 on a glass slide (UV-254 exposure), and PDA-3261 inside a nanoporous TiO₂ film (exposure by fluorescent lamp).

the nanoporous TiO₂ films by solution drop-casting from tetrahydrofuran (THF; 0.05 M). The polymerization was carried out by exposing the DA-3261/TiO₂ nanocomposites to fluorescent lamps (Sylvania Octron 4100K; 0.3 mW/cm²) and a series of monochromatic light within the fluorescent lighting spectrum.

Figure 1 shows the schematic solid-state polymerization of DA-3261 by the well-known 1,4-addition mechanism.¹¹ The DA-3261 monomer has two unsymmetric side groups, one of which is terminated with a carboxylic acid group for covalent attachment of the DA-3261 monomer to the TiO₂ surface.^{6,8}

As a control, the DA-3261 monomer was drop-cast on a glass slide from THF and then exposed to UV irradiation at 254 nm (UV-254). The polymerized DA-3261 film on the glass slide appeared blue with a golden luster. Under exposure by fluorescent lamp, the DA-3261 monomer deposited within the nanoporous TiO₂ film also turned blue. Figure 2 shows the UV-vis absorption spectra of the DA-3261 in THF, PDA-3261 on the glass slide (exposure by UV-254), and PDA-3261 within the nanoporous TiO₂ film (exposure by fluorescent lamp). The two absorption spectra of PDA-3261 are

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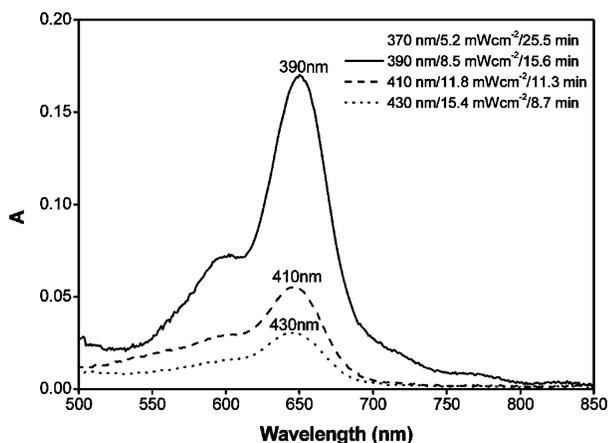


Figure 3. UV-vis absorption spectra of PDA-3261 in-situ polymerized within nanoporous TiO₂ films at different wavelengths.

not corrected for light scattering. The monomer in THF exhibits absorption below 350 nm with the peak absorption at ~ 250 nm. The monomer on the glass slide irradiated by UV-254 shows the characteristic absorption of PDAs in the visible region with an absorption peak at ~ 640 nm and a vibronic peak at the shorter wavelength.¹² The monomer within the nanoporous TiO₂ film irradiated by fluorescent lamp shows a similar absorption to that of the UV-254 polymerized DA-3261 on the glass slide.

Figure 2 also shows the Raman spectra of the DA-3261 monomer, PDA-3261 prepared on a glass slide by UV-254 treatment, and PDA-3261 in-situ prepared within a nanoporous TiO₂ film by fluorescent lamp illumination. The monomer DA-3261 shows a C \equiv C stretching vibration band at 2255 cm⁻¹. The PDA-3261 prepared on the glass slide under UV-254 illumination shows the characteristic Raman vibrational bands at 2074 and 1450 cm⁻¹, corresponding to the C \equiv C and C=C stretching vibrations of the polymer backbone, respectively. In comparison, the fluorescent lamp treated DA-3261 in the presence of nc-TiO₂ exhibits quite similar vibrational bands to those of the UV-254 treated DA-3261 on the glass slide.

Both the UV-vis and Raman spectroscopic studies clearly indicate that the DA-3261 monomer within the nanoporous TiO₂ film can be polymerized under fluorescent lamps. To determine the specific wavelength that facilitated the polymerization, the spectrum of the fluorescent lamp was characterized. The following emission lines are present below 450 nm: 319 nm (very weak), 367 nm (very weak), 404 nm (weak), 407 nm (very weak), and 433 nm (medium). A control experiment using a series of cutoff filters was conducted. It was confirmed that under fluorescent lamp illumination, wavelengths larger than 450 nm could not induce the polymerization of the DA-3261 monomer within the nanoporous TiO₂ film. Monochromatic light ($\Delta\lambda \approx 10$ nm) at 370, 390, 410, and 430 nm was then used to irradiate the DA-3261/TiO₂ nanocomposite films. Irradiation time was determined to provide the same energy exposure dosage.

It can be seen from Figure 3 that the 390-nm light shows the strongest effect on the polymerization of DA-3261 in the presence of nc-TiO₂, while the 430-nm light shows the weakest effect. The 370-nm light exhibited a different behavior and will be discussed later. Since there is no measurable absorption of the DA-3261 monomer at wavelengths larger than 350 nm, these results strongly suggest that TiO₂ plays a catalyst-like role in the solid-state polymerization of DA-3261 in the irradiation range of 390–430 nm. It is known that the Degussa P25 TiO₂ powder is a mixture of anatase ($\sim 70\%$) and rutile ($\sim 30\%$). Bulk TiO₂ has well-defined band gaps, corresponding to an absorption edge of ~ 400 nm for

anatase and ~ 420 nm for rutile,⁸ whereas TiO₂ nanoparticles have defect states which lead to an absorption tail into the violet-blue part of the spectrum. Therefore, the absorption of nc-TiO₂ is strong at 390 nm compared to 410 and 430 nm, resulting in the faster polymerization. By contrast, the slow polymerization at 430 nm can be attributed to the weak absorption of nc-TiO₂ in the absorption tail region. We propose that a photocatalytic process occurs at the TiO₂ surface after excitation even though the initiation mechanism of the polymerization is not understood yet at this time.

We also observed that the DA-3261 polymerization inside TiO₂ nanopores showed intensity dependence when irradiated at 370 nm or shorter wavelengths. Using the irradiation dosage shown in Figure 3, the 370-nm irradiated DA-3261/nc-TiO₂ area was completely bleached. Even if the exposure time was shortened by $\sim 75\%$, the obvious bleaching could still be seen. On the other hand, when the light intensity was reduced by $\sim 75\%$, the blue color signature of the polymerization was observed. Similar results were also observed at 350 nm. However, such bleaching was not observed at 390, 410, or 430 nm. It seems that upon excitation of TiO₂ by light at 370 nm and shorter wavelengths the DA-3261 monomer may have undergone two simultaneous, competitive processes: polymerization and photodegradation. The latter is consistent with the role of TiO₂ in waste disposal. These two processes probably depend on the photon energy and/or photon flux to some extent. The detailed mechanism is under investigation.

In summary, we have observed and investigated the visible light induced solid-state polymerization of DA-3261 in nanostructured TiO₂. This observation can be attributed to the photocatalytic effect of TiO₂ upon absorption of irradiation. Since visible light can be transmitted through the entire nanoporous TiO₂ film, it is possible to obtain complete polymerization of DA-3261 inside the TiO₂ nanopores, and this provides an approach toward fabrication of PDA/TiO₂ nanocomposite structures. This first demonstration of enhanced polymerization of diacetylene under visible light in the presence of TiO₂ may open up new possibilities for development of optoelectronic devices.

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Supporting Information Available: SEM image of the nanoporous TiO₂ film. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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