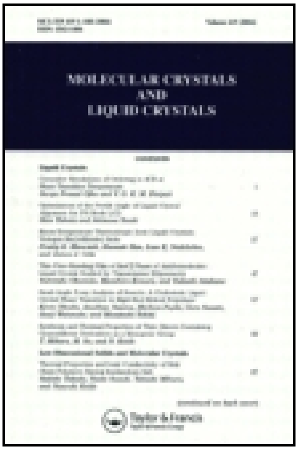

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Preparation of Polydiacetylene-Attached TiO_2 Nanoparticles

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Polydiacetylene-attached titania nanoparticles were synthesized by the reaction with 10,12-pentacosadiynoic acid (PDA). The surface of titania nanoparticles was modified with a silane coupling agent, 3-aminopropyltrimethoxy silane (APTMS). 10,12-Pentacosadiynoic acid (PDA) was also modified by the esterification of N-hydroxy-succinimide (HS) with 4-pyrrolidinopyridine as a catalyst. The modified PDA (HS-PDA) was attached to titania by the reaction between modified TiO_2*nanoparticles and HS-PDA. Products were purified and then further polymerized by the photochemical 1,4-addition reaction. These PDA-attached* TiO_2 *nanoparticles were characterized with NMR, IR and thermogravimetry (TG).*

Keywords: chemosensor; nanoparticles; polydiacetylene; titania

INTRODUCTION

Polydiacetylenes (PDAs) have received much attention due to their excellent material characteristics based on the strong optical absorption and fluorescence emission which vary with various stimuli, including temperature, pH, ions, solvent, stress, or ligand interactions [1]. These compounds contain the extended π-electron delocalization along the conjugated polymer backbones and their optical absorption occurs *via* π-to-π^* transition within the backbones [2]. Unpolymerized

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PDAs do not absorb visible light, whereas the absorption maximum of polymerized PDAs appears blue. The chromogeneic transition of polymerized PDAs is related with a significant shift from blue to red color which involves a shift in absorption from low to high energy bands of visible spectrum [3].

The sensor devices of PDA in the form of vesicle, liposome, thin film, and nanocomposite have been synthesized. Recent progress has been made on the immobilization of self-assembling PDAs on the various nano-engineered materials by exploring the well-defined surface and architecture [4]. Recently, it has been reported that PDA/silica nanocomposite thin films were with tunable mesostructure and reversible chromatic transition were synthesized using a simple sol-gel assembling process. It was also reported that the self-assembly of conjugated polymer/silica nanocomposite films with hexagonal, cubic or lamellar mesoscopic order was induced by using polymerizable amphiphilic diacetylene molecules as both structure-directing agents and monomers [5,6].

Here, we report the immobilization of PDA onto the surface of nanosized titania particles. Titania has attracted a great deal of recent attention, due to their application in catalysis, photovoltaics and photoelectronics. Titania-coated particles are very useful as catalyst, white pigment and electrophoretic particle.

EXPERIMENTAL

Materials

3-Aminopropyl-trimethoxysilane (APTMS, 97%), ammonia(2.0M solution in ethanol), N-hydroxy succinimide(HS, 98%), 4-pyrrolidinopyridine(98%), and N,N'-dicyclohexyl-carbodiimide (DCC, 99%) were purchased from Aldrich and used without further purification. Chloroform was purchased from Aldrich and distilled prior to its use. Nanometer-sized TiO_2 was used as received. 10,12-Pentacosadiynoic acid (PCDA) was purchased from GFS Chemicals.

TiO_2 Surface Modification with Coupling Agent

Dried TiO_2, silane coupling agent (3-aminopropyltrimethoxy silane, APTMS) were mixed in THF. Then, H_2O and NH_3 were added as catalysts. The mixed solution was stirred for 10 min and then dispersed for additional 15 min by an ultrasonic disintegrator. The reaction was completed after 48 hrs at room temperature.

Synthesis of N-hydroxysuccinimidyl-pentacosadiynoic Ester (HS-PDA)

10,12-Pentacosadiynoic acid (PCDA) was dissolved in acetone and then purified by filtration through a filter paper. Acetone remained in the sample was evaporated at room temperature. The purified PCDA was dissolved in a mixed solvent of THF/methylene chloride (MC) (vol. fraction of 1:1). N-Hydroxysuccinimide (HS) and 4-pyrrolidinopyridine were then added in the solution as catalysts, and the mixture was cooled to 0°C in an ice bath. DCC, dissolved in MC, were added dropwise. The mixture was stirred overnight, and the precipitated urea was filtered off and the solvent was evaporated. The product HS-PDA was isolated by column chromatography (silica, $CHCl_3$:MeOH = 29:1).

PDA-Attached Modified TiO_2 Nanoparticles

Several drops of triethylamine were added to a solution of HS-PDA in chloroform (analytical grade, anhydrous). Modified TiO_2 nanoparticles were dispersed in chloroform and added in the HSI-PDA solution while stirring. The mixture was stirred 3∼4 hrs. The solvent and amine were evaporated and the residue was dissolved in chloroform and extracted with water. Then, chloroform was evaporated and the sample was dried at room temperature.

Characterization of TiO_2/PDA Nanohybrides

Thermogravimetric analysis (TGA) was carried out with a Thermal Analysis Q50, under nitrogen over a temperature range from 25°C to 700°C at a scan rate of 20°C/min. ^1H NMR spectra were recorded on a Varian Unityinova 400 spectrometer at 400 MHz and were referenced to TMS. The solid state ^1H CP/MAS NMR spectra were also measured at 400 MHz Varian Unityinova 400 spectrometer with a sample spinning rate of 5 kHz at room temperature. Fourier Transform Infrared Spectra of the samples in KBr pellets were recorded on a S-2000 (Perkin Elmer) at room temperature.

RESULTS AND DISCUSSION

Most inorganic dioxide nanoparticles including titania contain free hydroxyl groups on their surface, and methoxy or ethoxy groups of APTMS readily react with these hydroxyl groups on the inorganic particle surfaces. We successfully demonstrated the modification of

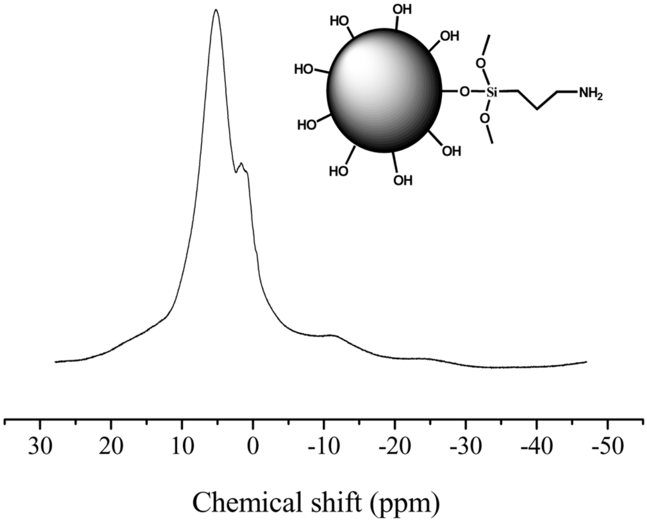


FIGURE 1 Solid state NMR data of the titania nanoparticles, modified by APTMS.

titania by using APTMS, as show in the solid state NMR data measured from the APTMS modified titania nanoparticles. In Figure 1, we found the peaks at 5.13 ppm and 1.66 ppm for $-NH_2$ and methylene groups of APTMS, respectively, confirming the successful attachment of APTMS on titania nanoparticles. A peak near -10 ppm appeared due to the hydroxyl groups on titania. The weakness of the peak arose from the reduced, relative concentration of $-OH$ unit after modification.

10,12-Pentacosadiynoic acid (PDA) was also modified by the esterification of N-hydroxy-succinimide (HS) with 4-pyrrolidinopyridine as a catalyst. The modification of PDA with HS and the chemical structure of HS-PDA were confirmed by ^{1}H-NMR data (Fig. 2) in $CDCl_3$. The modified PDA (HS-PDA) was attached to titania by the reaction between modified TiO_2nanoparticles and HS-PDA. Figure 3 shows the solid state NMR data of the PDA-attached titania nanoparticles. In this figure, we found peaks at $\sim$13 ppm and 1.66 ppm which appeared due to the NH groups and methylene group of APTMS after the reaction with HS-PDA. The peaks at 1.24, 0.84, -0.05 ppm were from the methylene group of diacetylene and the peak at -0.476 ppm was from the methyl group of diacetylene. These data confirmed that HS-PDA was successfully intercalated onto the surface of the modified titania surfaces.

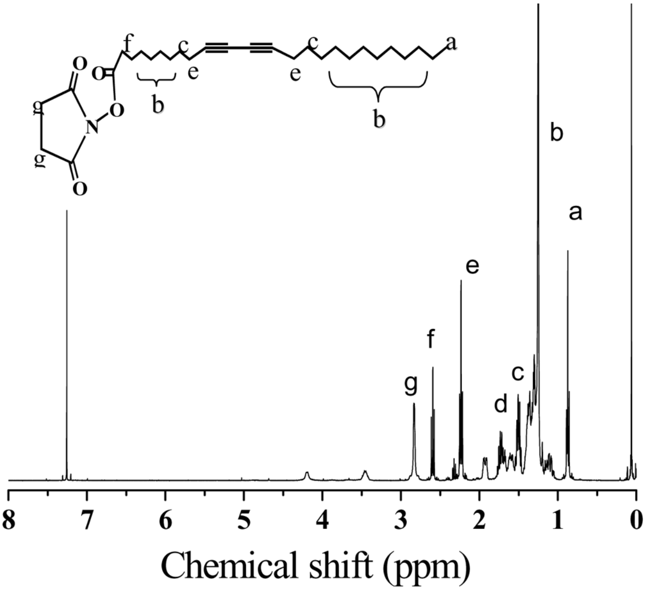


FIGURE 2 ^{1}H NMR of HS-PDA in $CDCl_3$.

TGA was also used to confirm the intercalation of HS-PDA onto the surfaces of titania nanoparticles. Figure 4 (a) showed the TGA data of PDA-attached titania nanoparticles, measured during heating in the temperature range between room temperature to 750℃. In these data,

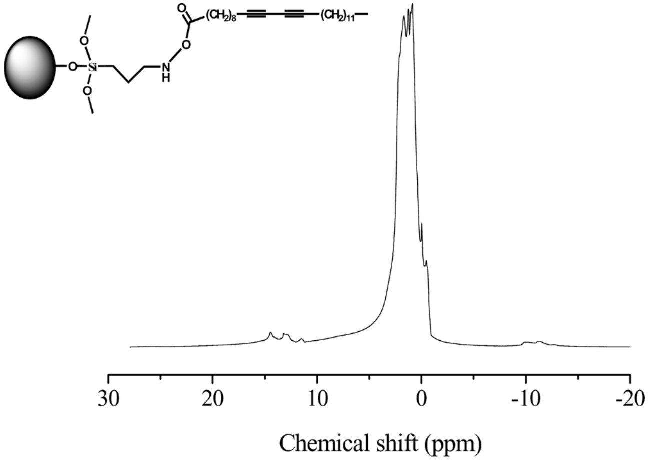


FIGURE 3 Solid state NMR data of the PDA-attached titania nanoparticles.

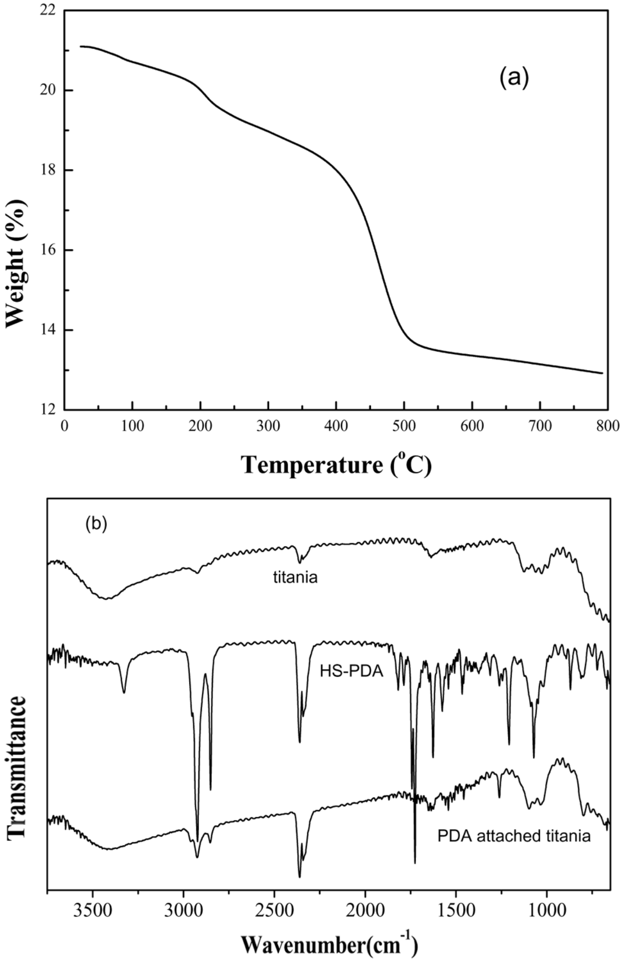
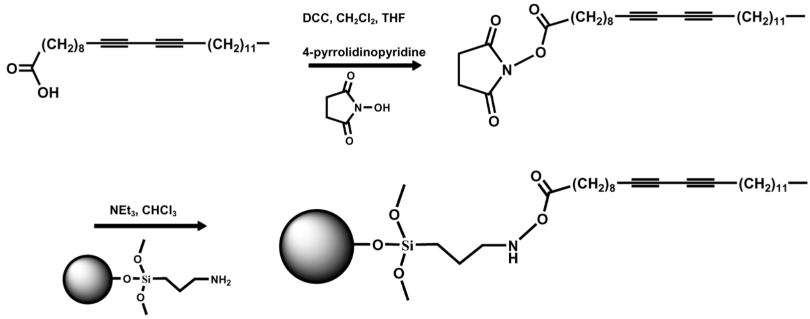


FIGURE 4 (a) TGA data of the PDA-attached titania nanoparticles; (b) FTIR data of the neat titania nanoparticles (top); HS-PDA (middle); and the PDA-attached titania nanoparticles (bottom).

we found a series of weight losses near 180°C and 450°C because of thermal decompositions of the PDA units and the coupled silane moieties attached on the titania surfaces. Figure 4 (b) showed the FTIR data of titania nanoparticles (top); HS-PDA (middle) and PDA-attached titania (bottom). In the FTIR data of PDA-attached titania, we found the peaks from the PDA moiety, indicating the successful attachment of PDA units onto the surface of titania nanoparticles.



SCHEME 1 Synthetic route of PDA-attached TiO$_2$ nanoparticles.

The schematic description of the synthesis of PDA-attached titania nanoparticles was shown in Scheme 1.

CONCLUSIONS

We successfully demonstrated the synthesis of PDA attached TiO$_2$ nanoparticles through a facile reaction pathway. The surfaces of neat titania were treated by a silane coupling agent and further reacted with the esterified PDA to obtain the final product. The solid state NMR data were used to confirm the chemical structures of the titania particles with the modified surfaces. The TGA and FTIR data were also used to confirm the intercalation of the PDA units on the modified titania surface. Because of nontoxicity of TiO$_2$ and sensing capability of PDA, PDA attached TiO$_2$ nanoparticles may be potentially useful for biosensing applications.

REFERENCES

[1] Geiger, E., Hug, P., & Keller, B. (2002). *Macromol. Chem. Phys.*, *203*, 2422.
[2] Okada, S., Peng, S., Spevak, W., & Charych, D. (1998). *Acc. Chem. Res.*, *31*, 229.
[3] Jelinek, R. (2000). *Drug. Develop. Res.*, *50*, 497.
[4] Kim, J. M., Lee, J. S., Choi, H., Sohn, D. W., & Ahn, D. J. (2005). *Macromolecules*, *38*, 9366.
[5] Errien, N., Vellutini, L., Froyer, G., Louarn, G., Simos, C., Skarka, V., Haesaert, S., & Joubert, P. (2005). *Phys. Stat. Sol.*, *9*, 3218.
[6] Mammeri, F., Bourhis, E. L., Rozes, L., & Sanchez, C. (2006). *J. Eur. Ceram. Soc.*, *26*, 259.