

Synthesis and Characterization of Soluble Polyaniline and TiO₂ Composite

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ABSTRACT: Soluble polyaniline was synthesized by attaching titanium isopropoxide (Ti(OPr)₃) to the amine group of the aniline. Approximately 1 to 1 molar ratio of aniline and Ti(OPr)₃ was mixed and polymerized with ammonium persulfate. The FTIR result showed clear difference between TiO₂-aniline composite (TiO₂An) and TiO₂-polyaniline composite (TiO₂PAn). Although the TiO₂An had negligible UV-visible absorption, the TiO₂PAn showed strong absorption in the UV-visible region. Photoluminescence (PL) peaks of TiO₂An were shifted toward red with the reduction of the excitation energy, which could be due to the multiple emission centers. The luminescence peak shift stopped at 501 nm. The PL spectra of TiO₂PAn exhibited three emission peaks at 2.88 eV (430 nm), 2.48 eV (501 nm) and 2.22 eV (558 nm). The new emission center (2.22 eV) was observed after polymerization. Field emission scanning electron microscope image showed crack-free composite film.

Key words: Soluble polyaniline, TiO₂, Composite, Photoluminescence

1. Introduction

Titanium dioxide (TiO₂) has been a great deal of research subject during the last decades due to the unusual structural, optical, magnetic and chemical properties. As a result, TiO₂ has been developed enhanced device applications including gas sensors¹, photoluminescence (PL) devices², energy efficient windows³, photocatalysts⁴, water and air purification systems⁵, UV protection creams⁶, and dye-sensitized solar cells⁷. Composites of inorganic metal oxides and organic conducting polymers have been considerable interest in research and development of various application fields. Nano- or micro-structures of TiO₂ and conducting polymers, such as polyaniline (PAn), polypyrrole (PPy), polythiophene, poly(3, 4-ethylenedioxythiophene) (PEDOT), and their derivatives have been shown promising for application devices including sensors, biosensors, electrochromic devices, and rectification diodes.

Many researchers have been investigated the preparation of TiO₂-PEDOT⁸, TiO₂-PPy^{8,9}, and nano-TiO₂-PAn¹⁰⁻¹². Among the conjugate polymers, PAn is one of the most important conducting polymers. It has been extensively investigated for

various applications including corrosion protections¹², transparent conductors¹³, sensors¹⁴, battery applications¹⁵, active electrodes¹⁶, rechargeable batteries¹⁷, and electrochromic displays¹⁸. Although the PAn has large variety of application fields, the major drawback of PAn is its insolubility in common solvents and its infusibility at elevated temperature, which makes poor processability. However, alkyl substitution to the aromatic ring of the aniline largely enhances its solubility. Only a few investigations of mono- or di-substituted PAn have been reported. Conductive core-shell microparticles with thin PAn layer have been fabricated in the presence of colloidal core particles. We report the synthetic process of soluble PAn with TiO₂ and the characteristics of TiO₂ and PAn composite including FTIR, UV-visible spectra, photoluminescence, and field emission scanning electron microscope (FESEM) image.

2. Experimental

2.1 Materials

Titaniumisopropoxide (Ti(OPr)₃, 97%), aniline (An, 99.5%), acetic anhydride (98%), and 2-propanol (99.5%) were purchased from Sigma Aldrich Co. Ltd. and used without further purification.

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Received July 21, 2015; Revised July 24, 2015;

Accepted July 29, 2015

2.2 Synthesis

Schematic view of the synthetic process is depicted in Fig. 1. To the 100 ml of round bottom flask with a magnetic stirring bar, 25 ml of 2-propanol, and 1 ml of aniline were added, and then 4 ml of $\text{Ti}(\text{OPr})_4$ was added to the flask. Finally, 1.2 ml of acetic anhydride was added to the flask and stirred at room temperature. Finally, the aniline and $\text{Ti}(\text{OPr})_4$ composite was polymerized by adding ammonium persulfate (TiO_2PAn).

2.3 Measurements

The TiO_2An or TiO_2PAn was directly dropped, dried to a KBr plate, and obtained FTIR transmission spectra using Nicolet iS5 FTIR spectrometer. Approximately 7 ml of methanol was added to a UV-visible cuvette, and added TiO_2An or TiO_2PAn to the cuvette, and obtained UV-visible spectra using Thermo Scientific Genesys 10S UV-visible spectrometer. PL spectra of TiO_2An or TiO_2PAn were obtained with Hitachi F-450 fluorescence spectrometer with the methanol- TiO_2An or methanol TiO_2PAn solution. The polymerized TiO_2PAn was spin-coated on a silicon wafer, and the FESEM image was obtained with field emission scanning microscope (JEOL ISM-7401F).

3. Results and Discussion

Heterostructures comprised of organic conducting polymers and inorganic oxides have been discovered an extensive interest in research and development for many practical applications with nono- and micro structures of TiO_2 and PAn. Since the $\text{Ti}(\text{OPr})_4$ is very quickly hydrolyzed by trace of water to form $\text{Ti}(\text{OH})_4$ and precipitate from the solution, many researchers have used diethanolamine as a stabilizer for $\text{Ti}(\text{OPr})_4$. The aniline was used as a stabilizer for $\text{Ti}(\text{OPr})_4$ instead of diethanolamine

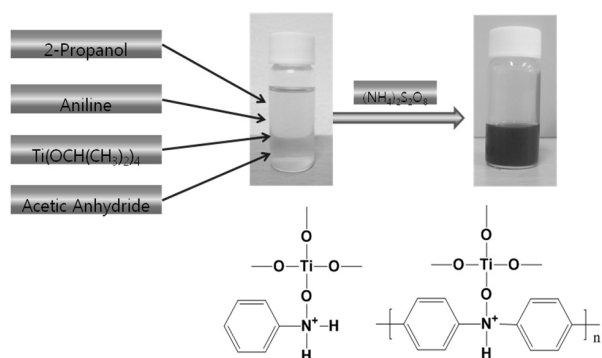


Fig. 1. Schematic representation of the synthetic processes of TiO_2An and TiO_2PAn

and used as a polymer backbone. Schematic view of synthetic processes is shown in Fig. 1. The synthesized TiO_2An color slowly changed from intense yellow to dark after addition of ammonium persulfate as shown in Fig. 1.

Fig. 2(a) and 2(b) show the FTIR spectra of TiO_2An and TiO_2PAn , respectively. The sharp and strong absorption peak at 3259 cm^{-1} is due to the $-\text{N}-\text{H}$ stretching vibration for TiO_2An . The absorptions peaks at 3070, 3038, 2974, 2929, 1600, 1555, 1540, 1498 cm^{-1} are attributed to $-\text{CH}$ stretching vibration. The absorption peaks at 1618, 1600, 1478 and 1437 cm^{-1} were observed due to the ring stretching vibration of the aniline. The bending vibrations of $-\text{CH}$ bonds are appeared at 1174, 1153, 1122 and 997 cm^{-1} . Deformations of $-\text{CH}$ bonds are at 905 and 752 cm^{-1} . The absorption peaks at 1663 and 1264 cm^{-1} represent the $\text{C}=\text{C}$ stretching vibration of the benzene ring and $\text{C}-\text{N}$ stretching vibration, respectively. The absorption peaks at 1026 and 662 cm^{-1} are due to the stretching vibration of $\text{Ti}-\text{O}-\text{Ti}$. Additional new peaks of $-\text{N}-\text{H}$ stretching vibration appear at 3263, 3194, and 3084 cm^{-1} after polymerization. Most of the absorption peaks of the TiO_2PAn are slightly shifted toward higher frequency, which implies that the polymerized molecule has more rigid structure than TiO_2An .

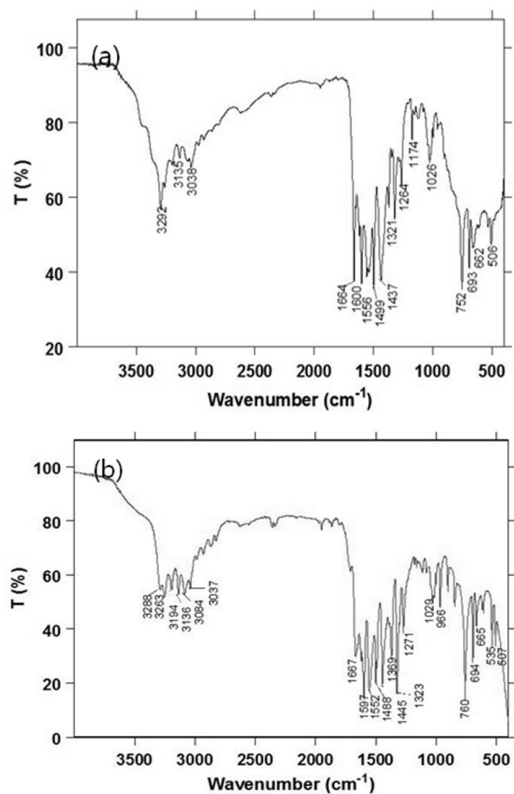


Fig. 2. FTIR spectra of (a) TiO_2An and (b) TiO_2PAn

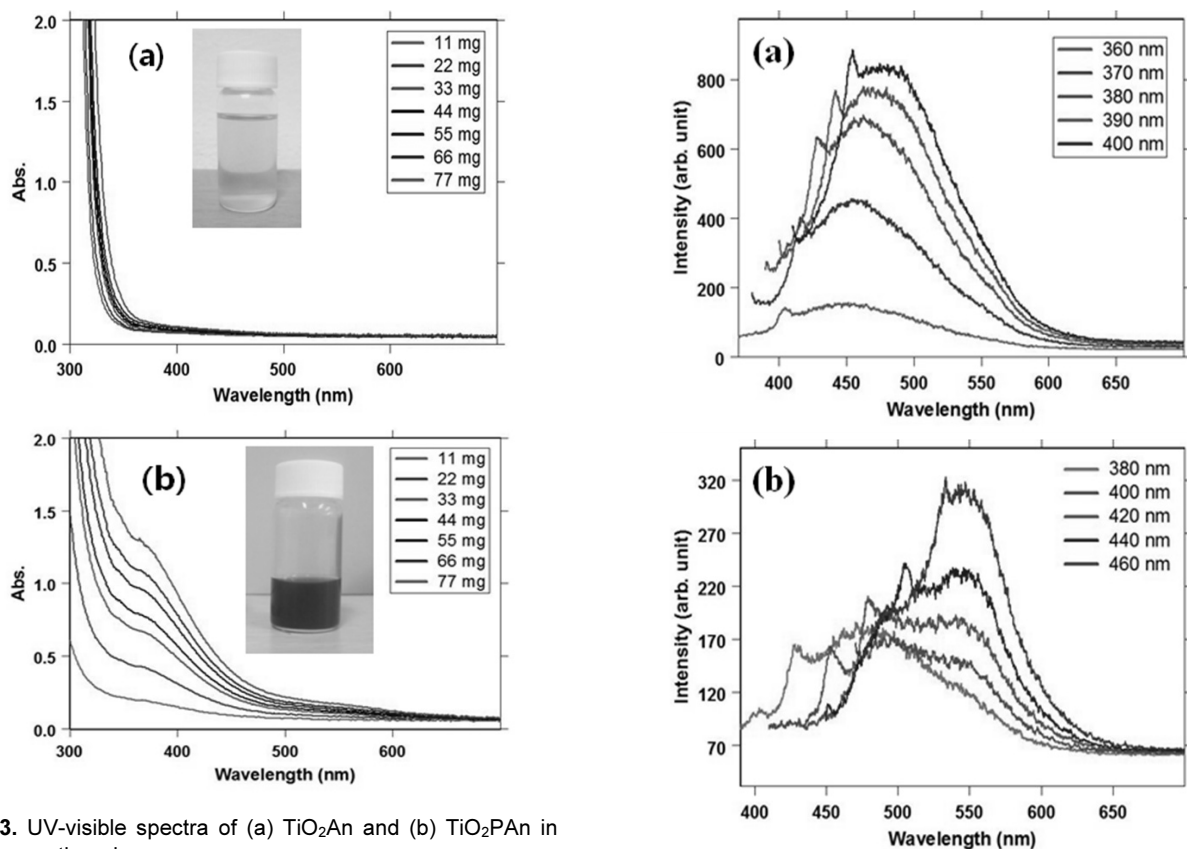


Fig. 3. UV-visible spectra of (a) TiO_2An and (b) TiO_2PAN in methanol

The colors of TiO_2An and TiO_2PAN are intense yellow and dark green, respectively, and the UV-visible spectra of various amounts of TiO_2An and TiO_2PAN in methanol are shown in Fig. 3 (a) and (b), respectively. Visible range absorption is negligible for TiO_2An with the increase of the amount of TiO_2An . However, UV-visible range absorption is drastically increased with increasing the amount of TiO_2PAN . The absorption peak obtained by UV-visible differential absorption spectrum with 77 mg of TiO_2PAN was at 365 nm.

Since the luminescence process competes with nonradiative process and exciton dissociation, the PL quenching is closely related with the degree of exciton dissociation and nonradiative process. Therefore, large amount of PL quenching indicates the possible success of solar cell development¹⁹⁾. The PL spectra in methanol for TiO_2An and TiO_2PAN with various excitation wavelengths are shown in Fig. 4 (a) and (b), respectively. The emission bands are at around 450 ~ 470 nm for TiO_2An with the excitation wavelengths between 360 to 400 nm. The emission peak is at around 490 nm for TiO_2PAN with the short excitation wavelengths (380 ~ 400 nm). However, when the excitation wavelengths increase, the second emission band becomes major emission band at 540 nm, which corresponds to the long tail of

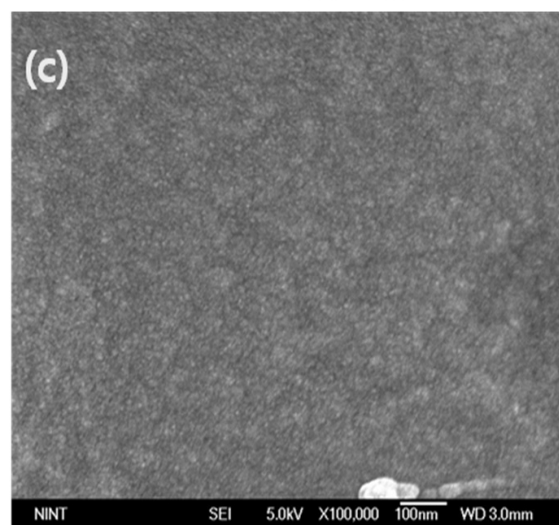


Fig. 4. PL spectra of (a) TiO_2An and (b) TiO_2PAN , (c) FESEM image of a TiO_2PAN film

the absorption band. Compared with the emission intensities of TiO_2An and TiO_2PAN , TiO_2PAN intensity is much less than the emission intensity of TiO_2An , which implies that the charge separation process is preferred process than emission process for the TiO_2PAN . The TiO_2PAN film was fabricated to the silicon wafer to identify the polymer film. Fig. 4 (c) shows the FESEM image of the TiO_2PAN film with a crack-free.

4. Conclusions

A soluble PAN and TiO₂ composite was fabricated by adding 2-propanol, aniline, Ti(OPr)₄, acetic anhydride and ammonium persulfate. The aniline was used as a stabilizer for Ti(OPr)₄. The PAN with Ti-OH became a soluble conjugate polymer in 2-propanol. The FTIR spectrum TiO₂PAN showed more complicate and rigid structure than that of TiO₂An. Although the UV-visible absorption of TiO₂An is negligible, the UV-visible absorption of TiO₂PAN is greatly increased. The luminescence peak shifted toward longer wavelength with increasing the excitation wavelength for both TiO₂An and TiO₂PAN due to the multiple emission centers. The emission intensity of the TiO₂PAN was much less than that of TiO₂An, which indicated that the charge separation process of the exciton was preferred process for the TiO₂PAN.

Acknowledgments

This work has been supported by Kyungil University in Korea.

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