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Effect of excess amount of aniline for TiO_2 and polyaniline composite

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ABSTRACT

Polyaniline and TiO_2 composite was fabricated with excess molar ratio of aniline (10 mol) against titaniumisopropoxide ($Ti(OPr)_4$) (3.3 mol) to find out the effect of an excess amount of aniline after polymerization. The composite was separated with soluble top layer (TPTOP) and insoluble bottom layer (TPBOT). FTIR spectra of TPBOT and TPTOP showed no clear difference. However, energy dispersive X-ray spectra (EDS) showed that the titanium weight ratios are 19.51 and 9.28 wt.% for TPTOP and TPBOT, respectively. Although field emission scanning electron microscope (FESEM) image of TPTOP film showed smooth surface without particle, FESEM image of TPBOT film exhibited particular shape with a diameter of approximately 60 nm. Strong UV–vis absorption in the range of UV–vis region was observed with the increase of the amount of TiO2PAn. The photoluminescence (PL) peaks of both TPTOP and TPBOT shifted toward lower energy with increasing to the excitation wavelength, which indicated the existence of multiple luminescence centers. The PL intensities of TPTOP were much stronger than those of TPBOT, which implied that the higher ratio of polyaniline (less TiO_2) led conducting process instead of a luminescence process.

1. Introduction

Titanium dioxide (TiO_2) has been a great deal of research subjects during the last decades due to the unusual structural [1], optical [2], magnetic [3,4], and electrical [5] properties. As a result, TiO_2 has developed widely enhanced device applications including gas sensors [6], photoluminescence (PL) properties [7], energy efficient windows [8], photocatalysts [9], water and air purifications [10], UV protection creams [11], and dye-sensitized solar cells [12]. Composites of inorganic metal oxides and organic conducting polymers have been considerable interest in research and development of various application fields. Nano-/micro-structures of TiO_2 and conducting polymers, such as polyaniline, polypyrrole, polythiophene, poly(3, 4-ethylenedioxythiophere), and their derivatives have been shown promising for application devices including sensors [13], biosensors [14], electrochromic devices [15], and dye sensitized solar cells [16].

Many researchers have been investigated the preparation of TiO_2-PEDOT [17], TiO_2-PPy [17,18], and nano-TiO_2-PAn [19–21]. Among the conjugate polymers, polyaniline is one of the important conducting polymers. It has been extensively investigated for various applications including corrosion protections, transparent conductors, electrostatic protections, sensors, battery applications, active electrodes, electro-optic devices, anti-static coatings, rechargeable batteries, energy storages, redox micro-template, electromagnetic interference protections, and electrochromic displays. Although polyaniline has such a large variety of application fields, the major disadvantage of polyaniline is its insolubility in common solvents and its infusibility at an elevated temperature, which makes poor processibility. However, alkyl or amine substitution to the aromatic ring of the polyaniline chain largely enhances its solubility. Only a few investigations of mono- or di-substituted polyaniline have been reported. Conductive core-shell microparticles with thin polyaniline layers have been fabricated in the presence of colloidal core particles. We report synthetic method to fabricating soluble polyaniline and TiO_2 composite (TiO_2PAn) and characteristics of TiO_2 and polyaniline composite including FTIR spectra, UV–vis absorption spectra, energy dispersive X-ray spectroscopy (EDS), and field emission scanning electron microscope (FESEM) images and PL spectra.

2. Experimental

2.1. Materials

Titaniumisopropoxide ($Ti(Opr)_4$, 97%), aniline (99.5%), 2-propanol (99.5%), and ammonium persulfate (98%) were purchased from Sigma Aldrich CO. Ltd. and used without further purification.

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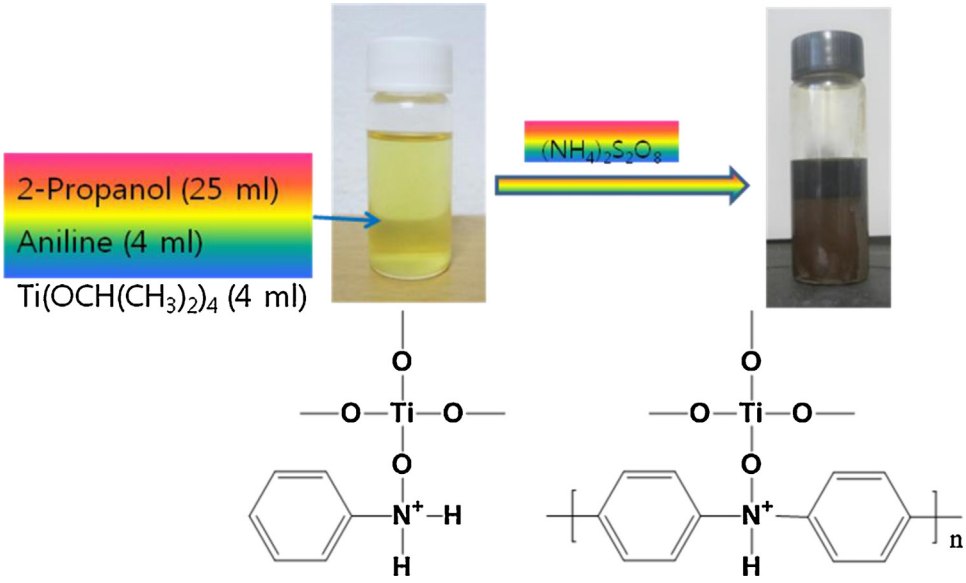

Fig. 1. Schematic representation of the synthetic process and possible chemical structures.

2.2. Synthesis

Schematic view of the synthetic process is depicted in Fig. 1. To the 100 ml of a round bottom flask with a magnetic stirring bar, 25 ml of 2-propanol, and 4 ml of aniline were added, and then 4 ml of $Ti(OPr)_4$ were added to the flask. Finally, 1.2 ml of acetic anhydride was added to the flask and stirred at room temperature. $Ti(OPr)_4$ and aniline composite was polymerized with ammonium persulfate (TiO_2PAn). The TiO_2PAn was centrifuged with the spinning rate of 1000 rpm for 60 s to separate the soluble top layer (TPTOP) and insoluble bottom layer (TPBOT).

2.3. Measurement

The TiO_2PAn was directly dropped and dried to a KBr plate. IR transmission spectrum was obtained with the KBr plate using Nicolet iS5 FTIR spectrometer. PL spectra of TiO_2PAn were obtained with Hitachi F-450 fluorescence spectrometer with the TPTOP or TPBOT with TiO_2PAn solution or solid. EDS spectra and FESEM images were obtained with field emission scanning electron microscope (JEOL ISM-7401F). Approximately 6 ml of methanol was filled in the UV–vis spectrometer cuvette and added various amounts of TiO_2PAn solution. UV–vis absorption spectra were obtained using Thermo Scientific Genesys 10S UV–vis spectrometer with the methanol solution.

3. Results and discussion

Heterostructures composed with inorganic oxides and organic conducting polymers have found an extensive interest in research and development for many practical applications. Since TiO_2 is one of the best photocatalyst and polyaniline is one of the best conducting polymers, TiO_2 and polyaniline composite is particularly interest with nano- and micro structures. The $Ti(OPr)_4$ are very quickly hydrolyzed and precipitated from the solution with trace of water. Therefore, many researchers use diethanolamine as a $Ti(OPr)_4$ stabilizer. In this research, aniline was used as a $Ti(OPr)_4$ stabilizer. Schematic view of synthetic processes is shown in Fig. 1. After addition ammonium persulfate, the solution color slowly changed to dark as shown in Fig. 1. The composite was separated two layers after one week; soluble layer on the top and insoluble layer on the bottom.

FTIR spectra of before and after acetic anhydride addition, before and after 2.5, 5, and 15 h ammonium persulfate additions are shown in Fig. 2(a)–(e), respectively. There are no big absorption peak change was observed after acetic anhydride addition. For the TiO_2PAn after ammonium persulfate addition, the absorption peaks at 3292 and 3135 cm^{-1} are due to the –N—H stretching vibration. The absorptions peaks at 3058, 2972, 2928, 1600 and 1556 cm^{-1} are attributed by —CH stretching vibration. The absorption peaks in 1667, 1600, 1478 and 1437 cm^{-1} represent the benzene ring stretching vibration. The bending vibration peak of —CH is appeared at 1122 cm^{-1}. Deformation peak of —CH is located at 753 cm^{-1}. The absorption peaks at 1021 and 665 cm^{-1} are due to the stretching vibration of Ti-O-Ti. Since the absorption peak positions between TPTOP and TPBOT are similar, it is difficult to identify the difference of the chemical compositions.

The colors of TPTOP and TPBOT are dark and brown, respectively, which indicate that the chemical composition would be different. Therefore, EDS analysis was performed. The compositions of TPTOP and TPBOT are shown in Table 1. The sulfur is from the catalyst (ammonium persulfate), which shows the chemical structure of ammonium persulfate on the bottom of Table 1. An ammonium persulfate has 8 oxygen atoms with two sulfur atoms. TPBOT has more oxygen and sulfur than TPTOP, which indicates that TPBOT has more polymerized chains than TPTOP. The amount of Ti of TPTOP has more than twice compared with that of TPBOT. This result shows that the TiO_2 increases the solubility of the polyaniline, and more than 19.5 wt.% of Ti requires to maintain soluble TiO_2PAn. Fig. 3(a) and (b) shows the FESEM images of TPTOP and TPBOT. Although TPTOP film has a smooth surface without particles, TPBOT film shows a particular shape with the diameter of approximately 60 nm. UV–vis absorption spectra with the various amounts of TiO_2PAn composite solution were shown in Fig. 4. The UV–vis range absorption drastically increased with the increase of the amount of the composite.

The PL quenching is closely related with the degree of exciton dissociation in a bulk heterojunction due to the luminescence process competes with nonradiative process and exciton dissociation. Therefore, a large amount of PL quenching indicates the