Synthesis and characterization of polyaniline nanofiber/TiO₂ nanoparticles hybrids

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The hybridization of polyaniline (PANI) and TiO₂ leads to unique materials, which exhibit the enhancement of photocatalytic properties. Further improvement requires high dispersion state of TiO₂ in the hybrid. In this study, highly dispersed PANI nanofiber/TiO₂ nanoparticles hybrids were obtained by modifying the surface charge of TiO₂ nanoparticles via layer by layer (LbL) technique. The structural studies of the hybrids confirmed the presence of PANI along with anatase TiO₂ nanoparticles. The degradation of methylene blue (MB) in an aqueous solution under visible light irradiation was carried out to study the photocatalytic activity of the hybrids. The hybridization of PANI nanofiber and TiO₂ nanoparticles resulted in an enhancement of photocatalytic activity for visible light.

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Key-words : Polyaniline nanofiber, Oxidation polymerization, Titania nanoparticle, Hybrid material, Photocatalytic property

[Received February 14, 2011; Accepted February 23, 2011]

1. Introduction

Hybrid materials of conducting polymer/inorganic nanoparticles with unique physical properties have attracted more attention. The combination of both materials with high level of dispersion at the nanoscale in the hybrid is considered to provide the best performance and expected to find applications in electrochemical devices, photoelectrochemical devices and non-linear optical systems.¹⁻⁵⁾

Polyaniline (PANI) draws much interest among the conducting polymers due to its ease of preparation, high conductivity, high chemical durability, and good environmental stability.⁶⁾ Conventional granular PANI powder was chemically synthesized from aniline by oxidative polymerization using ammonium peroxydisulfate (APS) in strong (sulfuric) and in weak (acetic) acids media.⁶⁾ However, PANI powder has a drawback concerning its process ability because it is hardly soluble in common solvents which are required in many applications. One of the recent solutions to this problem is to synthesize PANI as nanostructures. By reducing the polymerization rate using dilute concentration of aniline, PANI nanofibers and nanotubes were successfully acquired.⁷⁻¹⁰⁾ Nanostructures formed of conducting polymers receive great deal of attention due to the properties which differ from those of the coarse structures. The high conductivity and increasing surface area of conducting polymers make them an interesting material for sensor construction and gas storage.¹¹⁾ On the other hand, TiO₂ particles have been extensively studied and widely used in many applications including an effective photocatalyst. However, the band gap value of TiO₂ (3.2 eV) inhibits

the range of light source for photocatalytic reaction to only ultra violet (UV) light, it lowers the catalysis efficiency and limits the practical application.¹²⁾ One way to solve this setback is to use a sensitizer such as dyes with a narrow band gap.¹³⁾ PANI with 2.8 eV band gap is one type of the dye that can be used to enhance the catalysis efficiency of TiO₂. Polyaniline/TiO₂ nanohybrids have been successfully synthesized.¹³⁻¹⁷⁾ Furthermore, research works on obtaining good dispersion of TiO₂ nanoparticles in PANI matrix also have been extensively conducted based on ultrasonification.¹⁸⁾

In this study, we report a simple approach to obtain photocatalytic PANI nanofiber/TiO₂ nanoparticles hybrids. The flexible strategy to achieve high dispersion state of the hybrid is based on the surface charge by the layer-by-layer (LbL) self-assembly method.^{19,20)} By utilizing the electrostatic attraction between alternately deposited oppositely charged species, the surface charge of TiO₂ nanoparticles is modified to enhance the dispersion state of the hybrid during in situ polymerization of aniline. Following the surface charge modification of TiO₂ nanoparticles, PANI nanofiber was in situ prepared in hydrochloric acid solutions. The photocatalytic degradation of methylene blue (MB) dye with the resultant PANI nanofiber/TiO₂ nanoparticles hybrids was investigated.

2. Experimental

TiO₂ (AMT-600; TAYCA) nanoparticles were immersed to a poly(diallyldimethylammonium chloride) (PDDA; M_w 100,000–200,000; Sigma-Aldrich) solution with stirring for 10 min, followed by 10 min rinses in water to yield positively charged surfaces of the TiO₂ nanoparticles. The particles were then immersed to a poly(sodium 4-styrenesulfonate) (PSS; M_w 70,000; Sigma-Aldrich) solution with stirring for another 10 min, followed by 10 min rinses in water to yield negatively

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Table 1. ζ -potential data of LbL-modified TiO₂ nanoparticles and PANI nanofiber

Sample	ζ -potential (mV)
Initial TiO ₂ nanoparticles	-24.93
After PDDA-deposition	44.01
After PSS-deposition	-42.62
Initial PANI nanofiber	28.33

charged surfaces of the nanoparticles. The particles obtained were dried in an oven at 50°C for 12 h, and dispersed in the 1 M hydrochloric acid for 2 h with ultrasonic treatment. Afterwards, the TiO₂ suspension was mixed with 0.008 M concentration of aniline (Chameleon Reagent) for 24 h. The mole concentrations of aniline to dispersed TiO₂ were 20, 50, and 80%. Subsequently, the solution of ammonium peroxydisulfate (APS; Chameleon Reagent) was added by using a separatory funnel to the aniline/TiO₂ suspension in the beaker to perform in situ polymerization of aniline. At the end of polymerization, the dark-green precipitates were collected on a filter paper, rinsed with acetone and dried in an oven at 50°C for 12 h.

Surface charge measurements of LbL-modified TiO₂ nanoparticles were conducted using a ζ -potential analyzer (ELS-Z1NT, Photal Otsuka Electronic). The morphology of PANI/TiO₂ hybrid samples was observed with a field emission scanning electron microscope (FESEM, S-4800 Hitachi) and a transmission electron microscope (TEM, JEOL JEM-2100) recorded using RIGAKU RINT2000. Fourier transform infrared (FTIR) spectra of the samples were measured on a JASCO FT/IR-7300. The photocatalytic activities of the samples were evaluated by the degradation of MB in aqueous solution under the visible light exposure from metal halide lamp (HAYASHI LA-180Me; 3 mW/cm² at 405 nm) by cutting of the light below than 400 nm using a slide glass as an optical filter. Prior to irradiation, the samples were immersed in the MB solution and stirred first for 30 min in dark to saturate the MB adsorption. The remaining concentration of MB upon irradiation was characterized using a UV-visible spectrometer (UV-Vis, JASCO V-560).

3. Results and discussion

ζ -potential data of the LbL-modified nanoparticles are shown in **Table 1**. It is clearly seen that the surface charge of the TiO₂ particles was alternately changed by LbL assembly. The initial ζ -potential of TiO₂ nanofiber was -24.93 mV. After the deposition of PDDA polycation, the ζ -potential becomes +44.01 mV. Furthermore, upon the deposition of PSS polyanion, the surfaces of the nanoparticles were modified into more negatively charged particles with ζ -potential value of -42.62 mV. In contrast, the PANI nanofiber has a ζ -potential of 28.33 mV. Such a large difference in surface charge between PANI nanofiber and TiO₂ nanoparticles was expected to increase the electrostatic attraction force between the two hybrid components and to reduce the agglomeration rate of the nanoparticles.

Figure 1 shows the FESEM images of TiO₂ nanoparticles, PANI nanofiber/TiO₂ nanoparticles hybrids, and PANI nanofibers. The initial TiO₂ nanoparticles, with average size of 39 nm, were in agglomerated state [Fig. 1(a)]. At 20% PANI loading [Fig. 1(b)], the nanofibers, with diameter around 40–50 nm, wrapped the TiO₂ nanoparticles. By increasing the PANI loading to 50 and 80%, Figs. 1(c) and 1(d) respectively, the agglomerates of TiO₂ nanoparticles decreased and less PANI wrapped-TiO₂ nanoparticles were observed. Modification by LbL technique

Fig. 1. FESEM images of (a) TiO₂ nanoparticles, PANI-TiO₂ hybrids with (b) 20%, (c) 50%, (d) 80% PANI loading, and (e) PANI nanofibers. **Fig. 2.** FETEM images of PANI-TiO₂ nanohybrids with (a) 20% and (b) 80% PANI loading.

produced TiO₂ nanoparticles with more negative surface charge and hindered the attachment force between the particles under the presence of larger amounts of positively charged PANI. Such a phenomenon provides good attachment and high dispersion of TiO₂ nanoparticles in the positively charged PANI matrix.

Further analysis of the samples was conducted by FETEM. **Figure 2** shows the images of PANI nanofiber/TiO₂ nanoparticles hybrids with (a) 20% and (b) 80% PANI loading. Judging from the FESEM and FETEM data, it is seen that PANI not only has wrapped the TiO₂ nanoparticles, thin layer of PANI

Fig. 3. FTIR spectra of nanofiber PANI, nanoparticle TiO₂, and nanohybrid samples.

has also coated the TiO₂ nanoparticles. FETEM images could easily differentiate the crystalline TiO₂ nanoparticles with the amorphous PANI. The thickness of PANI coating layer was increased as the PANI loading increased. A thin layer of 3 nm PANI was observed on the hybrid with 20% PANI loading, whereas hybrid with 80% PANI loading provides PANI coating layer with thickness of 10 nm.

The FTIR measurements showed that the hybrid does not provide any new IR bands in comparison with the pure PANI sample (Fig. 3). The main bands observed at 1560 and 1474 cm⁻¹ are due to C–N stretching vibration of quinoid rings and C=C stretching vibration of benzenoid rings, respectively. The absorption bands at 1302 and 1245 cm⁻¹ are due to C–N stretching vibrations of secondary aromatic amine. The 1148 cm⁻¹ band can be assigned to a vibration mode of the –NH⁺= structure, which is formed by protonation. This –NH⁺= band in the hybrid is slightly shifted to lower wavenumbers and indicates the physical interaction between the positive sites (–NH⁺) present in the polymer chains and the negative sites present onto the surfaces of the modified TiO₂ nanoparticles.

Figure 4 shows the changes in MB concentration to indicate photocatalytic activities for visible light of PANI nanofiber, TiO₂ nanoparticles, and the PANI/TiO₂ hybrids. By introducing PANI to the TiO₂, photo degradation efficiency by visible light irradiation was enhanced. From the PANI/TiO₂ hybrids sample series, it was observed that 20% PANI loading is the optimum value to obtain a high efficiency. After 90 min of irradiation, the 20% PANI hybrid decomposed 30% of MB, whereas pure TiO₂ nanoparticles decomposed 15% of MB. A high PANI loading (50 and 80%) results in lower efficiency due to the roles of PANI which only acts as sensitizer for TiO₂ in photocatalytic reaction. Without sufficient amounts of TiO₂, the photocatalytic reaction will not efficiently decompose MB.

Fig. 4. Photocatalytic degradation of methylene blue by various PANI–TiO₂ hybrids with visible light irradiation.

Fig. 5. Mechanism of charge transfer during visible light irradiation of PANI–TiO₂ hybrids.

Under the irradiation of visible light, the MB was highly degraded by the PANI/TiO₂ hybrids compared with pure TiO₂ nanoparticles. The phenomenon of the MB degradation can be explained due to the charge transfer compatibility between TiO₂ and PANI.¹⁷⁾ As shown in Fig. 5, the PANI energy level π -orbital is located at higher electron energy state than the conduction band (CB) of TiO₂. The energy level π^* -orbital of PANI is located below the electron energy state of CB–TiO₂ and above the valence band (VB) of TiO₂.¹⁷⁾ As a result, during the visible light irradiation, PANI absorbs visible light to induce π – π^* transition, transporting the excited-state electrons to the π^* -orbital. The excited-state electrons could readily inject into the CB of TiO₂. Consequently, upon reaction with water and oxygen molecules, hydroxyl and superoxide radicals are expected to be formed and responsible for the enhancement degradation of the organic compound under visible light irradiation.¹³⁾ The function of PANI can be illustrated as an e^- injector into CB–TiO₂ conduction band under visible light irradiation which can trigger the formation of very reactive radicals.¹³⁾

4. Conclusions

Surface charge modification of TiO₂ nanoparticles via LbL technique method was conducted to obtain dispersed PANI nanofiber/TiO₂ nanoparticles hybrids. The structural studies of the hybrids confirmed the presence of amorphous PANI along with anatase TiO₂ nanoparticles. The degradation of MB in an aqueous solution under visible light irradiation was carried out and the hybrid samples performed high photocatalytic activity compared to the pure TiO₂ nanoparticles. Electrons supplied from PANI to valance band of TiO₂ along with a higher dispersion state of the hybrid are probably the main factor of the photocatalytic enhancement in the visible light region. After 90 min of irradiation, the 20% PANI/TiO₂ hybrid decomposed 30% MB in 10⁻⁵ M MB solution, although pure TiO₂ nanoparticles only decomposed 15% of MB in the solution.

Acknowledgements This work is partly supported by Japan Society for the Promotion of Science (JSPS) [Grant-in-Aid for Scientific Research (B)]. The authors are thankful to JSPS fellowship program, Toyohashi University of Technology in Japan and University of Tanta in Egypt. N.P. acknowledges ASEAN University Network/Southeast Asia Engineering Education Development Network (AUN/SEED-Net) and Japan International Cooperation Agency (JICA) for supporting his Ph.D. study at Toyohashi University of Technology.

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