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Photoluminescence of cellulose acetate and silica sphere composite



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ABSTRACT

Strong blue and green light emission has been observed from the cellulose acetate (CA) and silica sphere composite. Two different amounts of silica spheres were mixed in the CA solution to fabricate large area super-hydrophobic films. The silica spheres and CA solution ratios were 0.07:4.0 (SSCA-A) and 0.14:4.0 (SSCA-B). The milky color solution of SSCA-A and SSCA-B slowly turned to light yellow and red, respectively, with the time passed. The colors became intense yellow and red for the SSCA-A and SSCA-B, respectively, after 38 days. FTIR spectra show more absorption at 3478 cm^{-1} corresponding —OH stretching vibration, at 2963 cm^{-1} caused by —CH stretching vibration, at 1746 and 1713 cm^{-1} representing the C=O stretching vibration, and at 1100 cm^{-1} corresponding —R—OH and Si—O—Si stretching vibration for CA and silica. Therefore, aged SSCA-A and SSCA-B have more —OH , —CH , —C=O , and Si—O—Si groups than pure CA. UV-visible spectra show the absorption peaks at 410 nm for both SSCA-A and SSCA-B. Photoluminescence (PL) peaks were shifted toward longer wavelength with the increase of the excitation wavelength and became maximum at approximately 470 nm with excitation wavelength at 400 nm for the SSCA-A. There were two maximum luminescence peaks at 470 and 530 nm with the excitation wavelength at 400 and 470 nm , respectively, for the SSCA-B. The luminescence peak shift was due to the multiple emission center proved by the different excitation energy.

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1. Introduction

Polymer/inorganic composites have been focused on much attention as an interesting research subject due to their interesting physicochemical properties. Polymeric nanocomposites have been widely used in many industrial fields including catalysis [1], antibacterial agents [2], surface coatings [3], drug delivery [4], and enzyme immobilization [5]. Among the nanocomposites, cellulose and its derivatives have advantages, such as ubiquitous nature, green credentials, and abundance and widely utilized in cigarette filters, high absorbent diapers, semi-permeable membranes, biomedical utilities in the form of fibers and films. Cellulose acetate (CA) is particularly important in multiple industries along with textile and biomedical fields.

The silica surface comprised of two type of functional groups including siloxane (Si–O–Si) and silanol (Si–OH). Silica surface can be modified via nucleophilic substitution at the Si of the siloxane and direct reaction with the hydroxyl group of the silanol. Although much research effort has been focused on understanding origin of the luminescent properties, only a few cases have a conspicuous identification of the molecular structure of the luminescent center [6–8]. Most of the information is from theoretical models and experimental researches of natural or synthetic specimens. Sol–gel derived silica gel is of great importance due to the wide application in optics, sensors, and catalysts

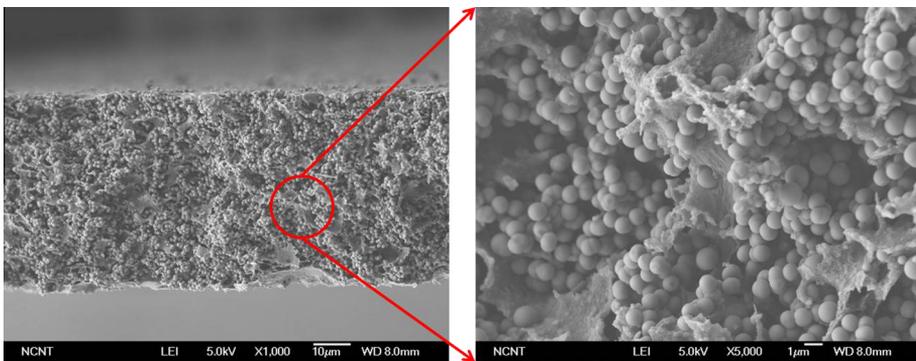


Fig. 1. FESEM cross-sectional images of CA and silica sphere composite.

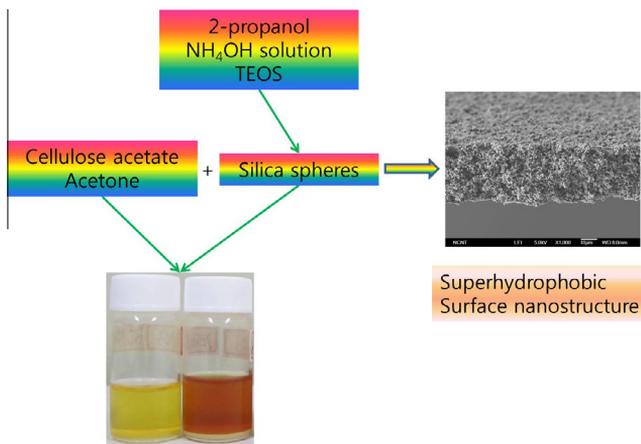


Fig. 2. Schematic representation of the overall this research.

[9,10]. Strong blue luminescence at 437 and 466 nm depending on the thickness of the amorphous-Si:H/SiO₂ multilayer were reported [11]. Intense violet–blue bands at 340–370 and 400–430 nm have been observed from the Si:H:O films [12]. However, many questions for the origin of the structure of the defect and mechanism still remain unsolved. Identification of the luminescent fragment from the silica material is difficult due to the strong absorption of the SiO₂ in the infrared regime. In this study we investigated the chemical functional groups and optical properties of CA and silica sphere composite after aging process. Field emission scanning electron microscope (FESEM) images, FTIR, UV–visible, and PL spectra with various excitation wavelengths are included in this report.

2. Experimental

CA (39.8 acetyl%) with molecular weight of approximately 30,000, acetone (99.9%), tetraethylsilane (TEOS, 98%), methanol (HPLC grade), 2-propanol (99%) and ammonium hydroxide (28%) were purchased from Sigma Aldrich Co. Ltd. and were used without further purification. Monodisperse silica

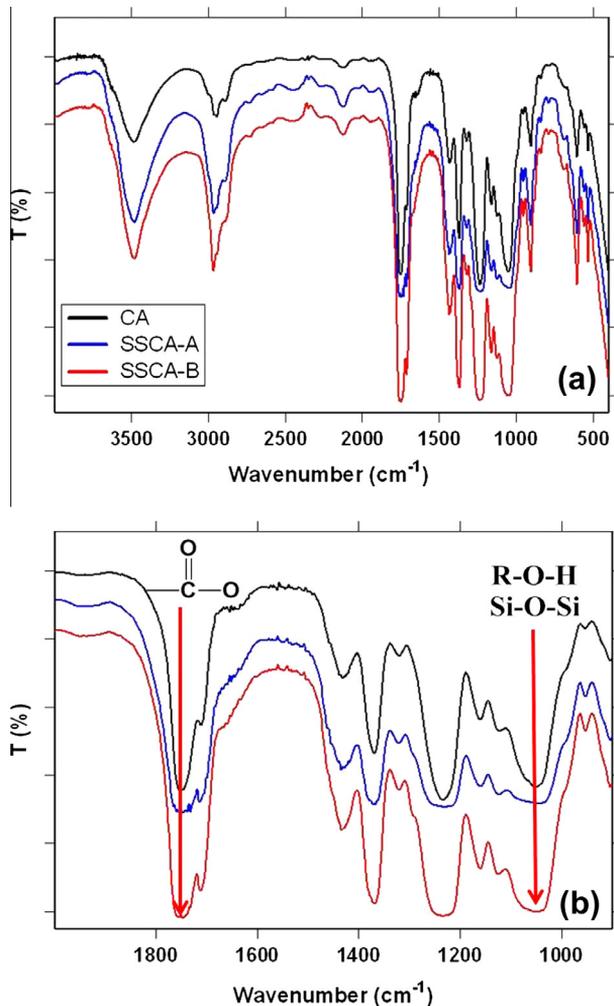


Fig. 3. FTIR spectra of (a) CA, SSCA-A, and SSCA-B and (b) expanded spectra of (a).

spheres were synthesized with Stöber synthetic route. The mixture of 2-propanol (100 ml) and ammonium hydroxide (100 ml) was placed in a 250 ml round bottom flask, then 3.5 g of TEOS was added to the round bottom flask and vigorously stirred. The spheres were separated and purified by repeated centrifuge-washing processes with methanol. The CA (12.08 g) was dissolved in acetone (100 ml). The CA solution (4 g) was poured into a 25 ml vial, and 0.07 g (SSCA-A) and 0.14 g (SSCA-B) of silica spheres were added to the vial. The CA solution was spin-coated to a glass substrate with spinning rate of 500 rpm. FESEM images of the CA and silica sphere composite films were obtained with JEOL ISM-7401F scanning electron microscope with acceleration voltage of 5 kV. The solution was left on the desk without any perturbation. After 4 days, the solution color changed noticeably. The color was monitored continually for 180 days. After 180 days, FTIR, UV-visible, and fluorescence spectra were recorded with Nicolet iS5, Thermo Scientific Genesys 10S, and Hitachi F-4500 fluorescence spectrometers.

3. Results and discussion

Large area nanostructures can be obtained by simply mixing silica spheres and CA to obtain super hydrophobic surface. Various amounts of silica spheres were mixed with CA, and the composites were spin-coated to the glass substrates. Fig. 1 shows FESEM cross-sectional images of the free standing film of silica spheres and CA composite. Although the film color did not change with the time passed, the solution color slowly changed as the time passed. The SSCA-A and SSCA-B had light yellow color after 4 days and became clear yellow color after 6 days. The color changed to bright/intense yellow and brown/intense red for the SSCA-A and SSCA-B, respectively, after 18/38 days. The color continually intensified until 80 days and did not change thereafter.

The conceptual representation of this research is shown in Fig. 2. Large area super-hydrophobic surface film can be fabricated with proper ratio of silica spheres and CA composite. The composite film was casted within one day and had white color. Even after several months, the film color maintained same. However, the solution color changed depending on the amount of silica spheres, which implied that the color change was mainly due to the acetone and silica spheres instead of CA. Both acetone and silica spheres are required components for formation of the light-emitting chromophore. This result promises that the photoluminescent super-hydrophobic films can be fabricated.

To analyze the chemical structural change of the composite, FTIR spectra were investigated. The FTIR spectra of CA, SSCA-A (excluded spheres), and SSCA-B (excluded spheres) were shown in Fig. 3(a). The absorption peak at 3478 cm^{-1} representing stretching vibration of Si—OH and R—OH increased for SSCA-A and SSCA-B compared with CA. The —CH absorption peak at 2963 cm^{-1} also

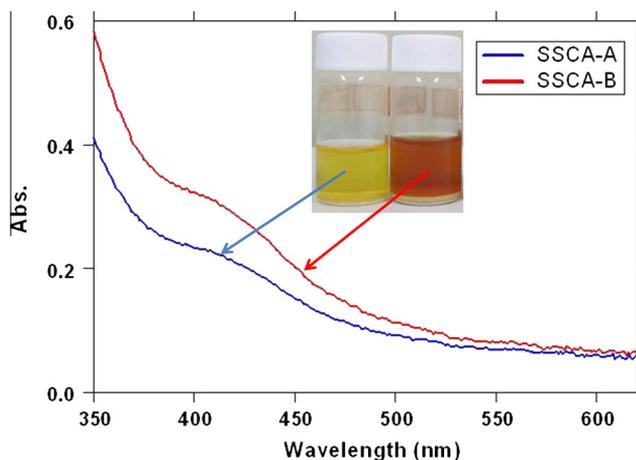


Fig. 4. UV-visible spectra of SSCA-A and SSCA-B.

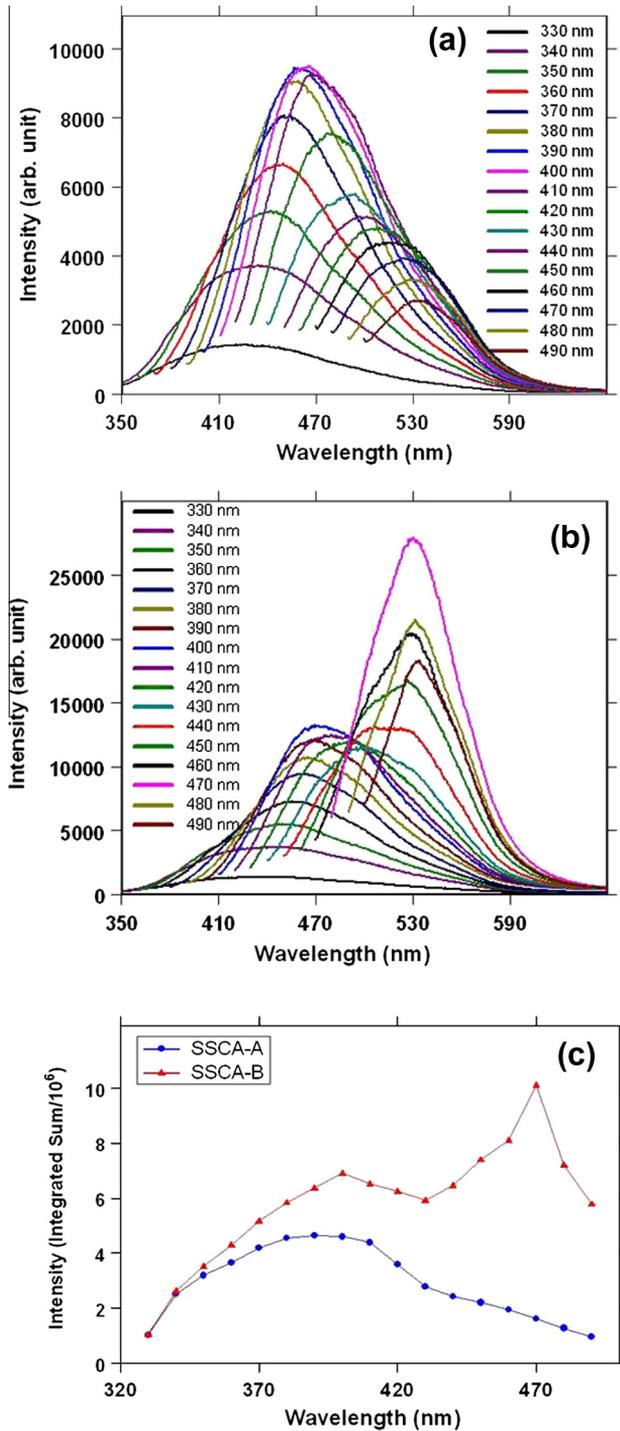


Fig. 5. PL spectra of (a) SSCA-A and (b) SSCA-B and (c) cumulative sum of PL spectra of (a) and (b).

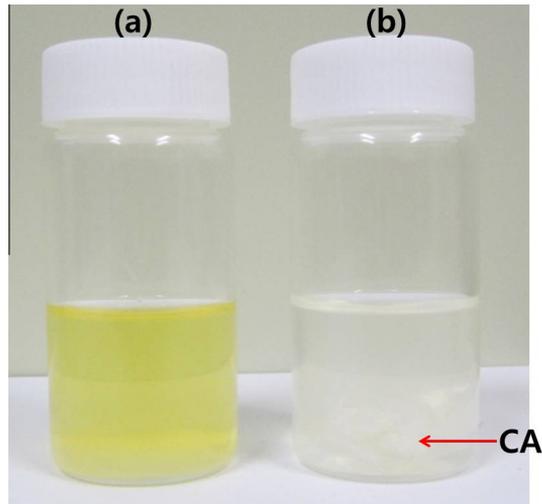


Fig. 6. Pictures of (a) the methanol/chromophore after washing once with methanol and (b) methanol/CA after washing twice with methanol.

increased for SSCA-A and SSCA-B. The absorption peaks at 1746 and 1713 cm^{-1} causing the stretching vibration of an ester became broader and stronger especially for SSCA-B. The broad peak at around 1100 cm^{-1} representing R—OH stretching vibration for CA and Si—O—Si stretching vibration for silica became much broader than that of CA as shown in Fig. 3(b). These results indicate that the SSCA-A and SSCA-B have more —OH, —CH, —C=O, and Si—O—Si groups than the CA.

UV-visible absorption spectra for SSCA-A and SSCA-B are shown in Fig. 4. The absorption peak for both SSCA-A and SSCA-B is at around 410 nm (3.02 eV), which is similar emission band gap energy of the silica. Fig. 5(a) shows PL spectra with different excitation wavelengths from 330 to 490 nm for SSCA-A. The emission peak is at about 410 nm for excitation wavelength at 330 nm. The maximum emission intensity is at approximately 470 nm with excitation wavelength at 400 nm, and the intensity continually reduced thereafter. The emission peaks shift toward longer wavelength with the increase of the excitation wavelength, which indicates possible multiple emission center or multiple emission components. This result shows that the SSCA-A also has some amount of longer wavelength emitting component. Fluorescence spectra for SSCA-B are shown in Fig. 5(b). The maximum intensity also is at 470 nm with excitation wavelength at 400 nm. However, the new emission peak appears and increases until the excitation wavelength at 470 nm. This result clearly shows that the multiple emission center or multiple emission components exist. The emission spectra was integrated and plotted with excitation wavelength as shown in Fig. 5(c). This plot shows the integrated emission intensity with various excitation wavelengths. This result indicates that the amount of longer wavelength light-emitting chromophore increases with the increase of the amount of silica spheres in the composite.

To prove that the CA was not involved in the formation of the chromophore, the chromophore and CA composite was washed with methanol. Fig. 6(a) and (b) shows the picture of the methanol/chromophore after washing one time and CA/methanol after washing twice the composite, respectively. After washing one time, only chromophore dissolved in methanol. After washing the composite twice, CA became colorless. This result proves that the CA is not involved in the formation of light-emitting chromophore.

4. Conclusions

Strong blue and green light emission was obtained with CA and silica sphere composite. Although the color of composite film remained the initial state, the solution color changed intense yellow and

red for SSCA-A and SSCA-B, respectively. The FTIR result shows that the aged SSCA-A and SSCA-B have more —OH, —CH, —C=O, and Si—O—Si groups than CA. The UV–visible absorption peak was approximately at 410 nm. PL peaks were shifted toward longer wavelength as the excitation wavelength increased, which indicated the existence of multiple emission components. Longer wavelength emitting element increased with the increase the amount of silica spheres in the composite.

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