

Photoluminescence Characteristics of the Light-Emitting Chromophores Obtained from Organic-Inorganic Hybrid Silica Spheres

Eun-Hye Park¹⁾ · Chang-Gi Jeong²⁾ · Kwang-Sun Kang²⁾

¹⁾Dasomdeul 50 Gamasilgil Hayangup Gyeongsan, Gyeongbuk, 38428, Korea

²⁾Department of New and Renewable Energy, Kyungil University, 50 Gamasilgil Hayangup Gyeongsan, Gyeongbuk, 38428, Korea

ABSTRACT: Light-emitting chromophores have been separated from silica spheres modified the surface with 3-(trimethoxysilyl)propylmethacrylate (TMSPM). The photoluminescence characteristics of the chromophores were investigated with various excitation wavelengths. The TMSPM was attached to the surface of silica spheres at 75°C. Large number of round shaped particles of the TMSPM was on the surface of silica spheres after 3 h reaction. The TMSPM was completely covered on the surface of the spheres after 6 h reaction. The surface modified silica spheres were soaked into acetone and stored for 20 days at ambient condition. The solution color slowly changed from light yellow to deep yellow with the increase of the storing time. The FTIR absorption peaks at 3348, 2869, 2927, 1715, 1453/1377, 1296, and 1120 cm⁻¹ represent C-OH, R-CH₃, R₂-CH₂, -C=O, C-H, C=C-H, and Si-O-Si absorption, respectively. The FTIR absorption peak at 1715 cm⁻¹ representing the ester -C=O stretching vibration for silica spheres stored for 20 days was increased compared with the spheres without aging. The UV-visible absorption peaks were at 4.51 eV (275 nm) and 3.91 eV (317 nm). There were two luminescence peaks at 2.51 eV (495 nm) and 2.25 eV (550 nm). The emission at 2.51 eV was dominant peak when the excitation energy was higher than 2.58 eV, and emission at 2.25 eV became dominant peak when the excitation energy was lower than 2.58 eV.

Key words: Light-emitting chromophore, Silica spheres, Photoluminescence, TMSPM, Large Stokes shift

1. Introduction

High photon emission in the range of ultraviolet, visible and infrared is one of the most well-known phenomena for the reduction of silica down to nanoscale¹⁻⁴⁾. Silica nanostructures can be developed diverse optical devices including solid state dye lasers, light emitting diodes, optical probes and displays. Although it is well accepted that the origin of the luminescence has relationship with the high specific surface of silica nanoparticles, the role and the structure of the specific optically active centers are poorly understood, which is due to the huge variety of defects at the surface sites and large number of molecular and atomic species^{5,6)}. Nevertheless, stable and bright luminescence has been reported by many researchers⁷⁻⁹⁾.

Recently, Yu et al.¹⁰⁾ reported blue emissions at 2.65 eV (470 nm) and 3.0 eV (414 nm). Similar blue luminescent band from silica nanowires has been reported by many other research groups¹¹⁻¹³⁾ and proposed that the luminescence is independent on the morphology of the silica nanostructure¹¹⁾. The 2.7 eV emission

attributed from neutral oxygen vacancy ($\equiv \text{Si}-\text{Si} \equiv$) and 3.1 eV emission caused intrinsic diamagnetic defect centers including the two fold coordinated silicon lone pair centers ($=\text{Si}:$) were reported in bulk silica¹⁴⁾. The difficulty to understand the cause of the luminescence in the nanostructure and the bulk silica is the existence of the luminescent chromophore in the silica matrix. The light-emitting chromophore (LEC) has been separated from silica spheres modified the surface with 3-(trimethoxysilyl)propylmethacrylate (TMSPM) by emerging silica spheres to acetone. The chromophore was analyzed with field emission scanning electron microscope (FESEM), UV-visible spectrometer, Fourier transform infrared (FTIR) spectrometer and fluorescence spectrometer.

2. Experimental

Tetraethoxy orthosilicate (TEOS, 98%), methanol (HPLC grade), 2-propanol (99%), ammonium hydroxide (28%) and TMSPM (98%) were purchased from Sigma Aldrich Co LTD. The monodisperse silica nanospheres were synthesized with Stöber synthetic route. The mixture of 2-propanol (50 ml) and ammonium hydroxide (50 ml) was placed into a 250 ml round bottom flask, and then 1.55 g of TEOS was added to the round bottom flask with vigorous stirring. After stirring for 6 h, 770

*Corresponding author: kkang@kiu.ac.kr

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mg of TMSPM was added to the solution, and the temperature was maintained at 75°C for 8 h. The spheres were centrifuged and washed with acetone three times. The surface modified spheres were soaked into acetone and stored for 20 days. After storing the solution for 20 days, the solution and the spheres were separated by centrifuge. The solution color became intense yellow, and the sphere color turned to weak yellow. The solution was completely dried to remove acetone. The dried solid diluted to the methanol, and the UV-visible spectra were obtained using Thermo Scientific Genesys 10S. FTIR spectra were recorded with Nicolet iS5 FTIR spectrometer. For acquiring fluorescence spectra of the dried chromophore, small quantity of the solid was diluted to the methanol. The solution was added to the quartz cuvette, and the fluorescence spectra were recorded with excitation wavelengths at 320 through 460 nm using Hitachi F-4500 fluorescence spectrometer.

3. Results and discussion

The blue luminescence from various silica structures has been reported¹⁵⁻¹⁷. In many cases, the blue luminescence of silica nanowires has been obtained by accident¹⁸⁻²⁰. However, there is no direct evidence for the origin of the luminescence and the detailed chemical structure of the luminescent fragment. Since condensation reaction between the silanol on the surface of the silica spheres and the silanol of the hydrolyzed TMSPM was not occurred at room temperature with NH_4OH catalyst, the elevated temperature (75°C) was used to attach the TMSPM on the surface of silica spheres with NH_4OH catalyst. The surface modified silica spheres were soaked into acetone and stored for 20 days. The acetone color changed to yellow after 20 days. The schematic view of the surface modification process and the silica spheres/acetone after 20 days is shown in Fig. 1.

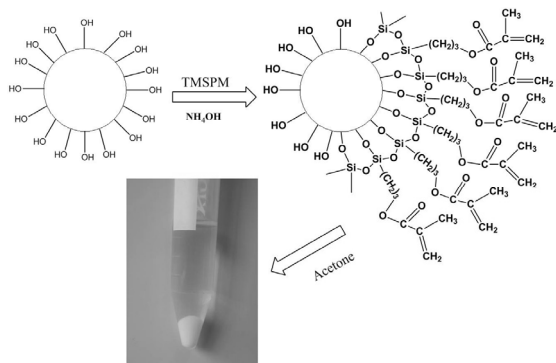


Fig. 1. Schematic representation of the surface modification process and extraction of the LEC.

Most of the silanol condensation reactions occur at room temperature with acid or base catalyst. However, the FTIR spectrum and FESEM image show no evidence that the TMSPM is attached on the surface of silica spheres after reaction with various ratios of TEOS and TMSPM at room temperature. Therefore, the reaction temperature increased from 50 to 75°C. The FESEM images of silica spheres reacted for 3 h and 6 h at 75°C are shown in Fig. 2(a) and 2(b), respectively. Fig. 2(a) shows many small TMSPM dots on the surface of silica spheres. After 6 h reaction, the TMSPM is covered all over the surface of silica spheres as shown in Fig. 2(b).

Silica spheres and acetone were separated by centrifuge after 20 days of storing time. Acetone was completely dried and collected the LEC solid before obtaining the FTIR spectra. Fig. 3(a) shows FTIR spectra for a pure TMSPM and LEC. For the LEC, the absorption peak at 3348 cm^{-1} represents C-OH stretching vibration. The absorption peaks at 2869 and 2927 cm^{-1} are due to the R-CH₃ and R₂-CH₂ stretching vibration, respectively. The strong absorption peak at 1715 cm^{-1} represents the C=O stretching vibration of an ester. The asymmetric and symmetric deformation peaks of the C-H are at 1453 and 1377 cm^{-1} , respectively. The

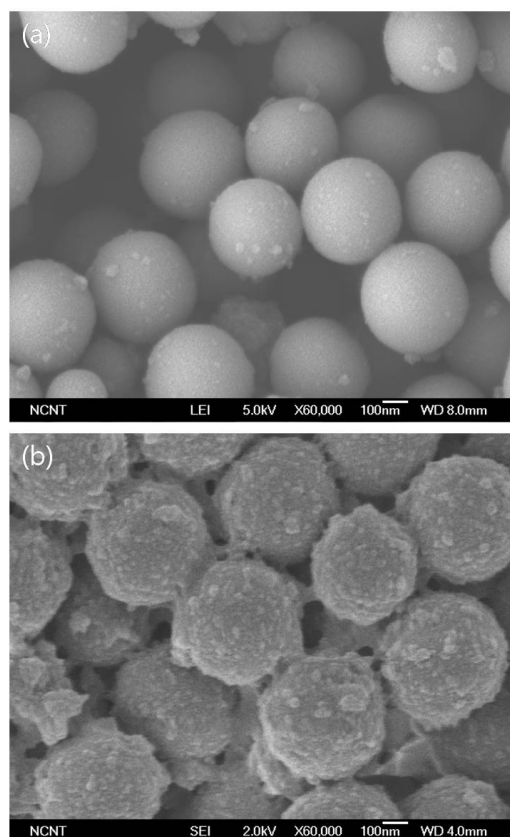


Fig. 2. FESEM images of silica spheres attached the TMSPM for (a) 3 h and (b) 6 h at 75°C

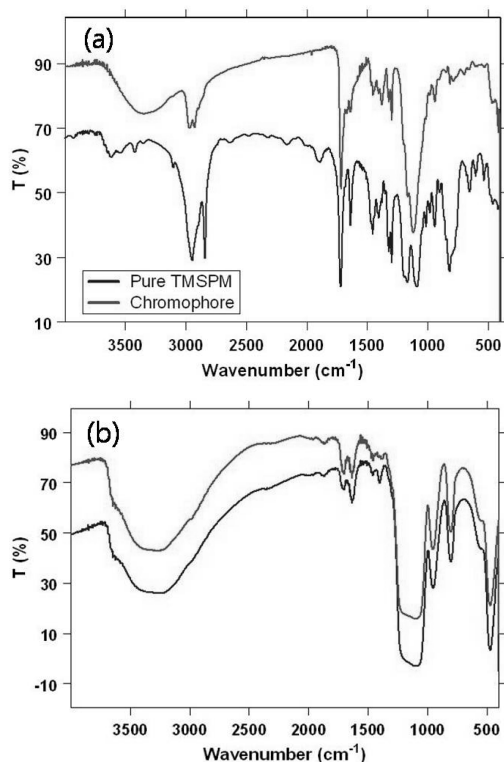


Fig. 3. FTIR spectra of the (a) pure TMSPM and LED and (b) surface modified silica spheres with TMSPM and silica spheres stored in acetone for 20 days.

absorption peaks at 1296 represents the C-H stretching vibration of the C=C-H group. The strong and broad absorption peak at 1080 cm^{-1} is due to the Si-O-Si stretching vibration. Therefore, the SLN-20 is comprised of C-OH, R-CH₃, R₂-CH₂, C=O, C=C-H, and Si-O-Si, and the main absorption peaks are closely matched with the TMSPM absorption peaks. Fig. 3(b) shows the FTIR absorption spectra for the as synthesized silica spheres and the spheres soaked for 20 days in acetone. Compared with the absorption peaks pristine silica spheres, the ester absorption peak at 1715 cm^{-1} for the soaked silica spheres increased, which indicates that the acetone may be involved in chromophore formation process.

Silica based excitation peaks at 5.2, 5.0, 3.9 and 3.2 eV are reported by Spallina *et al.*²¹⁾. Silica xerogel shows the excitation peaks at 5.12, 4.13 and 3.44 eV²²⁾. Therefore, wide range of excitation bands exist for the silica based materials depending on the structure and process conditions. Since LEC is separated from the silica spheres, characteristic absorption band of the pure LEC can be identified. The mixture of acetone and LEC was completely dried before analysis due to the acetone strongly absorbs UV-light shorter than 330 nm. Fig. 4 shows the UV-visible absorption spectrum for the luminophore in methanol,

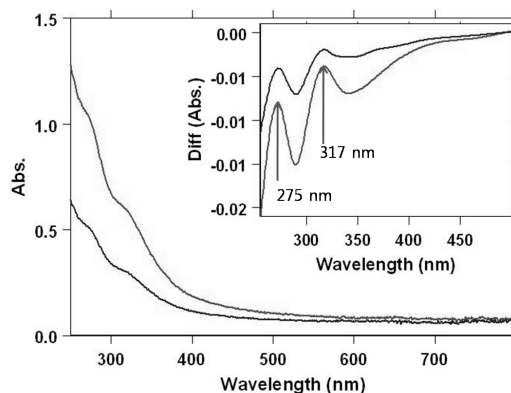


Fig. 4. UV-visible represents the differential absorption spectra of the LEC

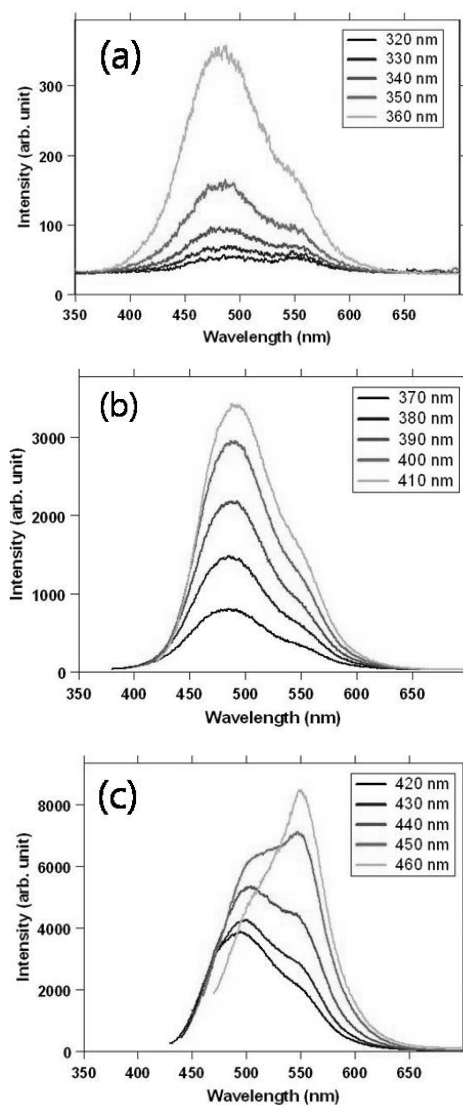


Fig. 5. Excitation wavelength dependent PL spectra. There are two emission bands at 495 and 550 nm. At high and low excitation energies, the main luminescence bands are at 495 and 550 nm, respectively.

which has two absorption shoulders. The differential absorption spectrum shows the clear absorption peaks at 4.51 eV (275 nm) and 3.91 eV (317 nm) as shown in the inset Fig. 4.

The luminescence of high surface area of silicas is presently accepted. However, the clear chemical structure and specific defects have not been established. Many researchers reported the silica based emission at 3.1 and 2.7 eV. Figs. 5(a), 5(b), and 5(c) show the PL spectra with excitation ranges of 3.88-3.44 eV (320-360 nm), 3.35-3.02 eV (370-410 nm), and 2.95-2.70 eV (420-460 nm), respectively. The emission peaks are at 2.51 eV (495 nm) and 2.25 eV (550 nm) for the excitation wavelength at 3.88 and 3.76 eV, and the 2.51 eV emission peak becomes dominant luminescent peak as the excitation energy reduces. As the excitation energy further reduces, the 2.25 eV luminescence peak becomes dominant peak as shown in Fig. 5(c). The luminescence band energy is slightly lower than the silica based emission, which may be due to the incorporation of TMSPM in this light-emitting chromophore. Compared with the absorption band, extra large Stokes shift is observed.

4. Conclusions

The LEC is separated from silica spheres modified the surface with TMSPM. The FESEM images of the modified silica spheres show the small particular shape of the TMPSM after 3 h reaction. The surface of the silica spheres was completely covered with TMSPM after 6 h reaction. The LEC has been extracted by soaking the silica spheres into the acetone. The FTIR absorption peaks exhibit the composition of the LEC comprised of C-OH, R-CH₃, R₂-CH₂, -C=O, C-H, C=C-H, and Si-O-Si. The increase of the FTIR absorption peak at 1715 cm⁻¹ for the silica spheres stored for 20 days indicates the involvement of the acetone to the formation of the LEC. The UV-visible absorption peaks for the LEC are observed at 4.51 eV (275 nm) and 3.91 eV (317 nm). Two characteristic luminescence peaks of the LEC are observed at 2.51 eV (495 nm) and 2.25 eV (550 nm). The emission peak at 2.51 eV is dominant when the excitation energy is higher than 2.58 eV, and emission peak at 2.25 eV becomes dominant peak when the excitation energy is lower than 2.58 eV. Compared with the absorption spectrum, extraordinary large Stokes shift is observed for this LEC.

Acknowledgment

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