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Separation of photoluminescent fragment from the silica spheres modified the surface with 3-mercaptopropyltrimethoxysilane

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ABSTRACT

Photoluminescent fragment was separated from the silica spheres modified the surface with 3-mercaptopropyltrimethoxysilane. The spheres were synthesized with the Stöber synthetic method, washed three times with acetone and stored in acetone for 12, 20, and 60 days. The solution color became yellow to dark red with the increase of the storing time. The UV-visible absorption spectra show absorption shoulder at 320 nm for only 60 days sample. Although the major Fourier transform infrared absorption peaks are similar for the 20 and 60 days samples, medium and small absorption peaks for the 20 days samples are not clear compared with 60 days samples. The absorption peaks at 3315, 2869/2968, 2928, 1703, 1294, 1185, 1219, 1080/1033, 971 and 864/761 cm^{-1} represent C–OH, R–CH_3, R_2–CH_2, –C=O, C–O, C=S, C–C, Si–O–Si, Si–O–C and Si–C absorption, respectively. The luminescent peak is between 2.7 and 3.0 eV with the excitation energies between 3.76 and 3.44 eV for both 12 and 20 days samples. However, the new luminescent peak is observed at near 2.5 eV for the 60 days samples, which may related with sulfur group.

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 nanoscale [1–4]. Therefore, it is promising for the development of 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 researchers [7–9].

Recently, blue emissions at 2.65 eV (470 nm) and 3.0 eV (414 nm) were reported by Yu et. al [10]. Many other research groups have reported similar blue luminescent band from silica nanowires [11–13] and have proposed that the luminescence is independent of the morphology of the silica [11]. The 2.7 eV emission attributed from neutral oxygen vacancy ($\equiv$Si–Si$\equiv$) and 3.1 eV emission caused intrinsic diamagnetic defect centers including the two fold coordinated silicon lone pair centers (=Si:) were also reported in bulk silica [14]. Therefore, the 2.65 and 3.0 eV emissions in silica nanowires are the origins of the 2.7 and 3.1 eV emissions in bulk silica.

The main difficulties to understand the cause of the luminescence in nanostructure and bulk silica and to systematically synthesize the luminescent silica chromophore are the existence of the luminescent chromophore in the silica matrix. The photoluminescent fragment has been separated from the silica spheres modified the surface with 3-mercaptopropyltrimethoxysilane (MPTMS) by emerging the silica spheres to the acetone for various times. The chromophore was analyzed with UV–visible, Fourier transform infrared (FTIR), and fluorescence spectrometers to identify the primitive chemical structure, characteristic absorbance, and luminescent property.

2. Experimental

Tetraethoxy orthosilicate (TEOS, 98%), methanol (HPLC grade), 2-propanol (99%), ammonium hydroxide (28%) and MPTMS (95%) were purchased from Sigma Aldrich Co. Ltd. The monodisperse silica nanospheres were synthesized with the Stöber synthetic route. The mixture of 2-propanol (100 ml) and ammonium hydroxide (100 ml) was placed into a 250 ml round bottom flask, and then 3.5 g of TEOS was added to the round bottom flask with vigorous stirring. After stirring for 6 h, 700 mg of MPTMS was added to the solution. The spheres were centrifuged and washed with acetone three times. The spheres were soaked into acetone and stored for 12, 20, and 60 days. After storing the solutions for

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12, 20, and 60 days, the solutions were completely dried before analysis. 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 methanol and chromophore solution was added to the quartz cuvette, and the fluorescence spectra were recorded with excitation wavelengths at 3.76, 3.65, 3.54 and 3.44 eV using Hitachi F-4500 fluorescence spectrometer.

3. Results and discussion

The blue luminescence from various silica structures has been reported [15–17]. In many cases, the blue luminescent silica nanowires have been obtained by accident [18–20]. However, there is no direct evidence for the origin of the luminescence and the chemical structure of the luminescent fragment. This research focuses on the obtaining the primitive chemical structures and characteristic properties of the luminescence chromophore. The uniform size silica spheres were synthesized using the Stöber synthetic process and were modified the surface with MPTMS [21]. The silica spheres were soaked in acetone and stored for various times, such as 12, 20, and 60 days. The acetone color changed to yellow after 12 and 20 days and turned to deep red after 60 days as shown in Fig. 1. The schematic view of the synthesis and color changed spheres soaked in acetone for 60 days is shown in Fig. 1.

The color changed acetone was separated from the spheres by centrifuge and completely dried before analysis due to the acetone strongly absorbs UV-light shorter than 330 nm. The solid chromophore was diluted to the methanol. Fig. 2 shows UV–visible absorption spectra for the luminescent fragment aged for 20 days (blue color) and 60 days (red color) in methanol. The inset pictures show the acetone color aged 20 and 60 days. The absorption profiles for the 12 and 20 days samples have no clear absorption peak, but show strong UV-light absorption in the range of shorter than 400 nm. The absorption profile for the 60 days sample show absorption shoulder at approximately 320 nm and shows strong UV-light absorption in the range of shorter than 420 nm.

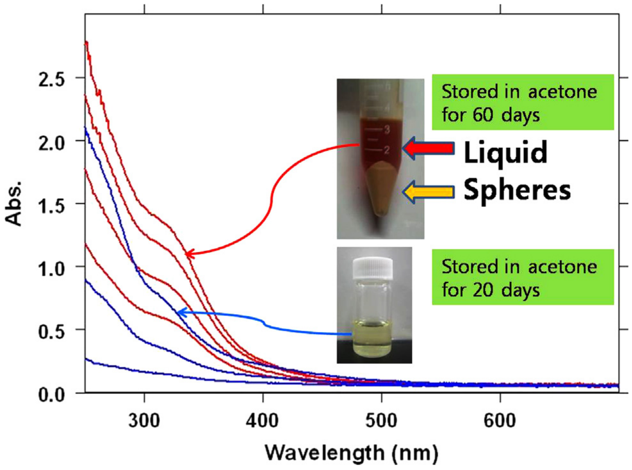

Fig. 2. UV–visible absorption spectra with 20 and 60 days aged samples.

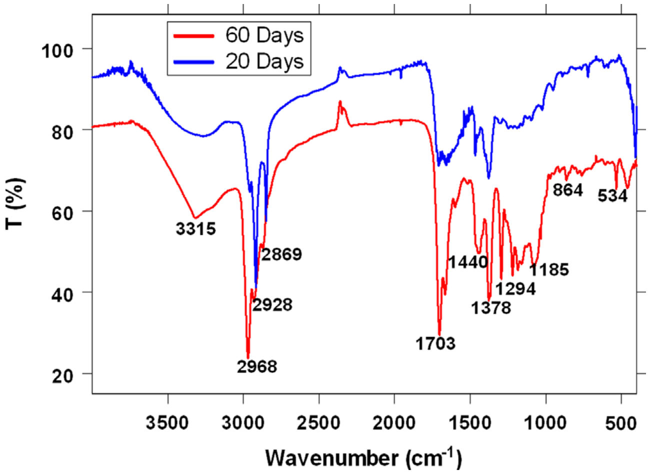

Fig. 3. FTIR spectra of the luminescent fragments soaked into the acetone for 20 and 60 days.

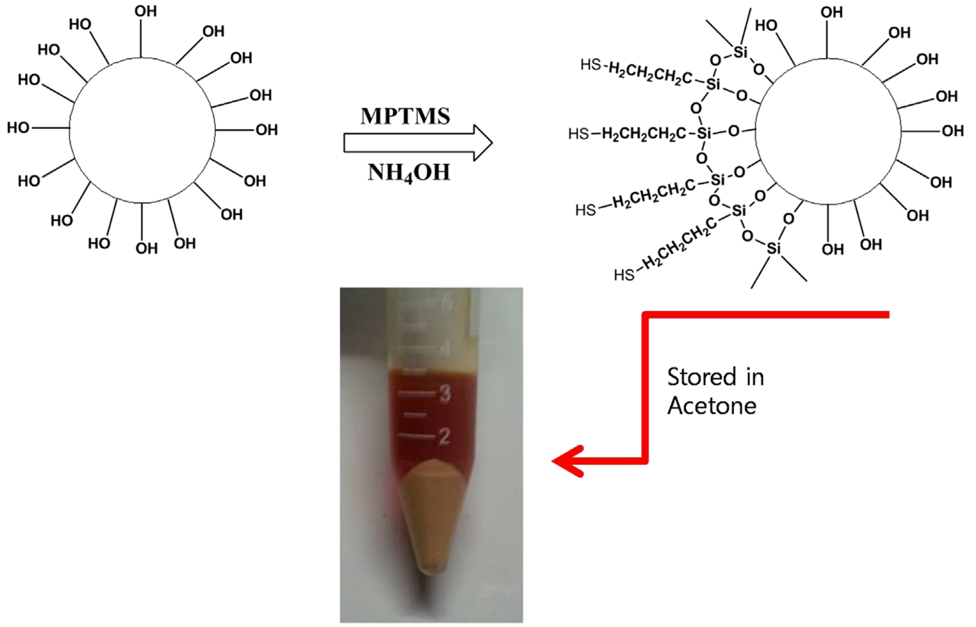

Fig. 1. Schematic representation of the synthesis of the surface modified silica spheres and soaked into acetone for 12, 20, and 60 days.