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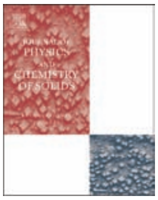

Characterization of luminescent chromophore obtained from silica spheres

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ABSTRACT

Blue light emitting chromophores have been separated from silica spheres by soaking them into acetone for 120 days. The luminescent chromophores were not obtained from other solvents, including ether, methanol, ethanol, 2-propanol, chloroform and tetrahydrofuran. According to the Fourier transform infrared spectrum, the luminescent material is composed of C–OH, $-CH_2$, $-CH_3$, C=O, and Si–O–Si. UV–visible absorption peak of the chromophore is at 5.17 eV (240 nm). Field emission scanning electron microscope images show small cracks on the surface of aged spheres. The luminescence peak was at 2.81 eV (441 nm) for excitation energy between 3.88 and 3.35 eV and slightly shifted toward lower energy for excitation energy lower than 3.35 eV. The deconvoluted luminescent spectrum shows two emission bands at 3.08 and 2.74 eV, which are well-matched the oxygen deficient center model. Compared to the absorption peak (5.17 eV) and the emission peak (2.81 eV), large Stokes shift (2.36 eV) is observed.

1. Introduction

Silicon dioxide is a useful amorphous material and has been focused to understand the properties of this material. Although much research effort has been focused on understanding the origin of luminescent properties, only a few cases have a conspicuous identification of the molecular structure of the luminescent centers [1–3]. Most of the information is from theoretical models. Sol–gel derived silica gel is of great importance due to the wide application in optics, sensors, and catalysts [4,5]. Strong blue luminescence at 437 and 466 nm depending on the thickness of the amorphous-Si:H/SiO_2 multilayer was reported [6]. Intense violet–blue bands at 340–370 and 400–430 nm have been observed from the Si:H:O films [7]. 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 SiO_2 in the infrared regime. The best way to identify the luminescent moiety is to separate the luminescent fragment from the silica matrix. Once it is separated, it can be analyzed with various spectroscopic methods to identify the structure and the composition. Therefore, in this paper we report the separation and analysis of the luminescent chromophore.

2. Experimental

Tetraethyl orthosilicate (TEOS, 98%), acetone (99.9%), methanol (HPLC grade), 2-propanol (99%) and ammonium hydroxide (28%) were purchased from Sigma Aldrich Co. LTD. The monodisperse silica spheres were synthesized by the Stöber synthesis route. A mixture of 2-propanol (50 ml) and ammonium hydroxide (50 ml) was placed in a 250 ml round bottom flask, and then 0.77 g of TEOS was added to the round bottom flask with vigorous stirring. The spheres were separated and purified by repeated centrifuge–washing processes with methanol. The spheres were soaked in various solvents, including methanol, ethanol, 2-propanol, ether, tetrahydrofuran, chloroform and acetone, for 120 days. Only the acetone color slowly changed to yellow. The acetone and spheres were separated by a centrifuge. The UV–visible spectra were recorded with the solution using a Thermo Scientific Genesys 10 S. FTIR spectrum of solid chromophore was recorded by a FTIR spectrometer (Nicolet iS5). The photoluminescence (PL) spectra of the chromophore solution were obtained with various excitation wavelengths using Hitachi F-4500 fluorescence spectrometer. Field emission scanning electron microscope (FESEM) images of

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silica spheres were obtained using a JEOL ISM 7401F field emission scanning electron microscope.

3. Results and discussion

Understanding the mechanism of the silica sphere formation is essential to predict the resulting silica particle size and size distribution. Theoretically many different models have been proposed for the dominant factors of particle sizes, including reactant supersaturation, reactant molecular diffusion, surface reaction, and particle coagulation. Generally silanol groups are formed by hydrolysis of silicon alkoxide groups, and then undergo condensation as follows: [8].

$$\equiv \mathrm{Si{-}OR} + \mathrm{H_2O} \longrightarrow \equiv \mathrm{Si{-}OH} + \mathrm{ROH} \tag{1}$$

$$\equiv \mathrm{Si{-}OH} + \equiv \mathrm{Si{-}OH} \longrightarrow \equiv \mathrm{Si{-}O{-}Si} \equiv + \mathrm{H_2O} \tag{2}$$

$$\equiv \mathrm{Si{-}OR} + \equiv \mathrm{Si{-}OH} \longrightarrow \equiv \mathrm{Si{-}O{-}Si} \equiv + \mathrm{ROH} \tag{3}$$

However, no clear mechanism has not yet been generally accepted. To understand the chemical structure of the luminescent material, it is necessary to separate the luminescent material from the silica matrix. Fig. 1 shows the experimental scheme and the result. As shown in Fig. 1, only acetone color is changed after 120 days. This result indicates that acetone is the key factor for the formation of light emitting chromophores.

To obtain the chemical information of the fluorescent fragment, FTIR analysis is performed. Fig. 2 shows the FTIR spectrum of the fluorescent fragment. The FTIR absorption peak at 3305 cm^{-1} represents the C–OH stretching vibration instead of Si–OH stretching vibration. The absorption peaks at 2969 and 2879 cm^{-1} represent R–CH_3 asymmetric and symmetric stretching vibration, respectively. The absorption peak at 2930 cm^{-1} can be assigned to R–CH_2 asymmetric stretching vibration. The characteristic absorption peak at 1698 cm^{-1} represents C=O stretching vibration of an ester. The FTIR spectrum shows absorption bands arising from deformation vibration of C–H (1462 and 1371 cm^{-1}), stretching vibration of C–O in the ester group (1294 cm^{-1}), stretching vibration of Si–O–Si (1106 cm^{-1}) and stretching vibration of Si–O (863 cm^{-1}). Therefore, the luminescent fragment is composed of –OH, –CH_2, –CH_3, C=O, and Si–O–Si. For silica spheres, there was no FTIR absorption difference between as-prepared silica spheres and aged silica spheres.

The FESEM images of as-synthesized silica spheres and aged silica spheres in acetone are shown in Fig. 3(a) and (b), respectively. As-synthesized silica spheres show no crack on the surface of the spheres. However the aged silica spheres generated cracks all over the surface, which were created by the reaction between silica and acetone, and they became light emitting chromophores.

Strong luminescence from the diverse silica nanostructures has been achieved by accidents in many cases [9–11]. The synthesized spheres were centrifuged to collect the spheres and washed three times with methanol. The purified spheres were stored in methanol, ethanol, 2-propanol, ether, tetrahydrofuran, chloroform and acetone for approximately two months. Only the acetone color slowly changed to bright yellow. The absorption band associated with the oxygen deficient center (ODC) is at approximately 5 eV, which is one of the most controversial issues for the defect research field of the SiO_2. Three models are proposed for the ODC including a neutral oxygen vacancy (≡Si–Si≡) [12,13], twofold coordinated silicon (=Si:) [13,14] and the unrelaxed oxygen vacancy (O≡Si · Si≡O) [14,15]. Although these models were supported by two-photon photobleaching experiment for the SiODC, the origin of the ODC is still controversial topic in this field [16]. Fig. 4 shows

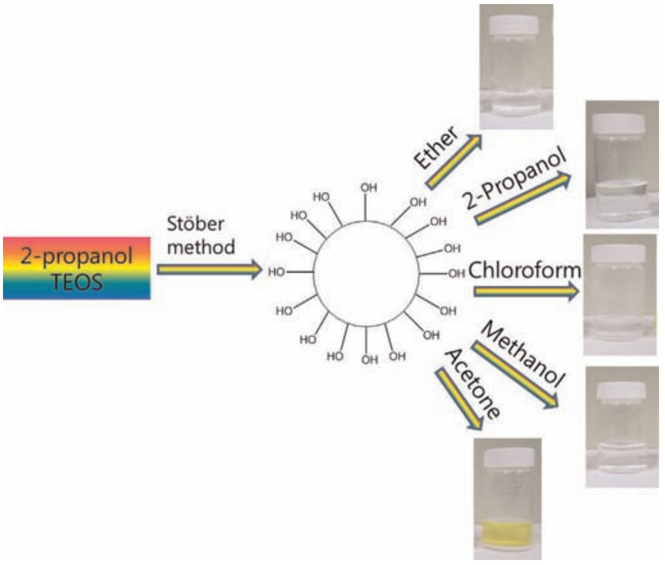

Fig. 1. Schematic view of this research.

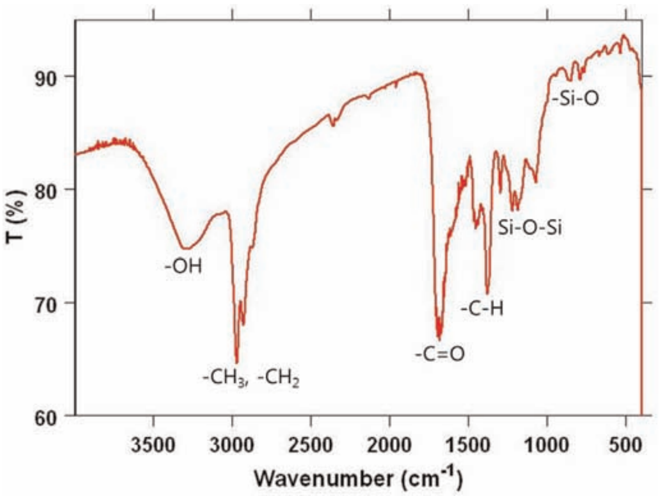

Fig. 2. FTIR spectrum of the chromophore comprised of –OH, –CH_2, –CH_3, C=O, and Si–O–Si.