Preparation of UV-dye TMQ-Doped Silica Film and Xerogel by Sol-gel Method

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UV dye TMQ-doped silica film and slab were prepared by sol-gel process with dioxane as cosolvent of the initial solutions. The maxima TMQ concentrations in the initial solutions for the transparent silica film and slab are 1.24×10^{-2} M and 1.5×10^{-3} M respectively. Luminescence quenching was not observed when TMQ concentration for the film is less than 6.2×10^{-3} M. Obvious red shift of absorption and emission maxima was observed, comparing with those of TMQ-cyclohexane solution.

The incorporation of organic dyes into silica glass prepared by sol-gel method has been extensively investigated in recent years because of their useful applications as laser materials, nonlinear optical materials, optical memories, high concentrators in solar cells and phosphors of ICCD (Intensified Silicon-Charge-Coupled Device) imaging detectors. A number of organic dye molecules, which are easily destroyed in the traditional glass forming process, have been successfully incorporated into silica matrix by the low-temperature sol-gel process.[1-5] However, most studies were focused on dyes in the visible region and little on dyes in the UV.[6] The main reason that UV dye-doped silica glass was seldom investigated is the great difficulty involved in the sample preparation because the commercially available UV dyes are nearly nonpolar and dissolve poorly in the normal initial polar solutions of the sol-gel process. Therefore the UV-dye concentration doped in the silica glass is too low to be effective. Since L. D. Ziegler and B. S. Hudson studied the laser properties of cyclohexane solution of UV-dye TMQ (2",3,3',3"'-tetramethyl-*p*-quaterphenyl) in 1980,[7] little has been reported on TMQ doped silica matrix in the literature up to now, to the authors' knowledge.

In this letter, dioxane was selected as the common solvent of the initial solutions during the sol-gel process after a large number of solvents have been tested. The concentration of TMQ doped in the initial solutions can be improved to be 10^{-2} mol/L (M), i.e. about 10–100 times larger than those of UV dyes reported. It is known that dioxane is one of the Drying Control Chemical Additives (DCCA) in the sol-gel process, which can prevent the drying gel from cracking.[8] TMQ-doped silica films were obtained by dip-coating method and the silica slab was obtained from the gelation of the sols. The absorption and emission spectra of the prepared samples were investigated.

The sample preparation procedures were briefly introduced as follows. Starting materials for synthesizing TMQ-doped silica film and slab are TEOS (tetraethoxysilane), dioxane, TMQ (EXCITON, INC.), hydrochloric acid and distilled water. All agents are Analytical Grade. The molar ratio of the initial solutions is TEOS: dioxane: H_2O: HCl = 1:4:2:0.00144. After vigorous magnetic stirring for 0.5 h, the mixing solution was refluxed for 6 h. TMQ dyes were added to the above sols under magnetic stirring and ultrasonic dispersing until the desired molar concentrations were reached. After aging for 24 h, TMQ doped silica films were prepared on fused silica substrate by dip-coating with the same rate of 6.7 cm/min and the silica slab was obtained from the gelation of the sols. The final transparent films and slab were obtained after being dried at 65 °C in the thermostat for about one week. The different concentrations of TMQ doped in silica film A, B, C, D and slab E were 1.24×10^{-2}, 6.2×10^{-3}, 3.1×10^{-3}, 1.5×10^{-3} and 1.5×10^{-3} M respectively. When the concentration is more than 1.24×10^{-2} M for the film and 1.5×10^{-3} M for the slab, the film and slab will become opaque.

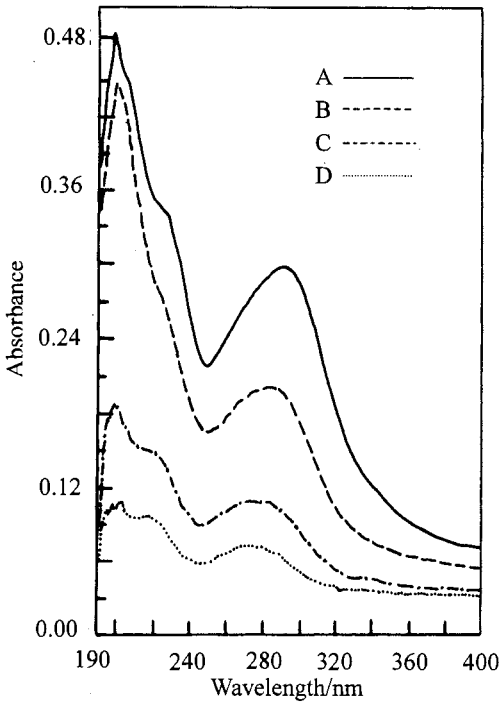

Figure 1. Absorption spectra of TMQ doped silica films

Transmittance of the TMQ-undoped silica film is above 90% in the range of 260–400 nm, which is a little higher than the fused silica substrate. Figure 1 shows the absorption spectra of TMQ doped silica films. The spectra profile is similar to that of TMQ-cyclohexane solution. However, 4–25 nm red shift of the absorption peak between 240–340 nm was observed, comparing with that of the TMQ-cyclohexane solution (266 nm).[7,9] In addition, the presence of several absorption peaks between 200–220 nm, i.e. the peak at 198 nm and peaks between 210–220 nm, can be attributed to the fine absorption structure of TMQ in the SiO_2 environment because these peaks are not seen in the absorption spectra of TMQ-cyclohexane solution.[7,9]

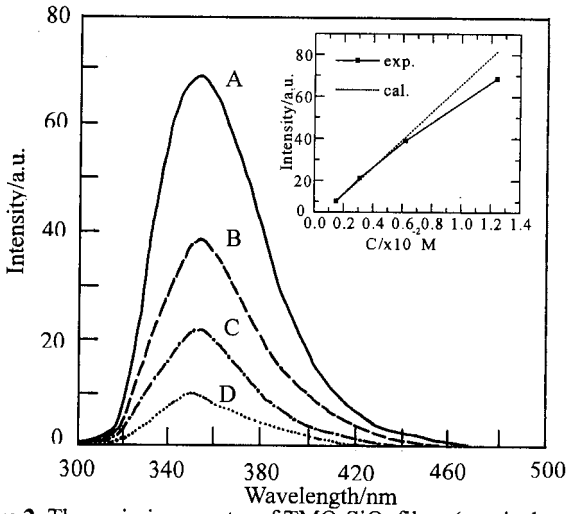

Figure 2. The emission spectra of TMQ-SiO_2 films.(exp.is the experimental curve and cal. is the calculated line).

Table 1. The data of emission spectra of the samples[h]

Sample	λ_{ab}[a] /nm	$A_{296.3}$[b]	λ_{em}[c] /nm	I_{em}[d] /a.u.	I_n[e] /x10^5	I_n/ $A_{296.3}$[f] /x10^5
Film A	291.2	0.296	361.7	68.6	2.9	9.8
Film B	281.8	0.181	359.3	39.0	1.8	9.9
Film C	271.8	0.108	358.7	21.3	0.91	8.4
Film D	270.2	0.060	357.1	10.2	0.46	7.7
Slab E[g]	Broad band	3.00	356.1	414.1	16.8	5.6

[a]absorption peak position. [b]Absorbance at 296.3nm(296.3nm is the excitation wavelength of fluorescence spectra). [c]emission peak position. [d]Intensity of emission peak. [e]Integral intensity of the emission band. [f]ratio of I_n and $A_{296.3nm}$. [g]Thickness of Slab E is 1.3 mm. [h]The thickness of the films are ~700 nm measured by the method of p-polarized reflectances[10].

Figure 2 shows the emission spectra of TMQ-SiO_2 films doped with different TMQ concentrations and the inset figure shows the intensity versus concentration plot. It can be seen from the inset that the intensity increases linearly when TMQ concentration is less than 6.2×10^{-3} M. However, the curve become crooked when the concentration is more than 6.2×10^{-3} M. Therefore it can be estimated that fluorescence quenching happens when TMQ concentration is more than 6.2×10^{-3} M. Table 1 lists the spectra data of the prepared samples. The quantum efficiency of the films can be estimated by the ratio of I_n/A(A is the absorbance under the excitation wavelength of emission spectra), as can be inferred in Ref. 11. The relative quantum efficiency increases with increasing concentration of TMQ when the concentration is less than 6.2×10^{-3} M while decreases as the concentration is up to 1.24×10^{-2} M, indicating concentration quenching takes place. It can also be found that the fluorescence maxima of the films and slab exhibit 6–12 nm red shift, comparing with that of the TMQ-cyclohexane solution (350 nm).[7,9]

The red shift of both absorption and emission peaks of the prepared samples can be illustrated by the polarity of the silica "cage" trapping TMQ molecules. The effect of polar solvent on dye molecules with (π, π^*) transition as their lowest energy transition can be seen in Ref. 5 and Ref. 11. The polarity of the silica cage mainly originates from the Si-OH group (one of the silica groups forming the walls of the silica "cage"). The Kosower Z value is an empirical scale to measure the solvent polarity[12] and Z value of the silica "cage" has been assigned as Z = 88,[1,5,13] which is between that of water (Z = 94.6) and MeOH (Z = 83.6). The main reason that concentration quenching does not happen when the concentration is less than 6.2×10^{-3} M is mainly due to binding effect of the silica "cage". The TMQ molecules were trapped in the rigid silica "cage" and their movements were restricted. Therefore the deactivation process originating from the collision and aggregation of the dye molecules can be avoided. It can be inferred that the pore size of the silica "cage" must be of importance to the nature of the dyes.

The pore size distribution curve for the undoped silica gel was measured by nitrogen adsorption/desorption method with the ASAP2010 physical absorption analyzer. The results show that most of the pore diameters are less than 2.5 nm.

UV-dye TMQ-doped silica film and slab were prepared by sol-gel process with dioxane as cosolvent of the initial solutions. Transparent TMQ-SiO_2 film and slab were obtained with the maxima dye concentrations of 1.24×10^{-2} M and 1.5×10^{-3} M respectively, which are 10-100 times larger than those of the reported UV-dye doped silica glass. Fluorescence quenching was not observed for the films with TMQ concentration less than 6.2×10^{-3} M because of the binding effect of the silica "cage". Due to the polarity of the silica "cage", obvious red-shift of the absorption and emission maxima was observed, comparing with those of TMQ-cyclohexane solution.

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