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The photoluminescence of coumarin derivative encapsulated in MCM-41 and Ti-MCM-41

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Abstract

Coumarin derivative encapsulated in various mesoporous sieves was prepared by impregnation method. The effects of pore size and Ti-containing amounts on the fluorescence properties were investigated. High dispersion of the dye molecules could be realized on the composite of mesoporous sieves, and the electron transfer from the excited dye molecule to titanium oxide occurred in the composite.

Keywords: C_n-MCM-41; Ti-MCM-41; Fluorescence; Decay; Coumarin derivative

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1. Introduction

Fluorescent dyes can be used as a tunable and amplifier laser materials. Dyes within various hosts represented attractive materials for their large fluorescent bandwidths covering the visible spectrum. The type of host will largely determine the characteristics of the laser performance. Dye lasers had been used in solution, but the fluid state was not very suitable for laser application. Therefore, dye lasers had been included in solid matrixes such as minerals [1], polymers [2] and sol–gel hosts [3]. The interactions between dye and solid matrix caused a variety of favorable properties of composites such as large Stocks shift. In addition, the interaction could also make dye molecules lose translational freedom and reduced the rate of dimmer formation. Compared with the above solid matrixes, mesoporous molecular sieves invented by Mobil scientists in 1992 [4,5] were optional hosts for dye molecules due to their high surface to volume ratio and regular pores to anchor the molecules [6].

Coumarin dyes constituted a family of highly fluorescent molecules which had enjoyed widespread use of blue–green laser dyes, optical bleaching agents and as fluorescence probes in a wide range of fundamental photophysical studies [7]. One particular member of this family, the coumarin derivative, 2H-Pyrano[3,2-*g*] quinolin-2-one,6,7,8,9-tetrahydro-4-methyl-coumarin (referred to as CD) was rigidified based on the original structure of coumarin. It has good lasing property and high value in application. The character of CD included in mesoporous material should be worth studying.

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2. Experimental section

2.1. Materials

TEOS (Tetra ethyl orthosilicate) (AR), $C_nH_{2n+1}(CH_3)_3$ NBr (CP), Ammonia (AR) and 15% $TiCl_3$ were all commercial products. Coumarin derivative [8] (CD) was prepared by our lab. Scheme 1 shows its structure.

2.2. MCM-41 synthesis

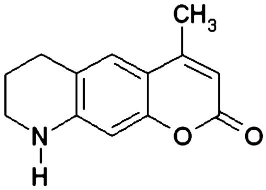
Siliceous C_n-MCM-41 molecular sieves with different pore sizes were synthesized from TEOS and $C_nH_{2n+1}(CH_3)_3NBr$ (n = 12, 14, 16) surfactants. Briefly, each kind of $C_nH_{2n+1}(CH_3)_3NBr$ surfactant was dissolved in 50 ml distilled water and then 30 ml ammonia was added. Following, 10 ml TEOS was dropped into the solution slowly with stirring. This mixture was stirred for at least 2 h. The molar composition of the final gel mixture was $1SiO_2$:0.012surfactant:$8.6NH_3$:$82H_2O$. The resultant gels were crystallized in Teflon-lined autoclaves at 120 °C for 2 days. After cooling to room temperature, the solid products were filtered, washed with distilled water and dried in air for one night. The products were then calcined at 550 °C for 5 h in air.

2.3. Ti-MCM-41 synthesis

Ti-MCM-41 was synthesized by the same procedure used for MCM-41 except that the required $TiCl_3$ was added after the TEOS was dropped completely.

2.4. Preparation of composite samples

All MCM-41 materials were dried at 250 °C in vacuum for 3 h to remove the physisorbed water before introducing coumarin. To encapsulate coumarin derivative, C_n-MCM-41 and Ti-MCM-41 were immersed in 2 ml toluene containing a suitable amount of coumarin. This slurry was stirred and allowed to equilibrium for 24 h, and the solvent was then removed under vacuum.



Scheme 1. The molecular structure of CD.

2.5. Characterization

X-ray power diffraction (XRD) patterns of all samples were recorded on Rigaku D/MAX-2550 diffractometer using CuKα radiation of wavelength 1.541 Å. The fluorescence spectra of all samples were recorded with Cary Eclipse. The decay curves were recorded on Edinburgh FLS920. The lifetimes were calculated from the decay curves by using the least-square method. All the above measurements were carried out at room temperature.

3. Results and discussion

3.1. MCM-41 and TiMCM-41 samples

The XRD patterns of siliceous C_n-MCM-41 molecular sieves with different pore sizes and Ti-MCM-41 with different Ti-doped amount are shown in Fig. 1. All samples showed three distinct peaks, suggesting that the samples have long-range order. Using Bragg's equation and comparing with reference studies [1,2], the pore size of calcined C_{16}-MCM-41 was estimated to be ca. 41 Å, C_{14}-MCM-41 ca. 39 Å, C_{12}-MCM-41 ca. 37 Å and Ti-MCM-41 ca. 40 Å, which are sufficiently large to allow coumarin derivative dye to be encapsulated into their pores.

3.2. Fluorescence of dye in solution

Fig. 2 showed the changes in the fluorescence spectra of dye dissolved in toluene depending on the dye concentration. There was only one peak in the excitation curve of 10^{-5} mol/l. While over the concentration of 10^{-4} mol/l, the main peak of excitation spectrum split into two peaks. The band placed at higher energies was defined as the H-band, and that at lower was defined as J-band [9]. It could also be observed that the intensity of the fluorescence increased when the J-aggregate formed (10^{-4} mol/l), which probably because of the flatness and rigidity of the molecules increased after the emergence of aggregations. And then the intensity decreased progressively with the increase of the dye concentration, which probably could be attributed to the long-range resonance coupling between the excited molecules and non-excited ones [10].

3.3. Fluorescence of CD/C_{12}-MCM-41

Fig. 3 showed the fluorescence spectra of dye encapsulated in the C_{12}-MCM-41 with various dye amounts. It could be observed that, with the increase of the dye content, the excitation band widened and

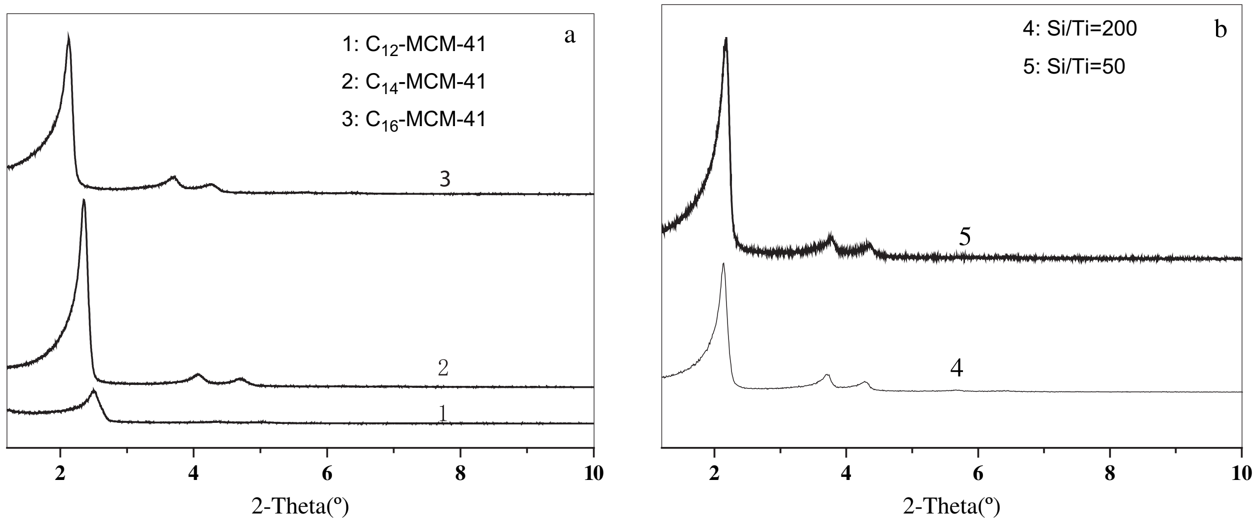


Fig. 1. (a) XRD spectra of MCM-41 prepared with different templates. 1: C_{12}-MCM-41, 2: C_{14}-MCM-41, 3: C_{16}-MCM-41. (b) XRD spectra of MCM-41 with different Ti-doped amount. 4: Si/Ti = 200, 5: Si/Ti = 50.

changed into two peaks like the situation in solution, and the maxima of the emission spectra shift to larger wavelengths from 450.9 nm (0.043 mg/g) to 459.8 nm (430 mg/g). The intensity of emission reached a maximum of 141.5 when the loading amount was 4.3 mg/g and it reduced to 1.3 when the loading amount was 430 mg/g. As the dye content was less than 4.3 mg/g, high dispersion of dye could be realized on the C_{12}-MCM-41 [11], dye existed as single molecules and the coupling of intramolecules of dye was low, which could explain that the intensity increases with increasing dye load. However, when the dye loading was more than 8.6 mg/g, the two clear peaks in the excitation curve indicated the formation of aggregates in terms of the exciton-splitting theory [9], the intensity decreased progressively with the increase of the dye loading, which probably could also be attributed to strong coupling between the excited molecules and non-excited ones. The shift of longer wavelength indicated a participation of the dye molecules in the dipole–dipole interaction with the host which decreased the energy of the electronic states in the dipolar excited state [12].

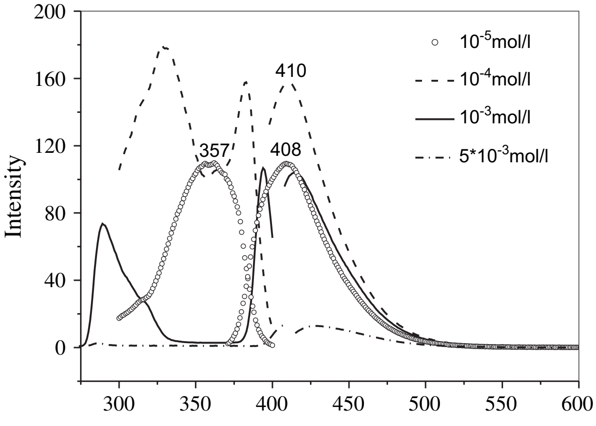


Fig. 2. The fluorescence spectra of different dye concentration in toluene. The left hands were the excitation spectra and the right hands were the emission spectra. The excitation spectra: 1×10^{-5} mol/l: monitor at 408 nm, 1×10^{-4} mol/l: monitor at 410 nm, 1×10^{-3} mol/l: monitor at 415 nm, 5×10^{-3} mol/l: monitor at 424 nm.

From Fig. 3, it could be known that the emission and excitation bands had considerably broadened compared to that in solution. On one hand, the near resemblance in emission bands of dye in the two media indicated that the dye was encapsulated into various MCM-41 without changing chemically. On the other hand, the difference between the excitation bands and emission bands implied that the local environment surrounding the dye molecules were not similar to that in solution. Meanwhile, the emission wavelength shifted from ca. 410 nm in solution to ca. 450 nm in composition. Those phenomena could be rationalized in terms of the stereo effects associated with the pore structure and more-than-toluene polarity of the local environment surrounding the dye molecules [13].

3.4. Fluorescence of CD/C_n-MCM-41

Fig. 4 showed the fluorescence spectra of 0.43 mg/g dye encapsulated in MCM-41 with different pore sizes. The fluorescence wavelength and intensity decreased in the order of C_{12}-MCM-41, C_{14}-MCM-41, C_{16}-MCM-41. From the above conclusion, we knew that the dye molecule existed as a single molecule and the coupling of intramolecules was low. And the contribution of dye molecular interaction to the change of emission spectra could be ignored. Therefore, the

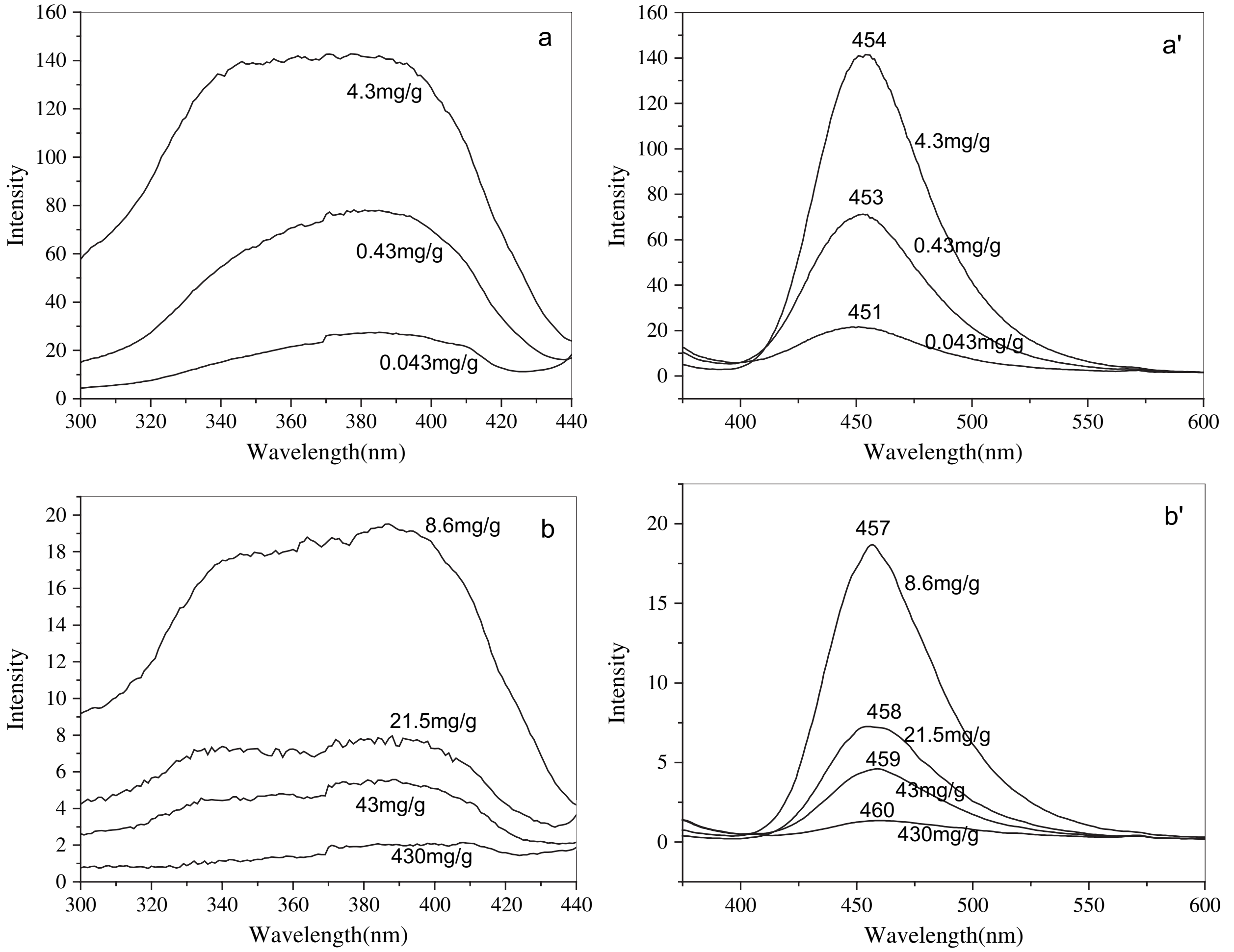


Fig. 3. The fluorescence spectra of dye encapsulated in C_{12}-MCM-41 with different dye containing amounts. (a) and (b), Excitation spectra; (a′) and (b′), emission spectra.

phenomenon probably resulted from the host–guest interaction. Steric restriction of MCM-41 increased as the pore size decreased, which led to stronger dipole–dipole interaction between the host and guest [13]. This may be the reason for the red shift and intensity decrease.

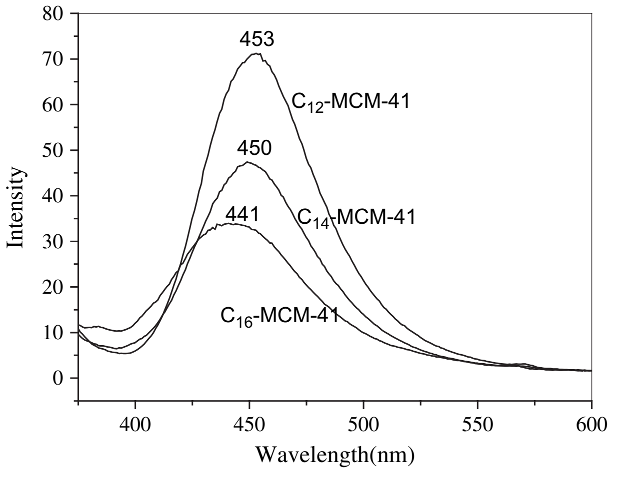


Fig. 4. The fluorescence spectra of 0.43 mg/g dye encapsulated in MCM-41 with different pore sizes.

3.5. Fluorescence of CD/Ti-MCM-41

Fig. 5 showed the dye (4.3 mg/g) encapsulated on various Ti-MCM-41 with different Si/Ti ratios. It could be observed that the fluorescence intensity decreased with the Si/Ti ratio increase. And these fluorescence intensities for CD/Ti-MCM-41 were lower than those observed with CD/C_n-MCM-41 system. At the same time, the fluorescence excitation spectra of Ti-MCM-41 showed only one narrow peak, which indicated that higher dispersion could be realized with the dye/Ti-MCM-41 systems than with the dye/C_n-MCM-41 system [14,15]. In addition, as shown above, the dye molecules in the solution formed aggregation (10^{-4} mol/l), but after impregnation, the dye molecules encapsulated in Ti-MCM-41 changed into monomer, which also indicated the high dispersity of the Ti-MCM-41. Probably, the isolated tetrahedrally coordinated titanium oxide in the mesopores could have a strong

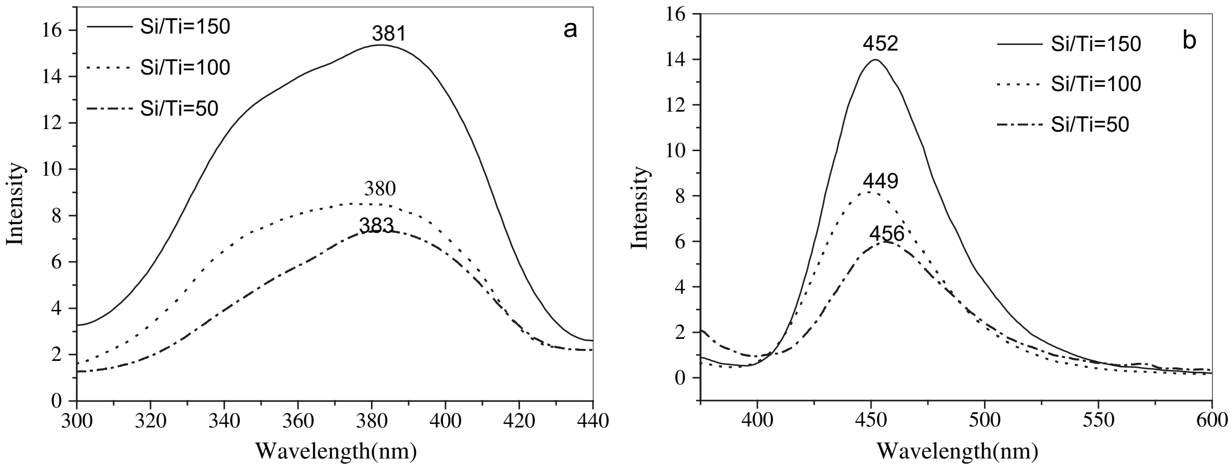


Fig. 5. The fluorescence spectra of 4.3 mg/g dye encapsulated on various Ti-MCM-41 with different Si/Ti ratios. (a) Excitation spectra; (b) Emission spectra.

interaction with CD molecules, which is effective in anchoring CD molecules in a highly dispersed state. Simultaneously, the isolated titanium oxide in distorted tetrahedral framework position acted as an acceptor for the electron and received the electron from the excited dye molecule, which decreased the fluorescence intensity of dye/Ti-MCM-41.

3.6. Fluorescence decay

Fig. 6 showed the fluorescence decay curves of various composites. All the curves displayed a double exponential function, which indicated that the dye molecules were not homogenously adsorbed on the surface of MCM-41. For 0.43 mg/g dye encapsulated in C_{16}-MCM-41 (Fig. 5a), it had two time constants of 1.77 ns (67.16%) and 8.87 ns (32.84%). Its excitation spectrum showed that no aggregation formed on the composite and the dye molecules adsorbed on the external surface could not be excluded. Therefore, it was induced that the longtime probably represented the dye molecules encapsulated in the inner surface of C_{16}-MCM-41 and the short time represented that in the outside surface [16]. In addition, G. Calzaferri et al. [12] had pointed out before that dyes could exist as organized systems in channel-structure sieves, the energy of excited molecules in the channels could be transported to the molecules on the surface, which prolonged the fluorescence lifetime of dyes. The molecules located on the external surface did not experience the energy transfer process, so it had short lifetime. However, 4.3 mg/g dye adsorbed on Ti-MCM-41 of Si/Ti = 150, the time constants of dye molecules on the inner surface was shorter than that on C_{16}-MCM-41, only ca. 4.5 ns. It could verify the explanation ahead that the electron transferred from the excited dye molecules to the

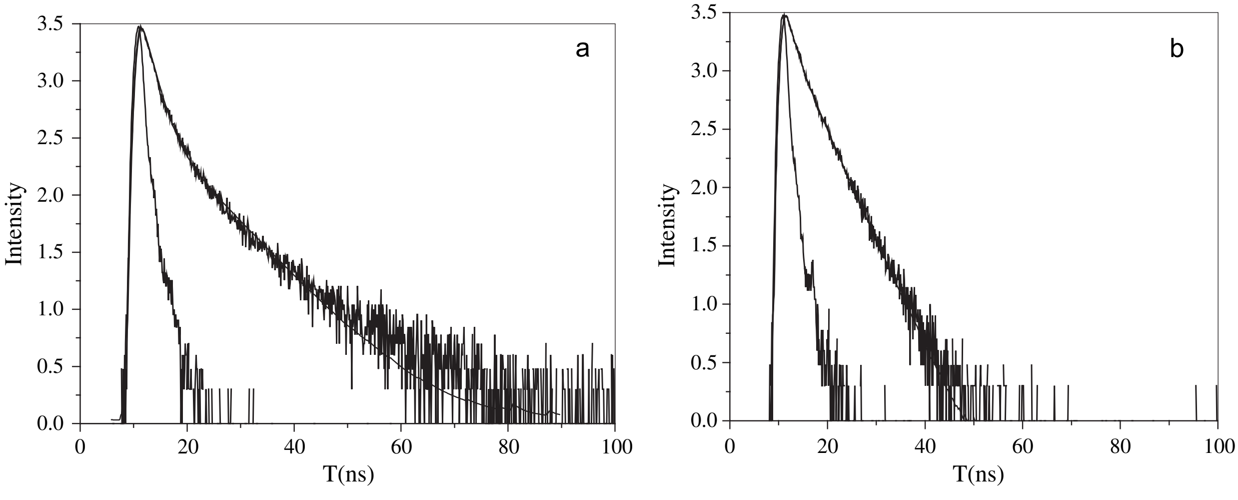


Fig. 6. Fluorescence decay curve observed with the 0.43 mg/g dye on C_{16}-MCM-41 (a), 4.3 mg/g dye on Ti-MCM-41, Si/Ti = 150 (b).

isolated titanium oxide, which quenched the fluorescence of the dye molecules [16].

4. Conclusion

The fluorescence properties of CD encapsulated in various mesoporous sieves were investigated to clarify the effect of the micro-environment on the guest-molecules. It had been found that high dispersion and decrease of aggregation could be realized compared with the properties of dye in solution. When the dye content was lower than 4.3 mg/g, the monomolecule dispersed on both the inner and outside surface of the mesoporous sieves. When the dye content was higher than 4.3 mg/g, the aggregation formed on the C_{12}-MCM-41. The Ti-MCM-41 was an especially useful host for achieving high dispersion of dye molecules. The results showed that the electron transfer from the excited dye molecules to the titanium oxide occurred within the system of CD/Ti-MCM-41.

Acknowledgements

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