

## A Transparent Thin Film with Hexagonal Mesostructure Containing Rhodamine 6G

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**Abstract:** A transparent thin film was prepared by depositing the sol-gel mixture for the synthesis of MCM-41 mesoporous molecular sieve doped with rhodamine 6G (R6G) dye on glass substrates. The film of silica-surfactant-R6G materials, which was identified to possess hexagonally ordered mesostructure, was composed of nanocrystallites about 35 nm in diameter and 1-10  $\mu\text{m}$  in thickness. Cleanness of the substrates, concentration of the sol-gel mixture and rate of evaporation of the solvent were the key factors affecting transparency and homogeneity of the film. Moreover, optical change and lack in dye aggregation were observed to the R6G-functionalized MCM-41 thin film in contrast with that in ethanol solution.

**Keywords:** transparent thin film, MCM-41 mesoporous materials, rhodamine 6G.

Organic dyes are superior to inorganic ones from the points of view of intensity of light absorption and the diversity available. The key problem in application as optical materials is to fix the organic substances into suitable matrixes so that the desirable optical functions might be stabilized. Inorganic glasses are suitable host materials due to the good optical properties, mechanical, thermal and chemical stability. But the high temperature required in glass manufacturing greatly limited the use. Recent development in low-temperature preparation of inorganic oxide-glass, *i.e.* the sol-gel process, opens the possibility to use the inorganic glasses as the hosts for the organic dyes instead of the organic carriers. This means, some dyes have successfully been doped into amorphous glass<sup>1-2</sup>, molecular sieve<sup>3-6</sup> and transparent silica or alumina thin film<sup>7-8</sup>.

In recent years, the synthesis of ordered mesoporous inorganic-based materials, especially MCM-41 by employing supramolecular assembly of surfactant to template the reaction of inorganic species is the subject of considerable research<sup>9</sup>. Since the films might be potentially applied as sensors, optical and electronic devices, to which monolithic samples could not approach, the preparation of thin films have attracted increasing interest<sup>7-8, 10</sup>. In our previous work, the fluorescein dye and rare earth europium complex with thenoyltrifluoroacetone have been encapsulated into MCM-41 mesoporous molecular sieve<sup>11-12</sup>. Here, a transparent R6G/MCM-41 thin film was prepared and characterized.

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## Experimental

Reagent in chemical pure grade were employed without further purification for tetraethoxysilane (abbreviated as TEOS), cetyltrimethylammonium bromide (abbreviated as CTMABr), ethanol, and hydrochloric acid. The organo-silica-surfactant thin film was prepared as follows: The surfactant CTMABr was dissolved in a mixed solution of deionized water and ethanol under an acidic condition ( $\text{pH} < 1$ ) and vigorously stirred for 0.5 h at room temperature. A stoichiometric amount of R6G in ethanol solution was subsequently mixed prior to the addition of the silica source TEOS. The sol-gel mixture obtained with a molar composition of 1 Si: 0.2 CTMABr:  $n$  R6G: 20  $\text{H}_2\text{O}$ : 30 EtOH was allowed to stand for another 2 h and then horizontally coated on a treated standard microscope slide. After slowly evaporating of the solvent at ambient temperature, a transparent R6G/MCM-41 thin film was obtained. Powder X-ray diffraction (XRD) data were collected on a Rigaku D/max-3A diffractometer. High-resolution transmission electron microscopy (HRTEM) images were observed on a JEOL JEM-2010 electron microscope. Scanning electron microscopy (SEM) observations were performed on a Hitachi S-520 electron microscope. And excitation and emission spectra were recorded on a SPEX FL-2T2 spectrofluorimeter.

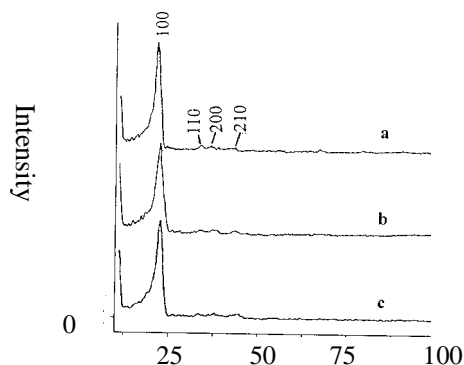
## Results and discussion

For the purpose to determine whether the R6G molecules were encapsulated into the pores or absorbed on the surface of MCM-41 thin film, a comparative dye-leaching experiment was performed according to the reference<sup>8</sup>. The colored film, which was obtained by directly dipping a pure MCM-41 film in an ethanol solution of R6G, promptly became colorless under running ethanol. In contrast, only small part of the dye was leached out from the other film, which was prepared *via* the sol-gel route described above. When peeled off from the slides, quite a few signals belonging to R6G were detected in the latter, but not in the former. This comparative test indicated that the R6G molecules were indeed encapsulated into the channels of the MCM-41 mesophase instead simply absorbed on the surface of the film. According to the supramolecular organization of alkaline and surfactant molecules occurred during the process of forming MCM-41 mesoporous materials<sup>13</sup>, the guest R6G molecules might be present as an additive within the surfactant micelles.

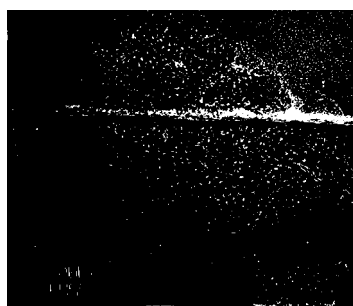
As shown in **Figure 1**, the XRD of the as-prepared thin film displayed a sharp peak along with three defined peaks in the low-angle  $2\theta$  region, which could be respectively indexed with 100, 110, 200, 210 in hexagonal symmetry and the corresponding d-spacing was  $d_{100} = 39.4 \text{ \AA}$ . The profile was characteristic of MCM-41 mesostructure and in close consistent with those reported for the MCM-41 mesoporous materials<sup>4,6</sup>. This mesostructure was further revealed under HRTEM observations (**Figure 2**). The resultant ultrafine particles exhibited a hexagonal set of lattice fringes and a uniform crystal size of about 35 nm. It was easily seen that the sol-gel process offered a promising pathway for the preparation of the inorganic-organic nanocomposite materials or thin films.

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**Figure 1** XRD patterns of the as-prepared films doped with various amount R6G dyes. (a- $1 \times 10^{-4}$  mol/L, b- $1 \times 10^{-3}$  mol/L, c- $1 \times 10^{-2}$  mol/l)



**Figure 2** HRTEM micrograph for the nanocrystallites composed of the film (1cm=35nm).

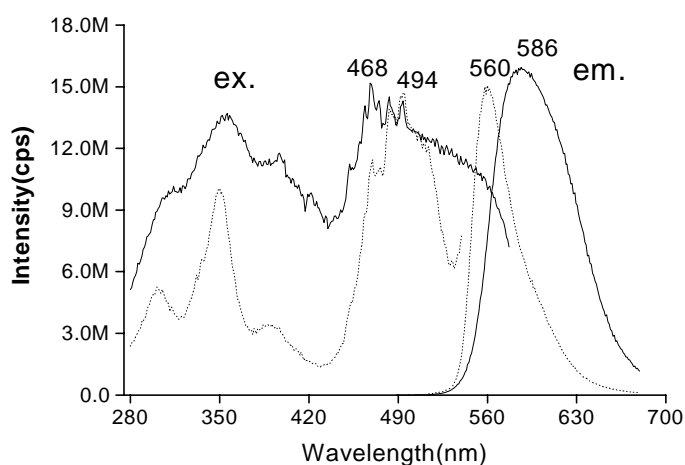


The SEM observations showed that the R6G/MCM-41 thin film was composed with fine particles less than 50nm in diameter and 1-10 $\mu$ m in thickness. The fact that no dye aggregation was noticed on the film indicated that R6G was homogeneously dispersed. Furthermore, it was found that cleanness of the substrates, concentration of the sol-gel mixture and rate of solvent evaporation played a key role during the formation of thin film. With the desirable molar composition described in the experimental section, a transparent and homogeneous film of R6G/MCM-41 was obtained.

As compared to the fluorescence spectra of R6G in ethanol solution (**Figure 3**), the characteristic emission band R6G in thin film has been remarkably broadened and red-shifted for about 26nm (from 560 to 586 nm). Also was the excitation band broadened. As proposed above that the guest R6G molecule was present as an additive within the surfactant micelles, the fluorophore molecular local environment was less polar<sup>7,8</sup> and quite different from that in ethanol solution. Thus the emission maximum of R6G dye considerably red-shifted when encapsulated into MCM-41 thin film. The broadening both in excitation and emission bands implied that the nearest-neighbor structure around the dye was not so simple as the cluster structure of solvation in the solution<sup>2</sup>. There might be a relatively strong interaction between the host MCM-41 and the guest R6G<sup>2</sup>, including Van der Waals force, the confinement and/or shield effect of the inorganic walls on the hosted molecules. It was worth noting that the undesirable concentration quenching caused by the dye aggregation, which was often noticed in

aqueous solution, was also largely hindered even at a concentration as high as  $5 \times 10^{-3}$  M due to the isolation effect of MCM-41 matrix. The luminescent R6G/MCM-41 thin film accordingly exhibited higher fluorescence quantum yield and better laser properties and their application as a photofunctional materials would be promising because of the good optical functions, the simple operation for the preparation, and transparency so on.

**Figure 3** Photoluminescence spectra of R6G dye in MCM-41 thin film (solid,  $\lambda_{\text{ex}}=468\text{nm}$ ,  $\lambda_{\text{em}}=586\text{nm}$ ) and in ethanol solution (dot,  $\lambda_{\text{ex}}=494\text{nm}$ ,  $\lambda_{\text{em}}=560\text{nm}$ ).



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