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The grafting of Rhodamine B onto sol-gel derived mesoporous silicas

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Abstract

Amorphous meseporous silica, silica foams and silica nanotubes have been prepared by the controlled hydrolysis of tetraethoxysilane in various environments. A self-similar structure was obtained in all cases. Rhodamine B was post grafted onto the meseporous silica foam which has been modified with γ-glycidyloxypropyl trimethoxysilane. The grafting and post grafting efficiency of γ-glycidyloxypropyl trimethoxysilane as well as the post grafting efficiency of Rhodamine B on meseporous silica foam were studied, respectively. Basic physicochemical properties of the modified particles are given. When the hybrid pigments were exposed to UV radiation pulses, the emission of the hybrid pigments was increased.

Keywords: Rhodamine B; Dyes; Pigments; Mesoporous material; Silica

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1. Introduction

The unique properties of organic laser dyes offer access to a variety of applications in spectroscopy, optics, and lasers. However, as problem arises in the case of the matrix that is used to host the dye. This phenomenon is not surprising, since the nature of the matrix affects virtually all of the characteristics of the dye. Spectral shifts in absorption or emission, photo stability and fluorescence are all affected. Therefore, attention must be nature of the given to solid matrices used. Powdered materials, colloids, high surface area porous glasses, polymeric thin films and blocks have been used to carry Rhodamine 6G as well as other dyes [1–12].

In contrast, due to its mild nature, the sol-gel process has been widely used for introducing dye molecules into an inorganic network. The inorganic and dye components can be mixed at the nanometric scale in virtually any ratio, leading to the so-called hybrid organic–inorganic nanocomposites. Such hybrids are extremely versatile in their composition and processing as well as optical and mechanical properties. Hybrid optical systems such as non-linear optical devices, solid state lasers and optical sensors have been developed in recent years [13–15].

The rapid development of the sol-gel technique in recent years has directed research towards the synthesis of solids which possess no conventional

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pore structure. Such materials enjoy application as heterogeneous catalysts, shape selective molecular sieving, or bio composites [16].

This paper reports the preparation of a silica matrix prepared by the controlled hydrolysis of tetraethyl orthosilicate in the presence of various organic agents, and its use for the grafting of γ-glycidyloxypropyl trimethoxysilane onto which Rhodamine B was subsequently grafted. The main absorption bands of Rhodamine B were found not to change since dye aggregation was avoided. Sol-gel methodology was chosen due to the mild experimental conditions.

2. Experimental

γ-Glycidyloxypropyl trimethoxysilane (GLYMO), sulfonic acid, DL tartaric acid, Triton X-114, tetraethoxy silane (TEOS), Rhodamine B, and anhydrous methanol were obtained from Fluka. Purity was checked using NMR and monomers were used as received. Deionised water was used throughout, and ethanol was dried over calcium hydride.

2.1. Characterization

The grafting efficiency of Rhodamine B was calculated from thermal gravimetric analysis (TGA), carried out using a Shimadzu System 50 DTA and TGA, respectively. Absorption spectra were measured on a Shimadzu UV 265 spectrometer and FT-IR analysis was performed on a Mattson 1100 FT-IR model spectrometer. Specific surface areas were measured using a static process by means of a Micromeritics ASAP 2010 instrument. The specific surface area was calculated by the BET method and the average pore size was calculated using Barrett, Joyner and Helenda (BJH) method. UV irradiation was performed at 20 Hz with a pulse width of 300 p/s and 250 kW peak power.

2.2. Procedures and methods

2.2.1. Amorphous mesoporous silicate synthesis (AMS)

13.86 g TEOS was dissolved in 8 g of ethanol and 8.26 g of ethylene glycol with stirring at 80 °C in an oil bath. After 1 h of stirring, a mixture of 24 g of ethanol, 6 g of water and a catalytic amount of acetic acid was added to the system. After 3 h of reaction under the same conditions a clear, transparent gel was obtained which was aged at ambient conditions for 2 days and dried in a vacuum oven at 110 °C, before being calcined at 500 °C for 12 h in a flow of O_2.

2.2.2. Preparation of silica nanotubes (MSN)

Silica nanotubes were prepared as previously described [17]. 10.08 g DL-tartaric acid and 30 g of water were dissolved in 2 l absolute ethanol. To this solution was added 365 g of TEOS and the mixture stirred for 5 min. with a magnetic stirrer. The mixture was allowed to stand for 30 min and 1 l of 25% aqueous NH_4OH solution was added. An Opal white gel formed after 1 h which was recovered by filtration, washed with water and dried at 110 °C in a vacuum oven.

2.3. Synthesis of macrocellular mesoporous silicate foams (MSF)

This method was based on a procedure given by Linn and Stein [18]. Triton X-114 (4.58 g) was dissolved in 30 g of water and the pH was adjusted to 1 by adding sulfonic acid. After stirring for 1 h, 13.86 g TEOS was added to the foam and stirring continued until the thick gel was formed. The resulting gel was aged overnight into a petri dish and dried in a vacuum oven at 110 °C.

Finally all samples were calcined at 500 °C for 12 h under an O_2 atmosphere.

2.4. Preparation of GLYMO modified mesoporous silica (MSF-2)

In order to enhance the number of silanol (SiOH) groups that can be used to attach GLYMO to the surface, etching of the above particles (grain size of 2–20 μm) with CH_3SO_3H was performed as described in the literature [19]. Grafting was carried out under a nitrogen atmosphere using different amounts of GLYMO and MSF. In each case 35 g of MSF-2 in 100 ml toluene was added GLYMO in methanol/water 3:10

Table 1
Major characteristics of the silica materials prepared

Silicate	BET surface area (m^2 g^{-1})	Pore diameter (Å)	Pore volume (ml g^{-1})
AMS[a]	305±5	25±12	0.56±01
MSN[b]	29±6	1678±23	0.28±0.1
MSF	896±6	43±2	1.10±0.2
HMSF[c]	932±4	41±4	0.90±0.3

[a] Amorphous silica.
[b] Silica nanotubes.
[c] Hydro thermally treated mesoporous silica foam.

ratio drop-wise to avoid gel formation of GLYMO. To this solution was added ethylenediamine and the pH adjusted to 8.6 or 9.2. The resulting solutions were heated to reflux and stirred for 24 h. The modified particles were then poured off and extracted with methanol in a soxhlet apparatus for 12 h. Finally, the dried particles were dried under reduced pressure at 120 °C for 24 h. The grafting efficiency of GLYMO on MSF was optimized as a function of GLYMO concentration.

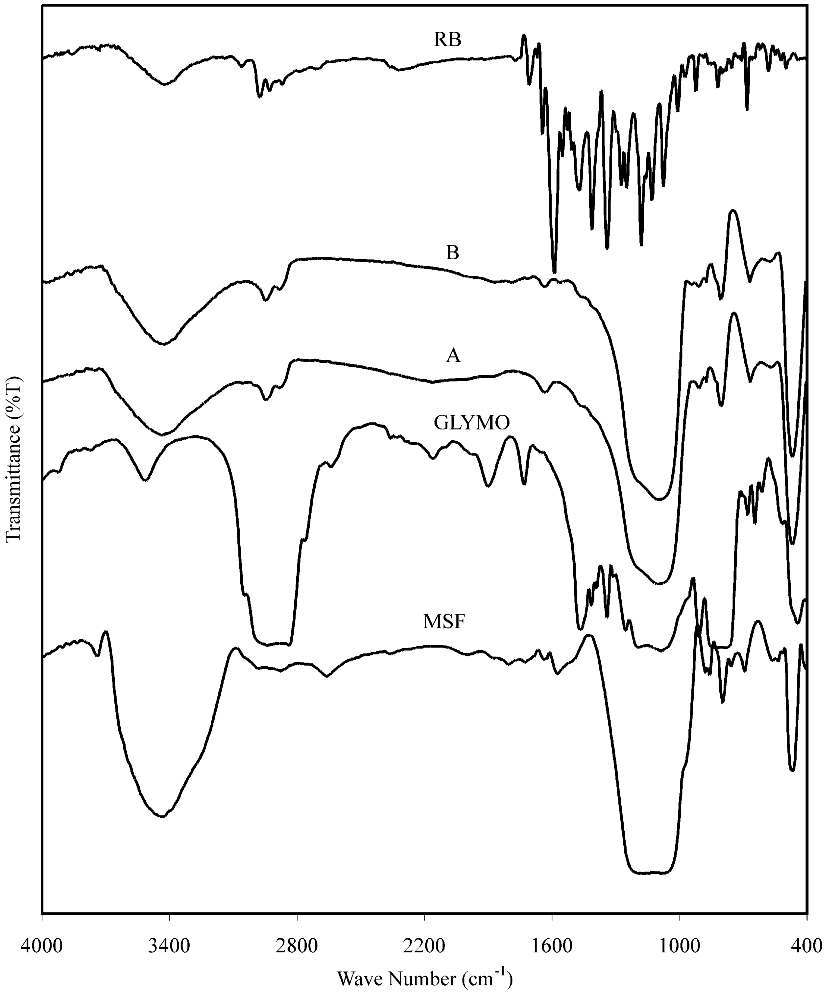


Fig. 1. FT-IR spectra of MSF, glymo, glymo modified MSF-2 (A), Rhodamine B grafted MSF-2 (B), and Rhodamine B (RB).

2.4.1. Procedure for the grafting of Rhodamine B on MSF-2 silicas

The GLYMO modified particles (5 g) were dispersed in 50 ml of DMF and 0.05–0.10 g of Rhodamine B was added under different pH conditions (adjusted by adding CH_3SO_3H); the mixture was heated at 95 °C with vigorous stirring for 20 h. The resulting solid particles were collected by filtration and extracted with methanol and dichloromethane in a soxhlet apparatus for 24 h to remove unreacted dye molecules. The samples were then dried in a vacuum oven at 110 °C for 2 h.

Table 2
The amount of epoxy groups present after grafting with Rhodamine B

Silica	Epoxy groups (mmol g^{-1})[a]	Post grafting (%)	Overall grafting (%)[b]
AMS-2[c]	0.45	2.4	14.6
MSN-1	0.01	0.5	2.1
MSF-2	0.89	3.4	20.1
HMSF-2[d]	1.13	4.6	22.7

[a] Calculated using TGA.
[b] Found by TGA analysis mass loss%.
[c] GLYMO modified AMS.
[d] GLYMO modified HMSF.

3. Results and discussion

The results showed that three different morphological types of silica gels had been synthesized. Completely amorphous silicates were obtained in the presence of alcohols, whereas those originating from DL-tartaric acid and Triton X-114 yielded silica nanotubes and silica foams, respectively. Nonporous silica spheres formation was observed along with nanotube formation. The characteristics of the products are given in Table 1. As expected, the silica foams had the largest and the silica nanotubes the smallest BET area. Pore size distribution calculated using the BJH method indicate that the nanotubes can be considered as essentially macroporous materials, while the majority of the pores of amorphous silica and silica foams fall within a mesoporous range. The

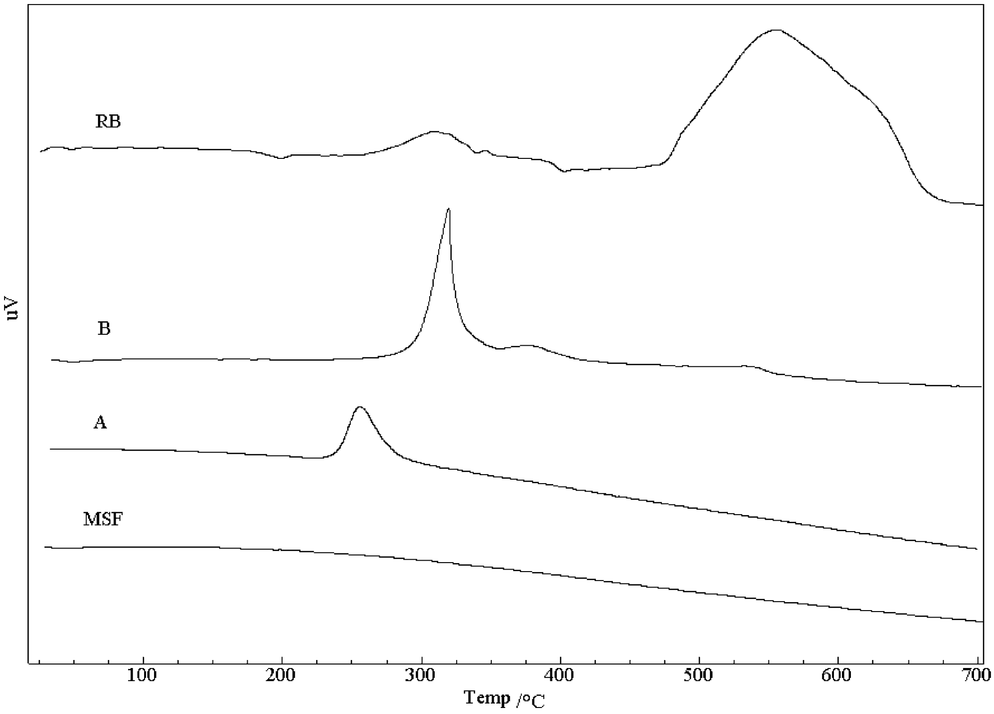


Fig. 2. DTA spectra of MSF, glymo modified MSF (A), Rhodamine B grafted MSF-2 (B) and Rhodamine B (RB).

results obtained were in accord with the results of Kukocevz et al. [20].

The grafting of γ-glycidoxyproyltrimethoxy silane onto a MSF network was investigated using FT-IR, TGA and DTA. In Fig. 1, the FT-IR spectra of MSF, GLYMO modified MSF and GLYMO are given. The CH_2 absorption bands at 2955 cm^{-1} (asymmetric stretching) and 2880 cm^{-1} (symmetric stretching) and 1440 and 1525 cm^{-1} (epoxy) can be clearly observed which are also present as the strongest peaks in the FT-IR spectrum of GLYMO.

Tentative assignments for the spectra of MSF are as follows; 1174 cm^{-1} ν_{as} (Si–O–Si), 1060 cm^{-1} ν (Si–O–), 938, 785 cm^{-1} ν^{s} (Si–O–Si), 620, 550 cm^{-1} ν_{s} (Si–O–Si). Polysiloxanes $[RSiO_{1.5}]_x$, show a broad, structureless absorption covering the entire region of 1160–1000 cm^{-1}. This suggests that GLYMO was successfully grafted onto the MSF surface. The silanol groups (SiOH) on the MSF play an important role in the surface modification process. Silica surfaces can be hydrophobic, as occurs when the surface chemical groups are mainly siloxane (Si–O–Si) groups, or hydrophilic, when contain the surfaces exposed silanol (Si–OH) groups. When silica groups are exposed to water for an extended time hydroxylation can occur.

This produces polymeric chains of Si $(OH)_2$–O–Si $(OH)_2$–OH groups, which can link up in many different ways to form a three-dimensional network or gel. The chemistry and chemical reactions of silica surfaces in aqueous solutions are generally considered within the earlier framework. Therefore mesoporous silica samples prepared in the presence of alcohols resulted in completely amorphous silica gels, in which polymeric chains form a three-dimensional network with hydroxyl groups present at the surface.

TGA revealed that the highest mass loss due to dehydroxlation was 6.4% for hydrothermal treated silica (HMSF), 4.9% for MSF, 0.95% for MSN, and 3.4% for AMS, respectively.

The grafting efficiency of GLYMO onto the prepared silica's is given in Table 2. The amount of Rhodamine B onto the MSF-2 was determined using TGA. Table 2 shows the epoxy group content of silicas after GLYMO grafting.

DTA analysis was performed on MSF, GLYMO modified MSF and Rhodamine B grafted MSF-2. The respective DTA curves are shown in Fig. 2. In the case of the Rhodamine B modified MSF-2, an exothermic effect was observed with a maxima at around 300 and 375 °C. The diffuse peak corresponds to silane decomposition at the surface. No such effects were noted for unmodified MSF; the slight exotherm at 550 °C was observed due to decomposition of the adsorbed silane.

The evidences of the FT-IR, TGA DTA elemental analysis support the successful grafting of GLYMO and Rhodamine B on the surface of MSF and MSF-2, respectively.

The absorption spectra of the laser active dye, Rhodamine B in ethylene glycol that of Rhodamine B grafted MSF-2 suspended in ethylene glycol, are given in Fig. 3.

The optimised structures of the hybrid pigment are depicted in Scheme 1. The absorption spectra revealed that the characteristics of the Rhodamine B were unchanged even after exposure to UV

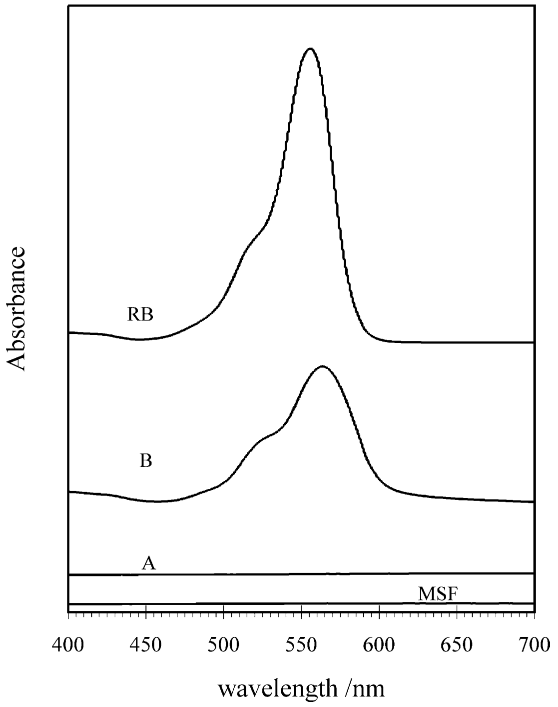
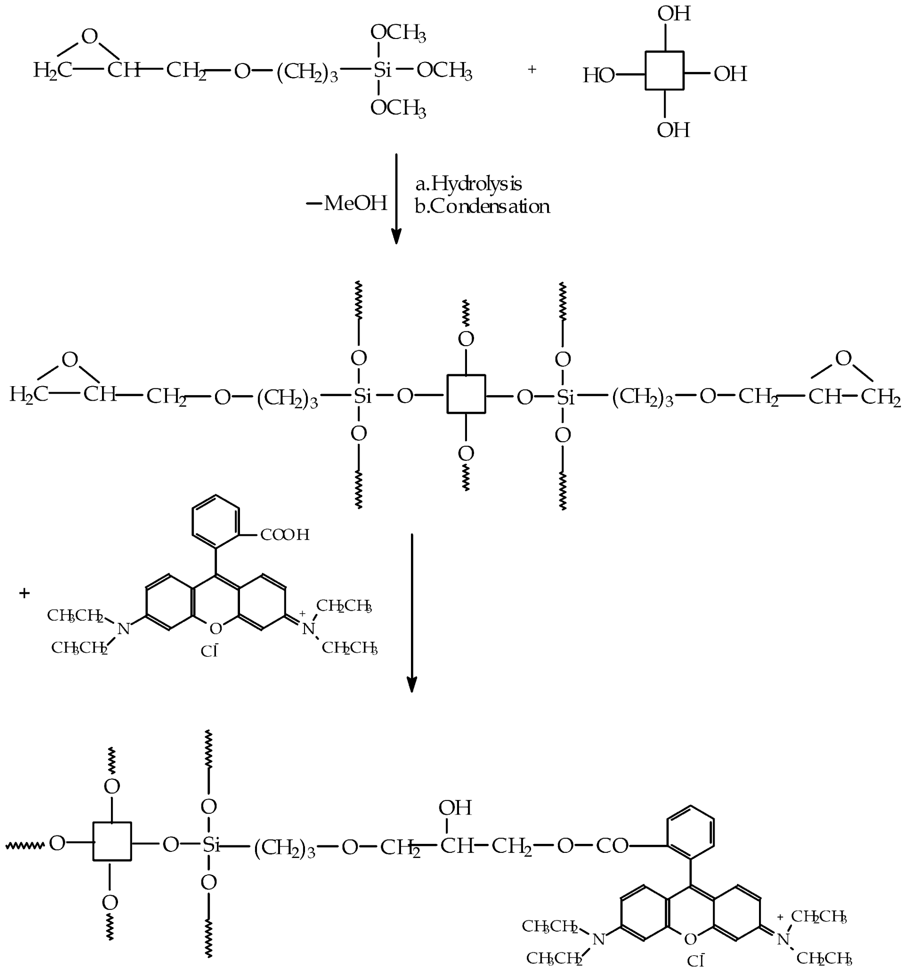


Fig. 3. UV/visible spectra of MSF, glymo, glymo modified MSF-2 (A), Rhodamine B post grafted MSF-2 (B), and Rhodamine B (RB).



Scheme 1. Synthetic route.

irradiation at 20 Hz, pulse width 300 p/s and 250 kW peak power. The absorption peak at 575 nm was enhanced after UV exposure. The electronic energy level common to organic dyes comprises a singlet ground state S_0, a singlet excited state S_1 and an intermediate, long-lived, triplet excited state T_1. $S_1 \rightarrow T_1$ transitions are allowed, but $T_1 \Longleftrightarrow S_0$ transitions are not. Therefore, when light excites the sample, the light is strongly absorbed by the molecules at the surface; two processes occur Firstly, some of the electrons decay to the T_1 level and remain there while others fall to the S_0 ground state and emit light. When UV light is absorbed bonds can be broken so some molecules are no longer active. This mechanism explains the usual photo degradation of laser dyes, which comprises the exponential decay of the emitted light from the dye. Moreover, because the molecules at the surface are either excited molecules in the T_1 state or have been photo degraded, the light can travel deeper inside the sample and find more active molecules, which are capable of emitting light, thus causing emission enhancement. However, as photo degradation continues, the electrons in the T_1 state decay and produce a second maximum. In the case of Rhodamine B, highly delocalised bands (C=C and –CO of –COOH groups) are mainly affected by which UV radiation can be the origin of the photo degradation.

Rhodamine B grafted onto MSF-2 may overcome this phenomena since the translational freedom of the dye is negated and intermolecular collisions prevented. Furthermore, photodecomposion products cannot migrate and therefore cannot facilitate further decomposition. Since the rotational relaxation of the excited state of laser dyes is one of the main modes of naonradiative energy loss [21], the MSF-2 matrix reduces the internal rotational modes to a great extent. Hence, the aggregational and translational collisions that stimulate the deactivation process of the laser dye have been prevented. Thus, the photo stability of the dye is higher than in the sol-gel matrix in which the dye was doped or in solution and also leaching has been overcome.

4. Conclusions

The grafting of Rhodamine B onto an epoxy functionalised matrix offers a suitable medium for hybrid pigment preparation. The characteristics of the dye in the grafted silicas are unchanged after UV irradiation. Morphologically different MSF could be used not only as a host for dye, but also as a matrix in which dye can be embedded. The MSF-2 matrix overcame dye decomposition.

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