

Preparation and optical properties of sol–gel materials doped with coumarin molecules

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Abstract New optical materials containing coumarin (3-(4-(dimethylamino)phenyl)propenoyl)-2*H*-chromen-2-one) in silica are reproducibly prepared by a sol–gel technique and characterized with UV/Vis and luminescence spectroscopy. The incorporation of the coumarin molecules in the silica gels is monitored with UV/Vis spectroscopy. The coumarin doped gels change their color with time which is attributed to a protonation of the dimethylamino group of the coumarin molecules during aging of the gels and is proved by UV/Vis spectroscopy. The process of protonation of the dimethylamino group is described as a second order reaction. The luminescence spectra of the coumarin doped gels at room temperature also are given.

Keywords Coumarin · Sol–gel method · UV/Vis spectroscopy · Luminescence spectroscopy

Introduction

Sol–gel method is used for preparation of porous gel glasses with desirable properties like optical transparency and chemical durability which can be produced at relatively low temperatures [1]. A new challenge of sol–gel

technologies is the preparation of organic modified ceramics (ORMOCER) and hybrid optical materials containing optical active organic molecules and inorganic ions. The organic components in such species are chromophores like dyes, nitroaniline, naphthalenes or coumarins, the inorganic components are *d*- and *f*- ions. In this way the strong absorption coefficients of the organic components are combined with specific emission properties of the inorganic ions. Such materials have demonstrated excellent optical properties: transparency, coloration and high quantum efficiency [2]. Moreover, substances containing coumarin complexes are materials with potential application in human medicine [3].

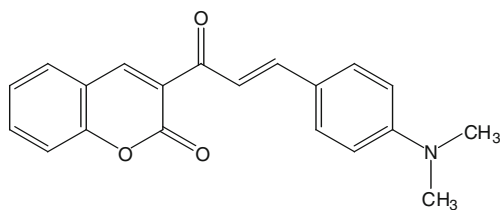
Recently we described the preparation and IR-characterization of SiO₂ gels, doped with Sm(III) ions and 3-(3-(4-(dimethylamino)phenyl)propenoyl)-2*H*-chromen-2-one (K2) for a first time [4, 5]. We demonstrated that the Sm(III) ions form octahedral complexes in the gels containing two K2 and two H₂O molecules. This suggestion was supported by IR and UV/Vis spectroscopy. The optical properties and color change during time of silica gels doped with K2, however, remained open. This paper is a continuation of our recent studies of embedded organic molecules in gel glasses, using sol–gel technology. Now we are describing the preparation and optical properties of gels doped with K2 using UV/Vis spectroscopy as a monitor for physicochemical processes taking place in the gels during aging.

Experimental details

The coumarin (K2), used as a doping compound is synthesized by the described in the literature method [6]. The chemical structure of the organic molecule is visualized on Scheme 1. The orange color of solutions, containing K2

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Scheme 1 3-(3-(4-(dimethylamino)phenyl)propenoyl)-2H-chromen-2-one (K2)

comes from the strong $\pi \rightarrow \pi^*$ electronic transition at about 450 nm due to conjugation of C=C and $N(\text{CH}_3)_2$ groups in the side chain. The solubility of K2 in ethanol is low. The color of K2 in solutions does not change during time proved by UV/Vis spectroscopy. The chemical structure of the coumarin molecule (K2) is shown below.

Large and transparent monoliths were obtained using the procedure shown on Fig. 1. The preparation scheme used is based on the addition of two catalyzing species: HCl for the hydrolysis and NH_3 for gelation. Thus, the overall rate of formation of the monoliths strongly depends on the mole ratio of the two catalysts. The experimentally obtained ratio 6/5 results in a reproducible gelation time of about 30 min, which allows performing coumarin doping under stirring. Higher amounts of NH_3 result in short gelation times in the range of few seconds, lower amounts lead to gelation times in the order of many hours. Monoliths containing coumarins were prepared by following the sequence: TEOS (98%, Aldrich) and absolute EtOH (99.8%, Riedel-de Haën) are mixed together in a 1:1 molar ratio. After homogenization of the mixture were added distilled H_2O in a 1:4 molar ratio and 0.23 M HCl for the hydrolysis. (hydrolysis time 10 min, pH = 2) we got transparent sol which contains one liquid phase. A mixture of 0.14 M NH_3 in a 1:4 molar ratio $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}$ was used to alkaline the solution before adding the coumarin solution. Gelation of monoliths takes place by pouring the sol into covered plastic Petri dishes.

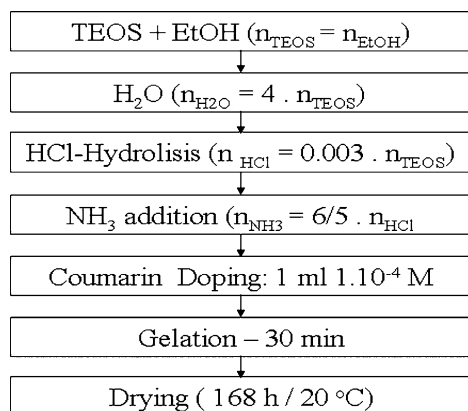


Fig. 1 Preparation sequence of monoliths containing coumarin molecules

They stayed covered for 24 h for gel aging. After aging the covers were removed and replaced by covers with three holes to allow slow solvent evaporation. The area of holes is about 1–2% from the cover area.

After 10 days for solvent evaporation we have stable, crack-free monoliths as can be seen on Fig. 2.

Received samples doped with coumarin are with diameter of 2.5–2.8 cm, thickness of 0.2–0.3 cm and weight of 1.8–1.9 g. They are orange colored, while these without dopand are colorless. The water amount of the gels is about 25%, obtained by weight analysis. SEM images of coumarin doped silica gels are presented on Fig. 3.

UV/Vis spectra were recorded on the monoliths using a Thermo Spectronic “Unicam UV 500” UV/Vis spectrophotometer at room temperature. The luminescence spectra were recorded with Varian “Cary Eclipse” fluorescence spectrophotometer. Scanning electron microscope investigations (SEM) are performed on a standard JEOL 5510 microscope. The samples are amorphous, proved by X-ray diffraction.

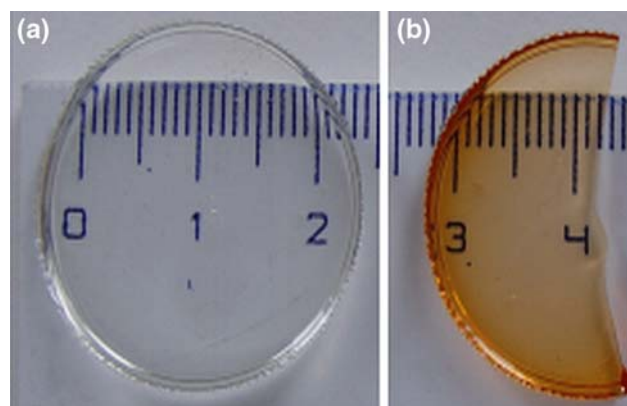


Fig. 2 Photo of **a** gel without modifying; **b** gel, modified with K2 (GK2)

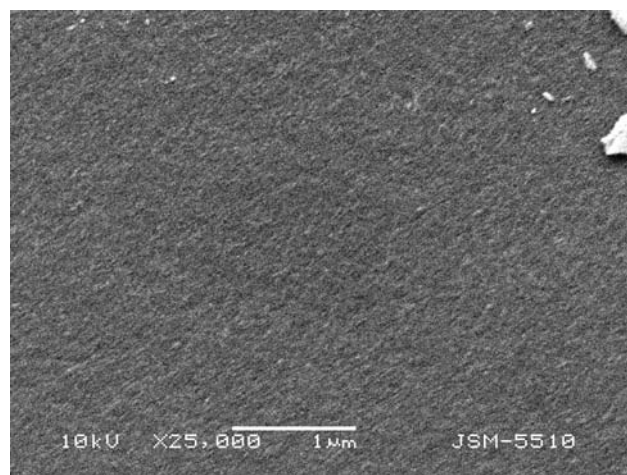


Fig. 3 SEM photograph of gel, modified with K2 (GK2)

Results and discussion

Absorption spectra of K2 in ethanol solutions and sol–gel monoliths are presented on Fig. 4.

The spectrum of SiO₂-monoliths is given for comparison. The monoliths prepared are of good optical quality and are transparent up to 250 nm. The gels display an absorbance at about 0.05–0.1 due to diffuse reflectance, caused by micrometer imperfections. The shoulder at 260–330 nm in non-doped gels comes from lattice defect in the gels [2]. It can be seen that the spectrum of GK2 has a peak at 452 nm due to conjugation of C=C and N(CH₃)₂ groups in the side chain which is responsible for the orange color of the gel. After more than 2 weeks the intensity of the orange color in K2 doped gels decreases significantly though all the samples are kept away from sunlight. This can be seen on Fig. 5 where absorption spectra of the gels at different times are given.

The absorption peaks in the spectra was quantified as overlapping Gaussian curves. The results of the Gaussian analysis for gels containing K2 are given in Table 1, the results are compared to the spectra of K2 in ethanol.

It can be concluded from Table 1 that the optical properties of gels can be explained by well known transitions in organic molecules [7]. In the last column the oscillator strength of the absorption transition is calculated using the expression [8]:

$$f = \frac{4.32 \times 10^{-9}}{C \cdot d} \int A(\tilde{\nu}) d\tilde{\nu} \quad (1)$$

Here, $\tilde{\nu}$ is the wavenumber in cm⁻¹, C is the concentration in mol L⁻¹, d is the thickness of the prepared gels in cm. The oscillator strength of the K2 transitions are changed

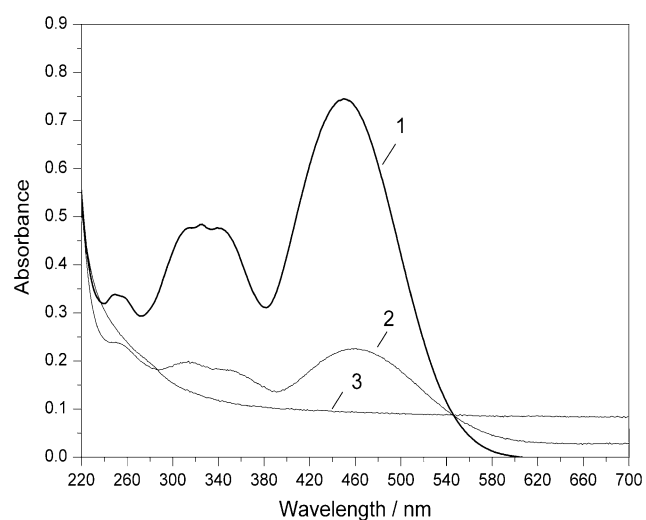


Fig. 4 UV/Vis spectra of (1) 1×10^{-4} M ethanol solution of coumarin (K2); (2) gel, doped with K2 (GK2); (3) gel without modifying

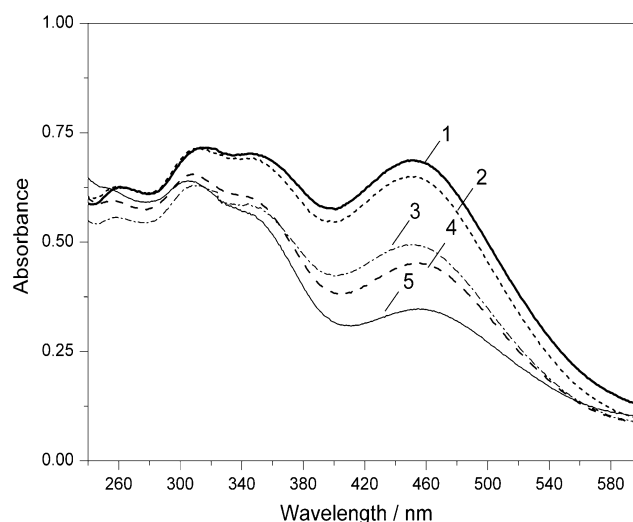


Fig. 5 UV/Vis spectra of GK2. The molar ratio K2/Si = 4.55×10^{-6} . Change of color intensity with time can be seen: (1) after forming of gel; (2) after 5 days; (3) after 8 days; (4) after 15 days; (5) after 30 days

after the coumarin is incorporated in the gel network, which is an indication for effective doping in the silica network of the coumarin molecules using the described preparation scheme. Both in gels and ethanol solution the most intense absorption peak in K2 is the $\pi \rightarrow \pi^*$ (C=C) transition at about 450 nm, the overall absorption of the coumarin molecules increases in gels, especially the coloration transition at 450 nm. The calculated half widths are typical for strong absorption transitions in organic molecules.

The absorbance of the doped gels is proportional to the concentration of the coumarin molecules (Beer's law).

$$A = \varepsilon \cdot C \cdot d \quad (2)$$

In Eq. 2, A is the absorbance, C is the concentration of K2 in mol L⁻¹, C₀ is the initial concentration of K2 in mol L⁻¹, d is the sample thickness in cm and ε the molar absorption coefficient in L mol⁻¹ cm⁻¹. In this way, the absorbance can be used for kinetical analysis of destroying of the coumarin molecules. We found that the protonation of dimethylamino group of coumarin process in gels can be well described as a second-order reaction. The results are fitted with the following equation, combining Eq. 1 and the integrated rate law for second order reactions:

$$\frac{1}{\varepsilon \cdot C \cdot d} - \frac{1}{\varepsilon \cdot C_0 \cdot d} = k \cdot t \quad (3)$$

The experimentally obtained molar absorption coefficient of K2 in solution used for the calculation is $\varepsilon = 19,619$ L mol⁻¹ cm⁻¹. A rate constant $k = 2.56 \times 10^{-3} \pm 3.14 \times 10^{-5}$ L mol⁻¹ s⁻¹ with a correlation coefficient $r = 0.98$ is obtained; C₀ is the initial concentration of K2 in the gels. The exact physical meaning of the rate constant,

Table 1 Absorption spectra of K2 in gels and ethanol solution

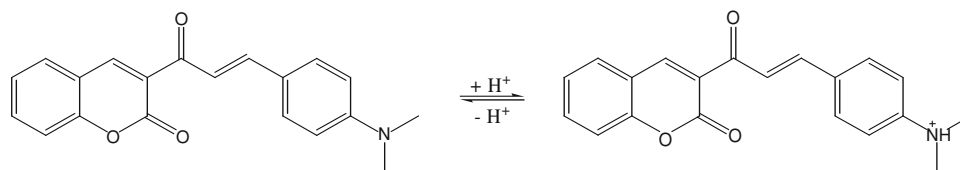
No.	Transition	x_c (cm ⁻¹)	A (cm ⁻¹)	ω (cm ⁻¹)	f
GK2 gel					
1.	$\pi \rightarrow \pi^*$ (C=C)	21996 ± 15	1207 ± 6	4925 ± 30	0.27 ± 0.03
2.	$n \rightarrow \pi^*$ (C=O)	28125 ± 40	45 ± 7	1857 ± 144	0.01 ± 0.001
3.	$n \rightarrow \pi^*$ (C=O)	31914 ± 69	317 ± 10	5268 ± 177	0.07 ± 0.001
1.13 × 10 ⁻⁴ M K2 solution					
1.	$\pi \rightarrow \pi^*$ (C=C)	22059 ± 7	2829 ± 9	3696 ± 14	0.11 ± 0.01
2.	$n \rightarrow \pi^*$ (C=O)	29089 ± 76	1164 ± 45	4065 ± 105	0.04 ± 0.002
3.	$n \rightarrow \pi^*$ (C=O)	32670 ± 72	583 ± 42	3095 ± 75	0.02 ± 0.002

The molar ratio K2/
Si = 4.55 × 10⁻⁶

Abbreviations: x_c peak maxima,
A integrated absorbance, ω full
half width of the peaks, f
oscillator strengths

its relation to the diffusion coefficient of protons in silica gels and to the gel morphology need additional investigations. We also checked the experimental data for zero order and first order reaction but, the correlation coefficient for second order reactions had the highest value.

The reversible protonation of the dimethylamino group of coumarin in solutions can be described by the well known reaction:



In order to check qualitatively this idea we performed the following experiment: equal amounts of 1 M HCl were added under stirring to a 1 × 10⁻⁴ M ethanol solution of K2 and UV/Vis spectra are recorded after the each acid addition. The spectra are given on Fig. 6. It can be seen, that a color change occurs almost immediately with adding the first portion of HCl and at about 30 min later due to HCl addition to the K2 solution the samples are bleached. The initial molar ratio between K2 and HCl is 100:1. The same process takes place in gels, however, with a lower rate. The spectra strongly support the idea that the protonation of the dimethylamino group of coumarin is pH-dependent.

We observed that adding of HCl acid to solution leads to a decreasing of intensity of the peak at 452 nm. The assumed protonation of dimethylamino group results in destroying of conjugation between C=C and N(CH₃)₂ groups in the side chain which is responsible for the orange colour of the gel. The second carbonyl group from the side chain is now free, does not participate in the conjugation and this results in increasing the intensity of the peak at 330 nm ($n \rightarrow \pi^*$, C=O) with adding of HCl acid. Large amounts of acid can destroy the organic molecule.

Figure 6 shows that in solutions the protonation of the dimethylamino group begins with adding of protons. In this

way we conclude that the colour change in the doped gels could also be explained by proton mobility in the gels leading to a protonation of the dimethylamino group of the organic molecules. The protons in gel, coming from the water included in the monoliths, can react with the dimethylamino group of the coumarin molecule. Aging of gels results in improving of the mechanical properties, density increase and water evaporation [1, 2]. Forming of

protonated N(CH₃)₂ group destroys the conjugation of the side chain. The second carbonyl group gets free which results in decreasing of intensity of orange color and increasing of intensity of the peak due to C=O group. Because of the rigidity of the matrix this process can take

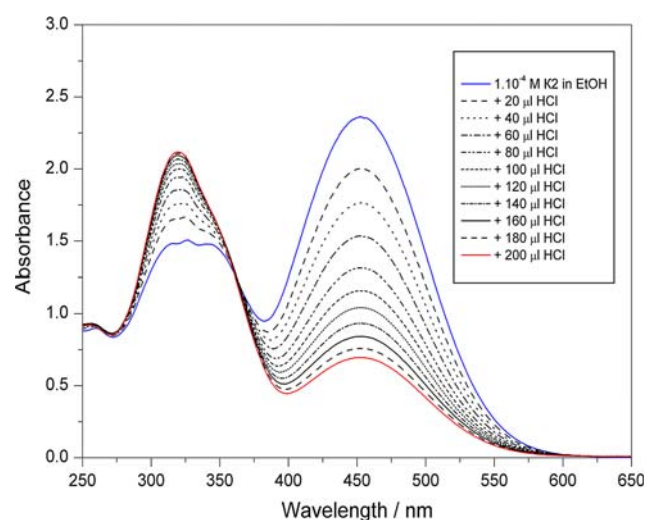


Fig. 6 UV/Vis spectra of 1 × 10⁻⁴ M ethanol solution of K2 under HCl addition. The acid has been added at intervals of 3 min

place if the protons and coumarin molecules are near each other, in the same cavity. The rate, however, is much slower than in solution as it is observed. The result obtained could be a starting point for research activities in order to explain the increased proton concentration in silica gels and their dependence from preparation conditions. Proton mobility is the reason for increased electric conductivity of silica gels obtained via sol–gel techniques [9, 10]. UV/Vis spectroscopy could be monitor for the changes in proton mobility in silica gels during aging using coumarin molecules as an optical indicator.

At 330 nm room temperature excitation the aged coumarin doped gels shows a weak luminescence with maximum at 425 nm ($\pi \rightarrow \pi^*$ C=C transition). A Gaussian deconvolution of the spectra displays two broad emission peaks at 412 nm ($24,272 \text{ cm}^{-1}$) to 461 nm ($21,692 \text{ cm}^{-1}$). Fresh prepared gels coumarin doped, however, do not luminescence due to absorption of the emission [7] (Fig. 7).

At 330 nm the $n \rightarrow \pi^*$ transition of the C=O group or lattice defects in SiO_2 are excited. Thus, the emission described is either a $n \rightarrow \pi^*$ transition or a lattice defect assisted transition. Following the discussion in previous papers [7–10], defects in the SiO_2 like non-bridging oxygen, Si–Si bonds, peroxy-bridges play an important role in the Tb(III) luminescence and in assisting the Ce–Tb(III) energy transfer. A comparison with the optical spectra, published in [11, 12] shows, that the optical transition in K2 partially coincide with spectral lines at 350 and 455 nm, attributed to defect transitions in the silica gels. That role of SiO_2 -defects and their relation to the optical properties remains still open and needs additional experimental and theoretical investigations. The optical spectra presented suggests that the potential applications of gels

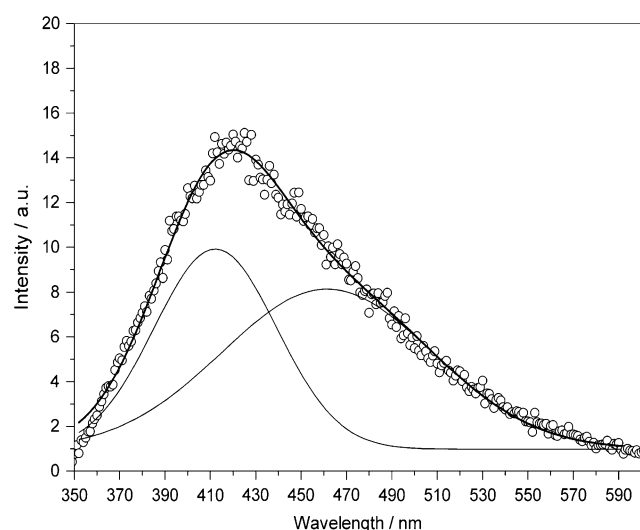


Fig. 7 Room temperature luminescence spectra of gels doped with K2. The results of the Gaussian analysis of the emission spectrum are given. The molar ratio $\text{K2/Si} = 4.55 \times 10^{-6}$

doped with K2 are materials for achieving external efficiencies of silicon solar cells via defect assisted energy transfer [11–14].

Conclusions

The preparation of large crack-free, transparent SiO_2 xerogels doped with coumarin molecules is possible by using a sol–gel preparation scheme based on acid catalyzed hydrolysis, gelation at pH 6.8 and soft drying conditions at room temperature. The peaks in the absorption and luminescence spectra of the gels come from strong C=C and C=O electronic transitions which can be used to convert UV-light into blue emission or to transfer energy to other optically active dopands. Gels change their color intensity with time which is attributed to a protonation of the dimethylamino group of the coumarin molecules during aging of the gels. The process, indicating proton mobility in the gels, can be described as a second order reaction and was easy monitored by UV/Vis spectroscopy.

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