

Optimization of the Intensity of Luminescence Emission from Silica/Poly(ethylene oxide) and Silica/Poly(propylene oxide) Nanocomposite Gels

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Transparent nanocomposite gels have been synthesized by the sol–gel method using hybrid precursors composed of two triethoxysilane groups and a mid polyether chain [poly(ethylene oxide) or poly(propylene oxide)] of various chain lengths. The end silicate groups are linked with the polyether chain through urea bridges (Ureasils). These nanocomposite materials can be visualized as silica nanoparticles dispersed in the organic phase provided by polyether chains. The gels are important room-temperature luminescent materials. Luminescence is the result of delocalized electron–hole recombination processes. The emitting centers are, most probably, located on the surface of silica clusters, where there is a concentration of NH and C=O groups. Larger clusters emit at longer wavelengths than smaller clusters. Precursor molecules tend to aggregate and they also emit luminescence. Gels obtained by hydrolysis in the presence of NH₄F favor larger cluster formation than gels obtained by hydrolysis in the presence of HCl and tend to emit at longer wavelengths. It has been found that luminescence intensity can be increased by modifying two major parameters. Shorter polyether chains give samples with higher luminescence intensity while larger chains cause a dilution effect that acts against luminescence efficiency. Doping with divalent or trivalent elemental cations of large atomic number results in an important increase of luminescence intensity. Heavy cations are then attracted close to the silica cluster surface and enhance luminescence by eliminating surface defects.

Introduction

Hybrid silica–polyether nanocomposite gels, where the organic/inorganic groups are united by urea bridges, thus named ureasils,¹ are important luminescent materials that recently attracted increasing interest. They have been originally synthesized to fabricate solid electrolytes^{2,3} where the covalent bond between the organic ionic conductor and the inorganic backbone would provide materials immune of phase separation⁴ and versatile with respect to their mechanical, optical, and thermal properties. Several structural characteristics of ureasils have been previously studied.^{5–7} They

can be thought in general as nanocomposite blends of organic and inorganic domains that form interpenetrating networks.⁶ Ureasils have been used as optical materials, namely, as host matrixes of lanthanide ion emitters.^{8–10} However, undoped gels are broad band photoluminescent materials by themselves that can be used as a new class of phosphors. In a recent publication by Carlos et al.¹ (see also a rich collection of related references therein), the following model has been presented as the origin of the observed luminescence in ureasils. As in the case of other silicon-based materials, electron–hole recombination processes, involving strongly correlated electron–hole exciton states, or radiative

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tunneling between localized states of electrons and holes may be the mechanisms responsible for luminescence emission. The localization and delocalization of states depend, of course, on the σ -conjugation of the silicon networks.¹ However, Carlos et al.¹ did not exclude the possibility of contribution of C=O and N-H groups of the urea cross-linkage bridge to the emission-spectrum characteristics. Similarly, in another class of silicon-based phosphors, introduction of carbonyl groups in the Si-O-Si network is considered responsible for the luminescence of silicate-carboxylate sol-gel hybrids.¹¹ Also, in still another case of a silicon alkoxide with a grafted propylamino group, gel formation by interaction with organic acids produces highly luminescent phosphors, where the amino group functionality is well distinguished.¹² It is a matter of fact that more work needs to be done in order that several questions related to these materials will be answered, so that the optimization of their emission characteristics will be advanced to a point where they will meet the applications they deserve.

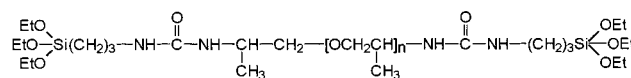
In the present work, we have exclusively studied the room-temperature luminescence of six different ureasils based on poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) chains of three different chain lengths each. We have thus examined the influence of the size of the organic groups on luminescence emission intensity and spectral structure. In addition, and this, to the best of our knowledge, has been done for the first time, we have examined the effect of the presence of positive ions of different valencies on luminescence characteristics. Indeed, in the course of studying the properties of terbium(III)-doped ureasils,⁸ we have found that the presence of the positive ion has an effect on the proper luminescence intensity of the gel. Thus, enhancement of luminescence intensity was observed in the presence of several cations. Finally, some additional parameters affecting structural evolution, such as pH of the precursor solutions, have also been examined in relation to the gel luminescence emission characteristics.

Experimental Section

Materials. Poly(propylene glycol)bis(2-aminopropyl ether) of molecular weight 4000, 2000, and 230 (2APPG-4000, 2APPG-2000, and 2APPG-230, Aldrich), *O,O*-bis(2-aminopropyl)poly(ethylene glycol) of molecular weight 1900, 800, and 500 (2APEG-1900, 2APEG-800, and 2APEG-500, Fluka), 3-isocyanatopropyltriethoxysilane (ICS, ABCR Chemicals), metal salts (Eu(NO₃)₃·5H₂O, Tb(NO₃)₃·6H₂O, Nd(NO₃)₃·6H₂O, Ce(NO₃)₃·6H₂O, Cr(NO₃)₃·9H₂O, Cd(NO₃)₂·4H₂O, Zn(ClO₄)₂, Cu(ClO₄)₂, InCl₃, LiClO₄, NaCl, Aldrich), and methanol and ethanol (spectroscopic grade, Merck) were used as received.

Synthesis of Hybrid Precursors. Six different unhydrolyzed hybrid silicon precursors were prepared basically using the preparation procedure of Dahmouche et al.¹³ who made poly(propylene glycol) (4000) and poly(ethylene glycol) (800) modified ethoxysilanes. 2APEG or 2APPG with different chain lengths and ICS (molar ratio [ICS]/[diamine] = 2) were mixed in tetrahydrofuran (THF) under reflux (64 °C) for 6 h. The isocyanate group of ICS reacts with the amino groups of 2APPG or 2APEG (acylation reaction) producing urea-con-

PP 4000/2000/230(n ~ 68, 33, 3)



PE 1900/800/500(n ~ 43, 18, 12)

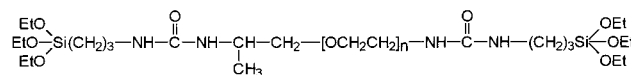


Figure 1. Chemical structure of the PPO- and PEO-containing precursors.

necting groups between the polymer units and the inorganic part. After evaporation of THF under vacuum, a viscous precursor was obtained, which is stable at room temperature for several months. We prepared similar hybrid precursors modified by both types of polymers with three different chain lengths for each type [poly(oxypropylene): 4000, 2000, and 230; poly(oxyethylene): 1900, 800, and 500]. The respective abbreviated names used in the present work are PP4000, PP2000, and PP230 for the poly(oxypropylene)-containing precursors and PE1900, PE800, and PE500 for the poly(oxyethylene)-containing precursors. The chemical structure of the precursors appears in Figure 1.

Sol-Gel Synthesis. Then, 4.5 g of precursor was mixed with 15 mL of methanol. After the mixture was stirred for 5 min, 0.5 mL of 0.1 M HCl was added and the resulting mixture was stirred for 30 min more. In the case of weak base-catalyzed hydrolysis, 0.04 M NH₄F was used in the place of HCl. After stirring, the fluids were put in uncovered square PMMA cuvettes and left to dry in air for 1 week. Dopants have been introduced by previous solubilization in methanol.

Experimental Methods. Measurements were performed at 20 °C. Absorption measurements were made with a Cary 1E spectrophotometer. Steady-state fluorescence measurements were made with a home-assembled spectrofluorometer using Oriol parts. Time-resolved fluorescence decay profiles were recorded with the single-photon-counting technique using light pulses provided by Synchrotron radiation (Super-ACO, LURE, Orsay, France).

Results and Discussion

Luminescence Spectra Characteristics of Hybrid Precursors and Nanocomposite Gels. Five of the monomers used in the present work are fluids except for PE1900, which is solid. These monomer fluids are luminescent. Figure 2 shows a typical luminescence spectrum of the PE800 monomer obtained at four different excitation wavelengths. Excitation at 340 nm gives the most intense luminescence peaking at 394 nm. The precursor solution consists of three well-distinguished emitting species peaking at 394, 418, and 458 nm. Changing of the excitation wavelength allows one to clearly distinguish them. Indeed, as seen in the inset of Figure 2, the three emitting species also correspond to three separate excitation spectra. The precursors undergo a slow ripening process so that samples several months old do not emit the 394-nm luminescence but their spectra contain only the 418- and 458-nm species. All monomers are soluble in several organic solvents. When the monomers are in solution, their luminescence completely disappears. We have performed light-scattering measurements in ethanolic solutions of the PE800 monomer and the results can be seen in Figure 3. The data show that in the absence of ethanol the monomers are aggregated with an apparent hydrodynamic radius R_H of 189 Å. R_H decreases fast in the

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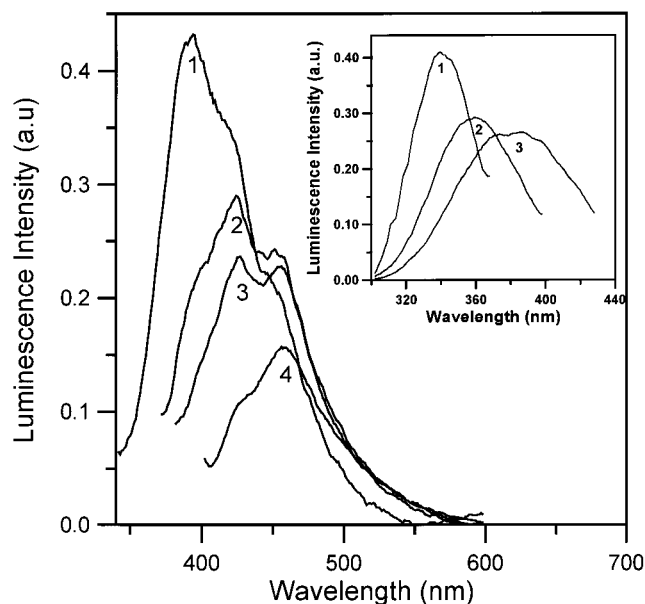


Figure 2. Luminescence spectra of the PE800 precursor. Excitation wavelength: (1) 340 nm; (2) 360 nm; (3) 370 nm; and (4) 390 nm. Spectral height was corrected for the lamp intensity at the four different wavelengths. Inset: Excitation spectra of the PE800 precursor. Emission wavelength: (1) 394 nm; (2) 418 nm; and (3) 458 nm.

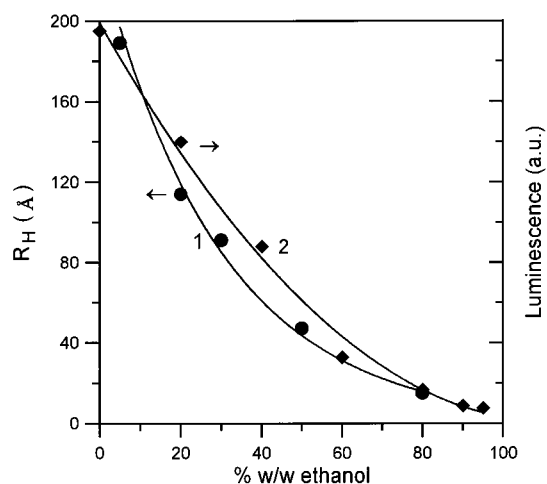


Figure 3. Apparent hydrodynamic radius R_H (1) and luminescence intensity (2) of the PE800 precursor aggregates in ethanol vs. weight percentage of solvent.

presence of alcohol and tends to zero at low precursor concentration, while a parallel decrease was also observed for luminescence intensity as can also be seen in Figure 3. A similar behavior was also observed for the rest of the precursors. Aggregation of monomers in precursor fluids could be due to two major reasons: (1) partial hydrolysis by atmospheric humidity and inorganic polymerization (Si–O–Si); (2) association of polymer chains induced by the difference in polarity between the apolar end silicate groups and the polar middle polyether chains, leading to organizing the material in alternating silicate-rich domains, covered with NH and C=O groups, and polyether-rich domains. Some limited inorganic polymerization, nondetectable by the presently used methods, cannot be excluded. However, it is hard to imagine that such strong bonds as Si–O–Si could be almost all destroyed by solubilization in ethanol. Dry gels are not soluble, anyway. For this reason,

Table 1. Variation of Luminescence Intensity (a.u.) in Both Precursors and Dry Gels with Respect to Polyether Chain Size

material	exc. wl. 340 nm	exc. wl. 390 nm	exc. wl. 360 nm
Precursors			
PP230	1270	470	
PP2000	799	179	
PP4000	508	45	
PE500	998	384	
PE800	857	299	
PE1900	678	176	
Dry Gels			
PP230			1140
PP2000			387
PP4000			208
PE500			897
PE800			698
PE1900			341

aggregation due to hydrophobic/hydrophilic balancing, in the general sense of the term, is responsible for monomer aggregation. Concentration of silicate groups in the same domain and of the attached urea groups on its surface creates conditions for luminescence emission. The mechanism of luminescence emission is obviously delocalized electron–hole recombination processes. This is concluded by the following observations: (1) Luminescence is not detected in diluted samples. (2) Luminescence is cluster-size-dependent (cf. Figure 2). Thus, mature precursors give higher apparent hydrodynamic radii and higher emission wavelengths. (3) The decrease of luminescence intensity in the presence of alcohol is not stoichiometric. And (4) when precursors are diluted in ethanol, long-wavelength luminescence is quenched faster than short-wavelength luminescence.

When the ether chains increase in size, both silicon and urea groups are essentially dispersed in an organic solvent. Dilution, apparently, increases defects on emitting clusters, thus also increasing luminescence quenching possibilities. Indeed, as seen in Table 1, an increase of poly(oxypropylene) or poly(oxyethylene) chain size resulted in decreasing luminescence intensity.

The dry gel obtained from the precursor solution, after sol–gel polymerization and drying, produced the spectra of Figure 4. These spectra are almost the same as those obtained with mature precursors. This means that similar recombination mechanisms take place in both silicate/urea-rich domains, held together because of hydrophilic/hydrophobic balancing and in silica/urea-rich domains, held together by inorganic Si–O–Si polymerization. It is then tempting to adopt that because the NH and C=O groups are common to the two situations; they are the most important factors providing states for delocalized electron–hole recombination and luminescence emission. Dry gels and mature precursors are, of course, expected to contain larger nanoparticles than the fresh precursor fluids. It is obvious that the emission wavelength is closely related to cluster size. This is expected for luminescence ensuing from electron–hole recombination processes and it is systematically observed also with other silicon-based materials¹² as well as with other luminescent semiconductors.¹⁴

The conclusion of this paragraph is then that the luminescence of both dry nanocomposite gels and pre-

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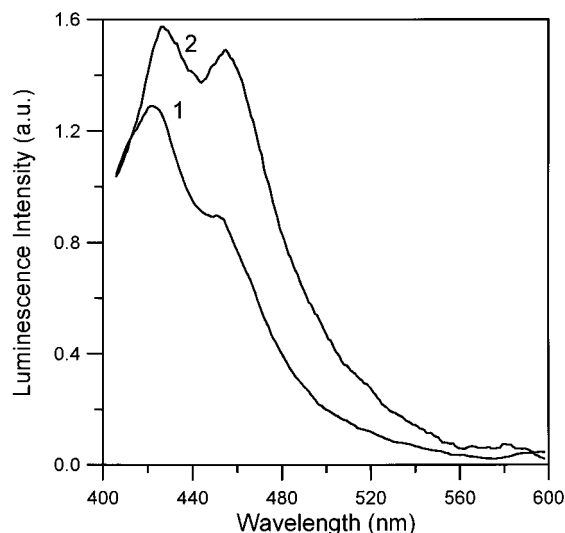


Figure 4. Luminescence spectra of the PE800 nanocomposite dry gel by excitation at 360 nm. Gel obtained by (1) acidic and (2) weak basic hydrolysis.

cursors originates from the urea-rich surface of silicon-containing clusters. The facility of formation of these clusters has an immediate consequence on luminescence intensity. The size of the clusters reflects on the emission wavelength. All the results are compatible with mechanisms involving electron-hole recombination processes, which are sensitive to cluster size.

Effect of Polyether Chain Size on Luminescence Intensity of the Gels. Table 1 presents a comparison of the luminescence intensity of the six dry gels made in the present work. It is noted that there exists a systematic decrease of luminescence intensity when the chain size increases. This is true for both PPO- and PEO-containing gels. Apparently, the dilution effect observed with precursors remains valid also in the case of final gels. The formation of luminescence centers in such materials is obviously primarily dependent on polyether chain size, that is, on organic volume fraction. We believe that when the organic volume fraction is excessively large, then the emissive clusters have a hard time forming themselves or they are formed with defects that tend to quench luminescence emission. Indeed, ²⁹Si CP-MAS NMR spectra previously reported¹⁵ have monitored the development of condensation of the silicon alkoxides and the formation of silica nodes, which act as cross-linking units of the polymeric network. Samples obtained from PEO precursors presented a condensation degree around 90% while those obtained from PPO precursors had a condensation degree varying from 80 to 70%. In this respect, the structure of the gel could be visualized according to the model presented in ref 7. Most of the material consists of an organic domain with spatial uniformity where small silica clusters are dispersed. Detection of only two emitting species suggests that size polydispersity is rather limited and at any rate much more limited than that observed in other cases.¹²

Effect of Solution pH on Gel Structure and Luminescence Spectra Characteristics. Figure 4 shows two luminescence spectra corresponding to gels obtained by hydrolysis of PE800 under acidic or weak

Table 2. Relative Luminescence Intensity and Luminescence Decay Times of PE800 Gels Doped with Elemental Cations (The Salt Concentration in the Original Sol Was Fixed at 10 mM (1 Ion per 170 Si Atoms or Urea Groups))

cation	relative luminescence intensity	decay time (ns) exc. wl. 325 nm em. wl. 418 nm	decay time (ns) exc. wl. 405 nm em. wl. 458 nm
no dopant	1.0	6.2	8.1
Li ⁺	1.0	6.1	
Na ⁺	1.0	6.2	
Cu ²⁺	1.2	6.2	8.2
Zn ²⁺	2.3		
Cd ²⁺	2.9	8.2	9.9
Cr ³⁺	1.1		
In ³⁺	1.5		
Ce ³⁺	1.7	6.0	
Nd ³⁺	1.7		
Eu ³⁺	1.9	8.0	
Tb ³⁺	2.2	8.4	10.1

basic conditions. In the second case we have observed that the long wavelength emitting species are more numerous than those in the case of acidic hydrolysis. In relation to the above, it is obvious that larger silica clusters are formed under weak basic hydrolysis conditions. The intensity of luminescence did not significantly differ in going from acidic to basic hydrolysis. Similar results have been obtained with all six studied precursors. It is then concluded that the ratio between the organic and inorganic volume fraction is the most important factor affecting luminescence intensity.

Enhancement of Luminescence Intensity in the Presence of Heavy Cationic Dopants. An interesting feature of the above materials is the enhancement of luminescence in the presence of some elemental cations. When several metal salts were dissolved in the original sols, we obtained gels that emitted enhanced photoluminescence. The most successful dopant was Cd²⁺, but lanthanide ions were also important. Table 2 shows relative luminescence intensities obtained with several doped versions of PE800. The structure of luminescence spectra did not change in the presence of dopants. The emitting species were again found at 418 and 458 nm, each well distinguished from the other by both steady-state and time-resolved analysis. Columns 3 and 4 of Table 2 show luminescence decay times of the two emitting species. The longer wavelength emission has also a longer decay time. This is true for both undoped and doped samples. This behavior is frequently observed also with other semiconductor nanoparticles, a characteristic example being CdS.^{14,16} Longer decay with larger clusters was also reported in ref 1. The decay times became longer in the presence of dopants, in the same direction as the increase of luminescence intensity. Monovalent ions did not at all affect luminescence intensity. Divalent ions had a large effect in the case of large elements while almost all trivalent rare earth ions significantly affected luminescence intensity. It is expected that multivalent ions will complex monomer chains through ether groups facilitating cluster formation.¹⁷ This may act in favor of luminescence intensity. It seems, however, more plausible to accept that cations may be attracted not only to ether oxygens but also to

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urea groups and silicate oxygens where negative charges are accumulated. The presence of cations at the surface of silica/urea clusters will cure surface defects, decreasing quenching processes and resulting in luminescence enhancement. A similar phenomenon has also been observed in the luminescence behavior of II–IV semiconductors, for example, ZnS.^{18,19} A preliminary FTIR study of nanocomposite gels in the presence of cations has revealed perturbations of the vibration modes of all involved groups, that is, ether oxygens, urea modes, and Si–O modes, giving shifts to lower wavenumbers. Perturbation of ether oxygens are more important for short PEO and PPO chains. The interesting result is that monovalent cations do not produce any detectable effect while the most extensive perturbation was observed in the case of Cd²⁺. This matter is being further studied in our laboratories.

Conclusions

Ureasils emit room-temperature luminescence both as precursor hybrid materials and as nanocomposite

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gels obtained through hydrolysis/condensation by the sol–gel method. Luminescence is the result of delocalized electron–hole recombination processes on the surface of silicon-containing clusters where there is a large concentration of NH and C=O groups. The luminescence intensity of ureasils is larger in the case of smaller polyether chains. The luminescence intensity can be increased by introducing large divalent or trivalent cationic species in the nanocomposite gels. These species solubilize themselves at the surface of the emitting centers and most probably enhance luminescence by eliminating surface defects.

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