

PHOTOLUMINESCENCE STUDIES ON HYBRID ORGANIC/INORGANIC NANOCOMPOSITE GELS

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ABSTRACT

Luminescent transparent organic-inorganic matrices have been synthesized by the sol-gel method and by using ureasil precursors. Photoluminescence is emitted by pure matrices and by matrices doped with lanthanide ions or semiconductor nanoparticles. These combinations provide interesting materials which can produce photoluminescence with a great variety of color choice.

1. INTRODUCTION

During the recent years, one of the most attractive fields in the development of new high-technology materials is the chemical design of 'hybrid organic-inorganic' nanocomposites¹⁻⁵. Among the different synthetic methods used for this purpose, the sol-gel method presents advantages as it allows the mixing of organic and inorganic components at the nanometer scale. Silicon alkoxides are the most popular precursors for inorganic polymerization by this method, where the alkoxide, first, reacts with water in the presence of an acidic or basic catalyst and then the reaction is followed by condensation through -O-Si-O-network formation⁶. In the last years, numerous silica based hybrid organic/inorganic materials have been synthesized via this method with many interesting mechanical, optical and thermal properties^{3,7}.

Silica/poly(ethyleneoxide) and silica/poly(propyleneoxide) nanocomposite hybrids have been synthesized from ureasil precursors via the sol-gel method and among other interesting properties, exhibit an intense room-temperature luminescence⁴. Ureasils are hybrid precursors composed of two triethoxysilane groups and a mid polyether chain [poly(ethyleneoxide) or poly(propyleneoxide)] of various chain lengths. The end silicate groups are linked with the polyether chain through urea bridges (Ureasils). They are almost full colored luminescent materials lacking metal activator ions which can be used as a new class of phosphors. Moreover, the sol-gel method offers the opportunity to introduce into these materials both inorganic and organic chromophores such as lanthanide ions, semiconductor nanoparticles or organic dyes⁷. Recent results have shown that all these sol-gel derived hybrids can be synthesized either by the conventional sol-gel method or by carboxylic acid solvolysis of the alkoxides in the absence of water^{8,9}, where they exhibit higher photoluminescence quantum yields.

In the present work, we have studied the room-temperature luminescence of a silica/poly(ethyleneoxide) nanocomposite hybrid derived from carboxylic acid solvolysis of the precursor ureasil material before and after the incorporation of Eu^{3+} ions and CdS nanoclusters. Doped hybrids could offer a wide range of optical applications such as luminescent displays, solid-state lasers, labels for time-resolved fluorometric assays and amplifiers for optical telecommunications⁷.

2. EXPERIMENTAL SECTION

All materials of the present work were purchased from Aldrich or Fluka and were used as received. Ureasil precursors were synthesized as described in previous publications⁴. Inorganic polymerisation was realized by acetic acid solvolysis in the absence of water by the following procedure: 0.5g of the hybrid precursor material was dissolved in 3mL of ethanol. Then, glacial acetic acid was added into the solution under stirring at a molar ratio of ureasil/acetic acid=1/10. After 30 minutes stirring, the mixture was poured in 1-cm square PMMA cuvette where was left to dry in air. Gelation was obtained in two weeks.

$\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ has been incorporated in the final matrices by previous solubilization in ethanol. The overall original concentration for the Eu^{3+} was 10mM. CdS nanoclusters have

been synthesized by arrested precipitation of CdS in hybrid precursor material, at room temperature, by mixing two equimolar precursor material solutions, one containing 1mM Cd(NO₃)₂ and the other 1mM Na₂S·9H₂O solution.

Steady-state fluorescence measurements were made with a home-assembled spectrofluorometer that consists of ORIEL parts in a standard configuration. Spectra were corrected for both lamp and photomultiplier spectral response profiles. Measurements were performed at 20°C.

3. RESULTS & DISCUSSION

As it is discussed in previous publications^{8,9}, alternatively to the conventional sol-gel process the silicon based materials could be prepared through carboxylic acid solvolysis of the precursors in the presence of ethanol, by a two-step reaction mechanism, previously proposed by Pope and Mackenzie¹⁰. A simplified reaction scheme is the following:

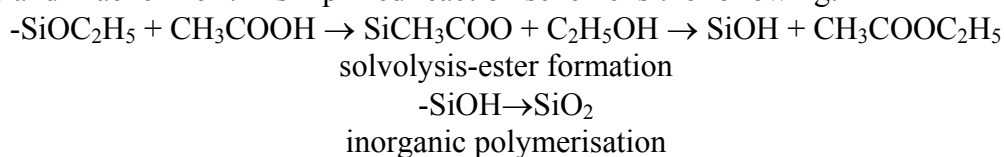


Figure 1 shows the photoluminescence spectra of one of the studied dry gels obtained from carboxylic acid solvolysis of the precursor ureasil PE-500. The chemical structure of the precursor is also shown in Figure 1.

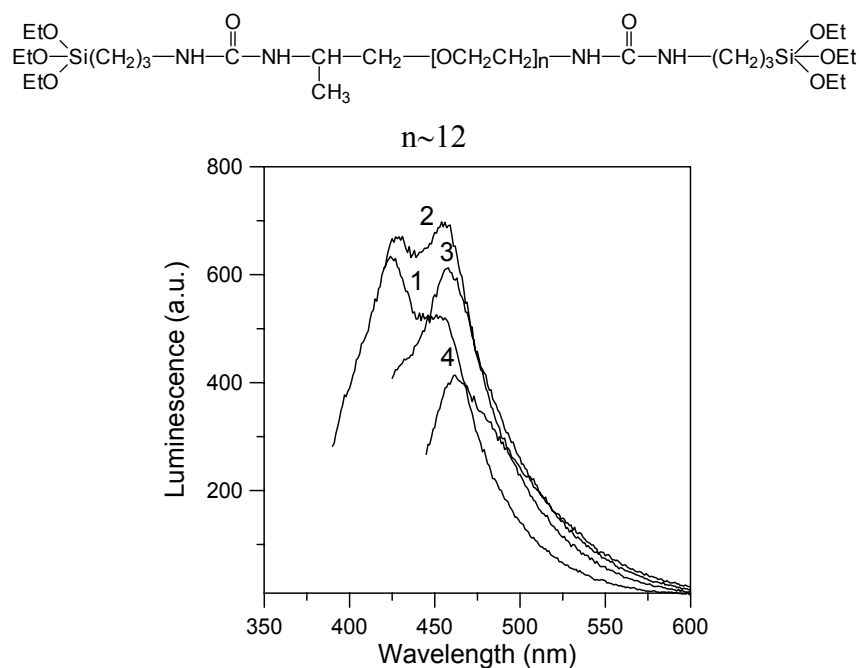


Fig. 1. Chemical structure of PE-500 and photoluminescence spectra of the ensuing acetic acid-catalyzed gel at various excitation wavelengths: (1) 340 nm, (2) 360 nm, (3) 370 nm, and (4) 380 nm.

As we can clearly see from the above figure, gels bear a very important characteristic: they give tunable photoluminescence by choosing the appropriate excitation wavelength. Light emission from these materials is a property of organic/inorganic hybrid nanoclusters generated by transitions between delocalized energy states associated with cluster size and cluster defects. Emission is red-shifted when the excitation is red-shifted because of nanocluster size polydispersity in these materials. As it is well known for several nanostructured materials, smaller clusters tend to absorb and emit at shorter wavelengths due to size defects¹⁰.

Due to the advantages of the processing procedure, e.g. low temperature, high sample homogeneity and purity, the above material is a potential matrix for the incorporation of lanthanide ions, CdS nanoclusters or organic dyes. Figure 2 shows the photoluminescence spectrum from the PE-500 dry gel after the incorporation of Eu^{3+} ions. The luminescence intensity of Eu^{3+} ions is greatly enhanced in this matrix because of the association of lanthanide ions with PEO chains, by interaction with ether oxygens. The resulting hybrid gives blue-green luminescence because of the matrix and red luminescence because of the lanthanide ions by single UV excitation.

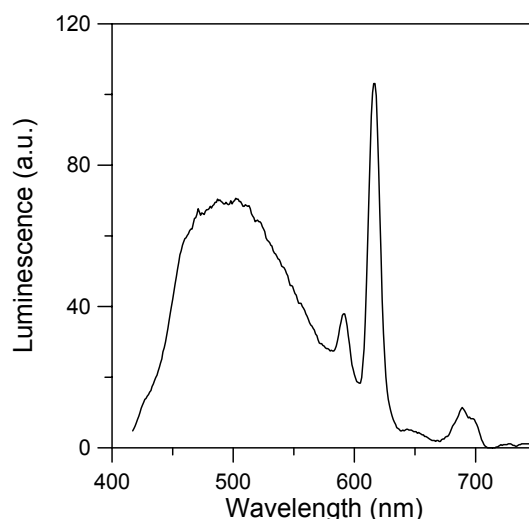


Fig. 2. Photoluminescence spectra of the ensuing PE-500 acetic acid-catalyzed gel with incorporated Eu^{3+} .
Excitation wavelength: 396 nm

Figure 3 shows the photoluminescence spectrum of the PE-500 dry gel after the incorporation of CdS nanoclusters. PE-500 provides a favourable environment for the suspension of high-luminescence-yield CdS nanoclusters due to the capacity of PEO to bind cations on ether oxygens¹⁰. Binding of cations is strong, and this results in further binding of compounds ensuing from ionic attraction, as in this case. Again, the resulting hybrid gives blue-green luminescence because of the matrix and red luminescence because of the semiconductor nanoparticles by single UV excitation.

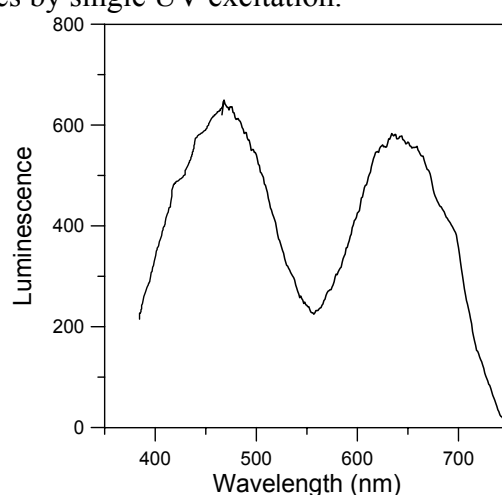


Fig. 3. Photoluminescence spectra of the ensuing PP-2000 acetic acid-catalyzed gel with incorporated CdS nanoclusters. Excitation wavelength: 370 nm

4. CONCLUSIONS

Ureasil gels are very efficient room-temperature luminescent materials. These materials can be used as host matrixes for lanthanide ions or semiconductor nanoclusters. This results to the formation of multiwavelength solid luminescent materials by single UV excitation.

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