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Tunable Photoluminescence from a Material Made by the Interaction between (3-Aminopropyl)triethoxysilane and Organic Acids

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Hydrolysis and polymerization of metal alkoxides produce oxide xerogels through a low-temperature chemical route, known as the sol−gel process.[1] Several materials based on SiO_2, TiO_2, and other oxides are nowadays made by this process. Pure SiO_2 matrixes and films are transparent insulators and they are immune of any electro-optical activity. However, impregnation of carbon impurities in the −O−Si−O− network introduces emitting states within the large silica energy gap, and the ensuing material becomes photoluminescent.[2] Thus it has been found that thermally oxidized porous silicon exposed to atmosphere for a prolonged aging process becomes photoluminescent, emitting in a broad blue band,[3] ascribed to carbonyl-related chromophores.[3] a-SiO_2:C films prepared by magnetron cosputtering gave a broad photoluminescence where the peak wavelength depended on carbon content.[2] States stretching into the forbidden energy gap are then held responsible for the broad expansion of the photoluminescence spectrum.[2] A simple room-temperature chemical process has been recently published[4] where white phosphorus (i.e. materials emitting a broad photoluminescence) has been prepared by the interaction between alkoxysilanes and carboxylic acids in an oxygen-free environment. In addition to the ease of preparation of this last material, what makes it most interesting is the high PL yield, which may exceed 35%.[4] Equally highly emissive photoluminescent materials have also been made in our laboratory by the interaction between (3-aminopropyl)-triethoxysilane (APTS) and acetic acid, where two distinct bright photoluminescence emissions (blue and yellow) were identified in the same material.[5] In the present work, we present the properties of an optimized material, obtained by interaction of APTS with a series of linear carboxylic acids. Gels were obtained through a slow sol−gel transformation process. Gels bore an important characteristic: they gave tunable photoluminescence by choosing the appropriate excitation wavelength, while the emitting colors possessed a startling brightness (cf. values of photoluminescence quantum yield given below). In addition, gels were soluble in protic solvents, directly providing colloidal solutions, i.e., without any dispersive agents, thereby preserving their main photophysical characteistics.

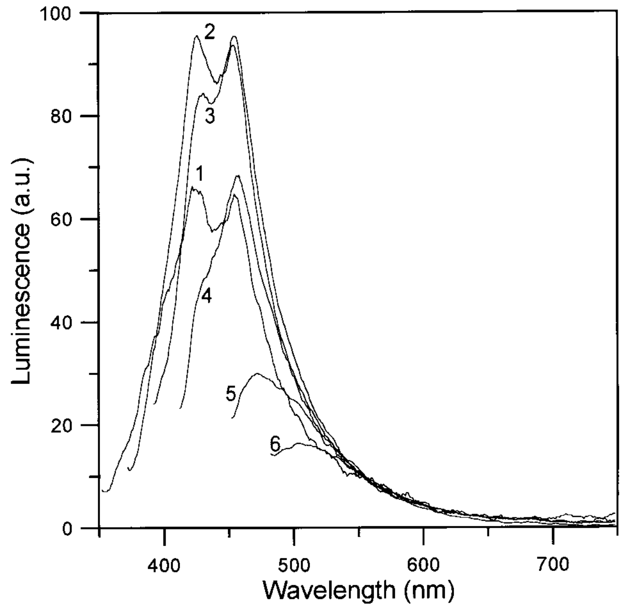

Figure 1. Photoluminescence spectra of a fresh material made by interaction of APTS with acetic acid. Excitation wavelengths: (1) 340 nm, (2) 360 nm, (3) 380 nm, (4) 400 nm, (5) 440 nm, and (6) 470 nm.

The preparation procedure was the following:[4,5] APTS was introduced in a closed container and was deoxygenated by the freeze−pump−thaw method. The carboxylic acid (formic, acetic, butyric, or valeric) was introduced with a syringe and mixed with APTS at the molar ratio APTS/acid = 1/3. The mixture was stirred for 0.5 h and the clear liquid was allowed to gel. The whole procedure was carried out at ambient temperature (∼25 °C). After about 10 days, the container was opened to the air. The viscous liquid content was then poured into a PMMA cuvette, covered with perforated aluminum foil, and left to dry at 50 °C for 10 more days. During this aging period, the gels remained transparent and progressively passed from colorless to deep yellow-orange. Gels made with formic acid were an exception. They remained colorless no matter how long their aging period lasted. The change in color upon aging of the gel was accompanied by variation in the absorption onset, which ranged from about 500 nm in wet gels and colloidal ethanolic solutions to above 600 nm in xerogels. The absorption spectrum (not shown) consisted of a structureless continuous absorption, typical of nanostructured semiconductor clusters, subject to size limitations.[6]

The luminescence emission behavior of the above material is presented in Figures 1−3. Figure 1 corresponds to relatively fresh samples and ethanolic solutions and Figure 2 to relatively mature samples. The emission of a long-aged xerogel can be found among the

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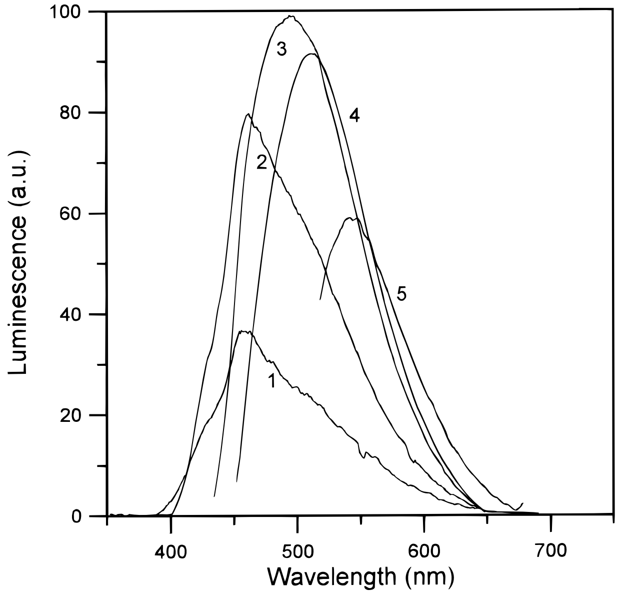

Figure 2. Photoluminescence spectra of a mature material made by interaction of APTS with acetic acid. Excitation wavelengths: (1) 340 nm, (2) 380 nm, (3) 440 nm, (4) 470 nm, and (5) 500 nm.

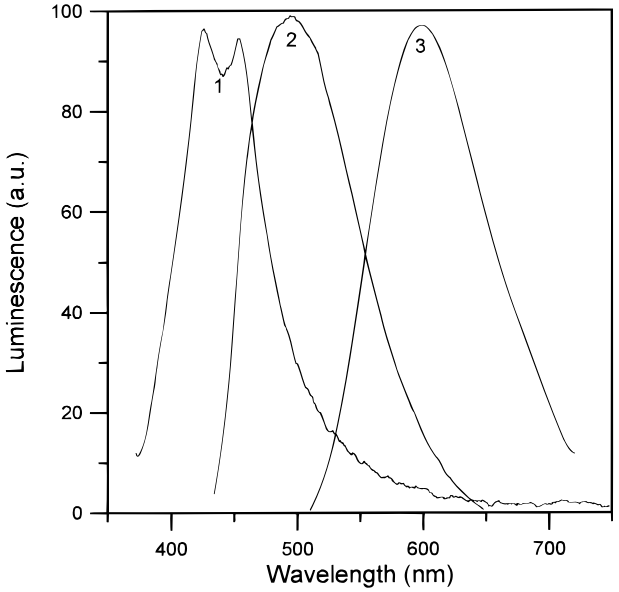

Figure 3. Comparison of photoluminescence emission spectra, corresponding to the major colors emitted by three samples of different ages. The three spectra were obtained by excitation at the wavelength which produces the most intense emission: (1) fresh sample, excitation at 360 nm; (2) sample aged for 30 days at 50 °C, excitation at 440 nm; and (3) sample aged for 60 days at 50 °C, excitation at 540 nm.

spectra of Figure 3. Figures 1 and 2 clearly show that emission depends on the excitation wavelength. The spectrum of maximum intensity covers all the rest as an envelope and it is the one with broadest color emission. Short and long wavelength excitations are, on the contrary, characterized by a higher colorimetric purity. The samples excited in the near UV offer a bright blue luminescence and samples excited around 470 nm offer a bright yellow luminescence.[5] Comparison of the spectra in Figures 1 and 2 and inspection of spectra in Figure 3 show that aged samples have the tendency to emit at longer wavelength. This is also in accordance with the absorption onset and it obviously characterizes a nanostructured semiconductor with cluster-size-dependent photophysical behavior. Obviously, aging affects the size of the luminescence centers. Mature samples consist of larger clusters, which absorb and emit light at higher wavelengths. We believe that this behavior is not due to quantum confinement effects,[7] since as it will be seen below, clusters are of a diameter of several tens of nanometers. It is more likely that their photophysical behavior is related with delocalized energy states associated with cluster size and cluster defects. In this respect, we have accepted the previously proposed model that the emitting states originate from the introduction of carbon impurities in the silica network,[2,3] which in the present case is achieved by the chemical route.[4] The extensive delocalization of the energy states, as indicated by the strong dependence on cluster size, may additionally indicate carbon clustering, as previously suggested[2].

The present material then demonstrates behavior typical of a nanostructured material consisting of semiconductor clusters. What, however, makes this material interesting is its particular photophysical and physicochemical behavior: (1) It possesses a high photoluminescence (PL) quantum yield,[4,5] q, emitting bright luminescence. Measurement of q in these materials presents some practical difficulties.[5] We have, however, previously estimated a lower limit for q that was 0.21 for blue and 0.12 for yellow PL. (2) The emitting colors are tuned through the excitation wavelength. (3) The material is readily soluble in water and alcohol, giving colloidal solutions. We have made dynamic light scattering measurements on alcoholic samples. The hydrodynamic radius of the particles, as extracted by extrapolation of the value of the diffusion coefficient to zero concentration, was found to be 95 Å, and it increased exponentially with material concentration. Alcoholic solutions then contain colloidal particles. Such colloidal dispersions and fresh gels have similar photophysical behavior. Aging obviously creates larger clusters in the gel with longer wavelength absorption onset and luminescence emission. Long-wavelength emission might also come from species ensuing from some slow chemical reactions, e.g., oxidation. Such a possibility cannot be excluded at the present stage. However, aging takes place also in a vacuum and it is reversible. For this reason, we believe that cluster growth is the main reason for the bathochromic shifts in both absorption and PL. Aging is accelerated by temperature increase. Thus a thin film casted on a glass support from an ethanolic solution can be rapidly aged by heating between 100 and 200 °C. Both wet gels and xerogels are easily soluble in protic solvents, giving colloidal solutions. Solubilization and drying of the material can be used to manipulate it and cast it in any desired physical state.

Samples made with formic acid were colorless and gave only blue photoluminescence. We have also observed that samples made with butyric or valeric acid aged faster than those made with acetic acid. It is likely that the alkane chemical group, bound to the COOH group and, through it, to the −Si−O−C−O−Si network,

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facilitates clustering, mainly by hydrophobic interactions. However, parallel mechanisms also affecting cluster formation, such as hydrogen bridging involving the butylamino group of APTS, seem of equally prime importance. As a consequence, addition of formamide to the original solution results in slow drying and colorless gels, similar to those obtained by the interaction between APTS and formic acid. This finding was a surprise, since formamide is used as a drying-control agent in sol–gel silica to obtain rapid aging and large clusters.[8] Apparently, this strong hydrogen donor is easily complexed with the butylamino group of APTS by hydrogen bridging, neutralizing the role of the amino group in cluster formation.

In view of the large interest that these materials can attract, thanks to their bright and tunable photoluminescence capacity, the detailed study of their structure can create several subjects of interesting research.

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