Communications

Luminescent Si Nanoparticles in Sol−Gel Matrices Stabilized by Amino Acids

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The ability of glass materials to stabilize semiconductor nanoparticles remains an area of extensive interest.[1−10] In addition to well-known commercial glass filters containing nanocrystallites of composition CdS_xSe_{1-x},[6,9] a diverse range of semiconductor materials can be incorporated into sol−gel glasses, including fullerenes[11] and wide-bandgap III−V materials such as GaN.[12] In this work, the preparation and properties of silica sol−gels incorporating luminescent Si nanocrystallites are described; the Si nanoparticles are stabilized by the presence of an amino acid such as alanine, phenylalanine, tyrosine, or tryptophan during the hydrolysis of tetraethoxysilane. The stability imparted by an amino acid physisorbed on a Si nanoparticle surface is 2-fold: (a) it serves to inhibit Si nanoparticle oxidation during sol−gel formation and (b) it importantly acts to passivate nonradiative pathways for electron−hole pair recombination at the Si nanoparticle surface.

For sol−gel processing methods, the inclusion of group IV semiconductor nanoparticles such as Si poses a special problem as a consequence of the thermodynamic tendency of Si to oxidize.[13] In 1990 it was reported that an electrochemically anodized thin film on crystalline Si (known as porous silicon) exhibits visible photoluminescence,[14] and this account has initiated extensive studies designed to understand the fundamental origins of the observed light emission and exploit its potential applications in light-emitting diodes (LEDs), chemical sensors, biomaterials, antireflection coatings in solar cells, etc. The active lumophore in this material is small silicon nanocrystallites (1−5 nm),[15,16] which can be liberated ultrasonically into other media such as organic solvents[17] and polymers.[18]

In a previous report[19] we described the effects of fatty acid addition on the stability of luminescent Si nanocrystallites doped into silica sol−gel matrixes. These Si nanocrystallites have been previously characterized in our laboratories by high-resolution electron microscopy (HREM) with an average Si nanocrystalline particle size of 4.6 nm and a relatively broad size distribution.[20] Such nanocrystallite solutions typically exhibit a broad photoluminescence (PL) spectrum with a peak maximum near 620 nm upon UV/visible excitation. While the presence of the long-chain carboxylic acid introduces excellent long-term (>1 month) stability to the Si nanoparticle luminescence, the hydrophobic character associated with the alkyl chains results in a phase segregation problem and agglomeration of the Si nanocrystallites within the gel. Thus it is necessary to utilize a water-soluble carboxylic acid to inhibit such agglomeration and segregation; amino acids are excellent candidates not only for such a purpose but also ideally permit the additional modification of the photophysical properties of the material by choice of functional group at the α carbon of the amino acid.

The Si nanocrystallites used in these experiments were prepared by sonication of porous Si samples for approximately 35 min in an aqueous solution containing 1.0% (w/w) of a given amino acid (L-alanine, DL-phenylalanine (Sigma Ultra grade, > 99%); *N-t*-BOC-L-alanine, *N-t*-BOC-L-phenylalanine (Sigma, 99%); tyrosine (Matheson Coleman & Bell, 99%); DL-tryptophan (Eastman Kodak, 99%)). The concentration of Si crystallites in the suspension was roughly 0.1 mg/mL. Silica-based sol−gels were then prepared by the hydrolysis reaction of 0.5 mL of tetraethoxysilane (TEOS, Gelest Inc.) with 1.0 mL of the Si crystallite/amino acid solution (pH 1, adjusted by HCl or HNO_3) in a plastic vial. Gelation was completed within 1 week. To form powders, the gel was exposed abruptly to air after 1−2 days aging. To form sol−gel monoliths, the gel was kept in a sealed vial. All samples used for measurements were dried for 1−2 additional days at room temperature until no obvious shrinkage was observed. The cylinder-shaped monoliths were roughly 1.0 cm in diameter and 0.3 cm in height.

To date we have explored the effects of incorporating the following amino acids into a sol gel matrix along with the Si nanocrystallites: L-alanine, DL-phenylalanine, L-tyrosine, and DL-tryptophan, as well as protected

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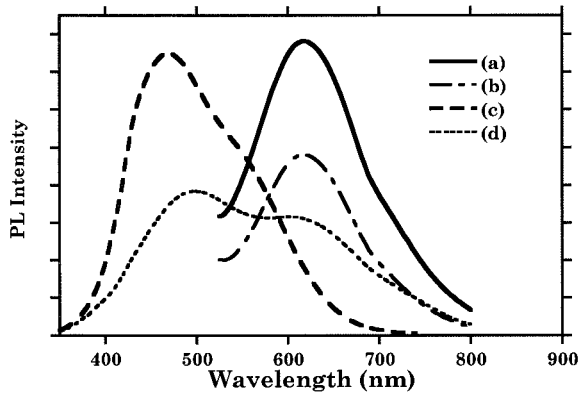

Figure 1. Comparison of room-temperature PL spectra of different sol−gel samples at an excitation wavelength of 375 nm: (a) nano-Si/alanine/sol−gel; (b) nano-Si/*N*-*t*-BOC-alanine/sol−gel; (c) tryptophan/sol−gel; (d) nano-Si/tryptophan/sol−gel.

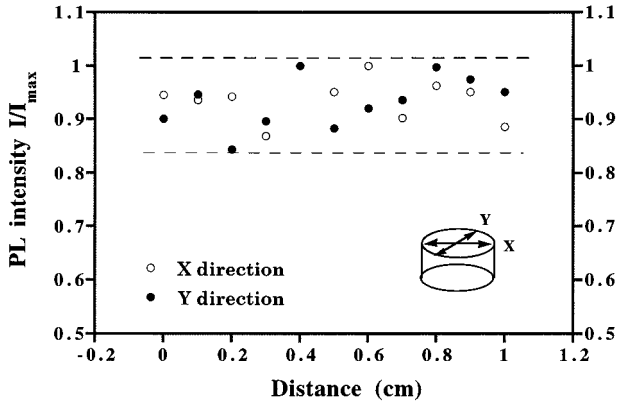

Figure 2. Distribution of PL intensities across the diameter of a sol−gel monolith with Si nanocrystallites stabilized by alanine. The integrated intensities were mapped across othogonal directions along arbitrary *X* and *Y* axes (as shown in the inset). Open circles represent PL intensity values at a given position along the *X* direction, while the filled circles represent PL intensity values along the *Y* direction.

analogues possessing the *tert*-butoxy ester moeity at the amino nitrogen (*N*-*t*-BOC-L-alanine and *N*-*t*-BOC-L-phenylalanine). In terms of physical characterization, conventional BET methods involving nitrogen absorption/desorption at 77 K were employed. For parent sol−gels with no Si crystallites or amino acid added, the typical surface area (*S*) was 400.7 m^2/g and the total pore volume (*V*) was 0.243 cm^3/g. The average pore diameter (*d*) was 25 Å, estimated from $d = 4V/S$. Such values are comparable to those we have reported previously for silica sol−gels doped with Si nanoclusters stabilized by fatty acids such as myristic acid.[19] In contrast, it is interesting to note that use of a water-soluble carboxylic acid such as alanine (along with the Si nanocrystallites) produces porous gels with a typical surface area (*S*) of 514.6 m^2/g, a total pore volume (*V*) of 0.536 cm^3/g, and an average pore diameter of 42 Å. One important contribution to the larger pore structure of the amino acid-doped gel is the presence of extensive hydrogen bonding between the amino acid and the silica framework during the condensation process, something that is not feasible in the case of the hydrophobic hydrocarbon chains of a fatty acid. Such a conclusion is also consistent with the previous studies of sol−gel condensation reactions in the presence of formamide, where a network of hydrogen bonds sterically shields the reaction centers and promotes the formation of branched structures of larger micropores.[21] These results are also consistent with the previous report that the use of surfactants as templates in sol−gel processing will affect the microstructure.[22] FT-IR spectra of these Si nanocrystallite/sol−gel composite powders (suspended in KBr) show the presence of carbonyl modes associated with the acid at 1632 cm^{-1}. In this case strong SiOH vibrations of the silica framework mask the N−H and C−H modes of the acid.

Photoluminescence spectra of some of these amino acid/nanocrystalline Si-doped sol−gels are illustrated in Figure 1. For a rather simple amino acid such as alanine, the PL from the composite amino acid/nano-Si sol−gel mirrors the emission line shape from the original Si nanocrystallite suspension quite closely. However, it is also important to evaluate the role of pH in the relative luminescence intensity of the amino acid/nano-Si sol−gel samples. When the amino acid molecules are dissolved into H_2O, they exist mainly in zwitterionic form as the solution is just slightly acidic (pH ∼ 6). By acidifying the TEOS/amino acid/Si nanocrystallite/water mixture to a pH ∼ 1, the luminescence intensity of the sol gel monoliths is enhanced by a factor of 5 (relative to the pH 6 samples). Another origin for the diminished PL in the pH 6 samples could involve interactions between amino groups and the Si nanocrystallite surface, as a number of previous studies by our group have established the facile quenching ability of porous Si PL by exposure to organoamines.[23] Thus, the presence of any unprotonated amine group in amino acid molecules may induce such quenching. However, in this pH range it is more likely that it is the COO^- moieties that are responsible for the diminished PL. Carrying out the sol−gel formation reaction at relatively low pH values carries the added benefit of accelerating the gelation process and inhibits the Si nanocrystallites from extensive aggregation in a polar protic solvent. It must be stressed that control experiments have verified that it is not simply the acidic environment alone responsible for the enhanced, stable Si nanocrystallite PL, but both an amino acid and an acidic environment.

To deliberately remove any possible luminescence diminution of Si PL by amino groups in the gel, both *N*-*t*-BOC-L-alanine and *N*-*t*-BOC-L-phenylalanine have been employed as stabilizers. Strong PL with a peak maximum at 620 nm from Si nanocrystallites is observed in the sol−gel monoliths with either derivative; the specific case of a *N*-*t*-BOC-L-alanine/Si nanocrystallite sol−gel sample is illustrated in Figure 1.

Unlike the fatty acid-doped monoliths, which drive agglomeration of the Si nanocrystallites into micron-sized domains within the gel,[19] an improved uniformity of luminescence is observed from the amino acid/Si nanoparticle-doped sol gels. Such an observation has been quantified by PL mapping experiments involving a spectrograph-CCD detector system interfaced to a fluorescence microscope. As shown in Figure 2, the

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variation of integrated PL intensity as the luminescent monolith sample is rastered along both X and Y directions is within 15%, indicating that luminescent Si nanocrystallites are uniformly dispersed within the sol−gel matrix.

The role of the functional group at the α carbon of the amino acid on the luminescence of the Si nanocrystallites in the gel has also been analyzed. In the case of phenylalanine it seems that the aromatic group does not significantly impact the luminescence intensity of the Si nanocrystallites, in contrast to the known ability of benzene vapor and related aromatic compounds to quench the PL of porous Si.[24] In general, there is no appreciable difference in the Si nanoparticle PL properties (intensity, emission maximum) between alanine, phenylalanine, and tyrosine in the amino acid/nano-Si-doped sol gels. However, in the case of the tryptophan/nano-Si-doped sol gel, a very different luminescent spectral line shape is observed relative to the other samples excited at the common wavelength of 375 nm (Figure 1). Only very weak PL near 620 nm is observed from the Si nanocrystallites, and a second emission maximum at ∼500 nm (green-yellow) is also detected. The overall emission intensity of the sample is relatively weaker than that of the other amino acid-doped samples. This yellow band at ∼500 nm originates from acidifed tryptophan (and related indole derivatives) and has been attributed to phosphorescence from this chromophore.[25] This strong yellow-green emission is also observed in control experiments of sol−gels containing only tryptophan, but not in any of the other amino acid-doped gels. Taken in concert, this would initially suggest that the indole residues associated with the amino acid are interacting with Si nanoparticle photophysics in some manner. Mechanistic details of these observations are still under investigation, but preliminary studies probing the influence of excitation wavelength on the PL of the tryptophan/Si nanoparticle silica sol−gel have been explored (Figure 3). At an excitation wavelength of 330 nm, the PL spectrum is dominated by emission emanating from the Si nanoparticles with only a minor feature associated with the tryptophan at 500 nm observed. However, as the excitation wavelength is increased to longer wavelengths (from 325 to 400 nm), the relative intensity of the yellow-green band is enhanced while the orange emission band from Si nanocrystallites decreases significantly. In contrast, excitation spectra for sol−gels containing only tryptophan (Supporting Information) reveal that the 500 nm emission reaches a maximum value at an excitation wavelength of ∼350 nm but then drops with increasing excitation wavelength after that point. On the other hand, the excitation spectrum of a Si nanocrystallite/sol−gel sample with a nonphotoactive amino acid such as alanine (Supporting Information) indicates that the 620 nm Si nanocrystallite PL should be increasing in intensity as the excitation wavelength increases from 325 to 380 nm. While such phenomena are consistent with energy transfer between the excited states of Si crystallites and tryptophan, further experiments evaluating this possibility are underway.

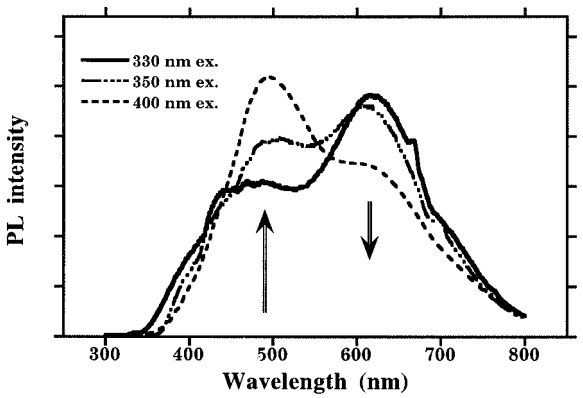

Figure 3. PL spectra recorded at different excitation wavelengths (from 330 to 400 nm) from a sol−gel monolith doped with Si nanoparticles stabilized by tryptophan. The arrows point to the increase of the 500 nm emission along with concomitant decrease of the 620 nm peak as the excitation wavelength is increased.

To summarize, we have successfully incorporated Si nanocrystallites extracted from porous Si into porous silica-based sol−gels. The Si crystallites show stable and strong PL when an amino acid is added as a passivation agent. Results acquired to date suggest that incorporation of a photophysically active functional group permits modulation of the Si nanocrystallite luminescence.

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Supporting Information Available: Photoluminescence excitation spectra for (a) nanocrystalline Si/tryptophan/sol−gel samples and nanocrystalline Si/alanine/sol gel samples (emission is monitored at 620 nm for both of these samples) and (b) nanocrystalline Si/tryptophan/sol gel samples and tryptophan/sol gel samples (emission is monitored at 500 nm for both of these particular samples) (2 pages). Ordering information is given on any current masthead page.

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