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LUMINESCENT STUDIES OF FLUORESCENT CHROMOPHORE-DOPED SILICA AEROGELS FOR FLAT PANEL DISPLAY APPLICATIONS

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ABSTRACT

The remarkable optical and electronic properties of doped and undoped silica aerogels establish their utility as unique, multifunctional host materials for fluorescent dyes and other luminescent materials for display and imaging applications. We present results on the photoluminescence, absorption, and photoluminescence excitation spectra of undoped silica aerogels and aerogels doped with Er^{3+} , rhodamine 6G (R6G), and fluorescein.

INTRODUCTION

Aerogels represent a novel class of open-cell nanoporous materials with remarkable optical, electronic, thermal, and structural properties. Many of these properties are ideal for host matrices in which luminescent materials are incorporated for flat panel display (FPD) applications. Some of these properties include low weight, minimal optical and electronic interactions with the chromophore, and physical robustness. Silica aerogels can have densities as low as 3 mg/cc, or roughly be 99.8% air and 0.2% material backbone. The backbone structure of colloidal aerogels is made up of clusters of materials which are 4 to 10 nm in diameter. They have interconnected pores and extensive internal surface areas ranging from 500 to 1200 m²/g. Aerogels are physically robust, able to support 1600 times their own weight and stable in air and vacuum. Aerogels can be doped with a variety of atoms and molecules including metals, metal oxides, salts, and phosphors. In addition, silica aerogels are non-hazardous and non-flammable.

We studied the optical properties of silica aerogels doped with a luminescent materials Er^{3+} , rhodamine 6G, and fluorescein. We report on the photoluminescence (PL), absorption, and photoluminescence excitation (PLE) spectra of these doped aerogels, and evaluate their performance for FPD purposes. We contrast the optical properties of these doped aerogels with those observed for each chromophore and find that silica aerogels serve as an ideal host matrix. Our results demonstrate the potential utility of these silica aerogels as host materials for fluorescent dyes and other luminescent materials for display and imaging applications.

EXPERIMENT

The preparation of the aerogels studied in this paper is discussed in detail in reference 1.

Transmission and absorption spectra were recorded with an absorption spectrophotometer. Optical excitation for PL studies was provided by three sources: (1) the ~100 fs output from a self-modelocked Ti:sapphire laser was frequency-doubled with an appropriate KDP crystal to give excitation pulses varying from 355-400 nm and at a 82 MHz repetition rate, (2) the ~150 fs output from a Ti:sapphire regenerative amplifier was frequency-doubled to give 400 nm excitation pulses at a 1 kHz repetition rate, and (3) a commercial fluorimeter. Photoluminescence spectra were recorded with a fluorimeter and also with a 0.25 m monochromator equipped with an intensified optical multichannel analyzer. The PL spectra were corrected for the spectral response of the optical system. Photoluminescence excitation spectra were recorded with a fluorimeter.

RESULTS

Figure 1 shows the PL spectrum for a typical low density silica aerogel excited at 264 nm. This spectrum can be compared with figures 2-4, which show the photoluminescence spectra for the chromophore-doped silica aerogels. The luminescence of the aerogel host is much smaller in magnitude than the intensity of the dopant in the aerogel. Also the peak of the luminescence of the undoped aerogel occurs far below the peaks of the doped aerogels.

Figure 1. PL spectrum of a 30 mg/cc low density silica aerogel excited at 264 nm.

Figure 2. PL spectrum of R6G in silica aerogel excited at 365 nm.

Figure 3. PL spectrum of Fluorescein in silica aerogel excited at 266 nm.

Figure 4. PL spectrum of Er^{3+} in silica aerogel excited at 450 nm.

Absorption spectra are shown in figures 5-8 for undoped aerogel, R6G in aerogel, fluorescein in aerogel, and Er^{3+} in aerogel. Here again, we see that absorption in the aerogel does not affect the absorption of the doped aerogel.

Figure 5. Absorption for different low densities of silica aerogels.

Figure 6. Absorption peak for R6G in silica aerogel.

Figure 7. Absorption peak for Fluorescein in silica aerogel.

Figure 8. Absorption peaks for Er^{3+} in silica aerogel.

The PLE spectra are shown in figures 9-12 for undoped aerogel, R6G in aerogel, fluorescein in aerogel, and Er^{3+} in aerogel. In the PLE spectra we monitor the main PL peak in for each aerogel to ensure that the contribution to that peak is due solely to the dopant and not to the aerogel matrix.

Figure 9. PLE spectrum of 30 mg/cc silica aerogel monitoring the PL peak at 428 nm.

Figure 10. PLE spectrum of R6G in silica aerogel monitoring the PL peak at 555 nm.

Figure 11. PLE spectrum of Fluorescein in silica aerogel monitoring the PL peak at 544 nm.

Figure 12. PLE spectrum of Er^{3+} in silica aerogel monitoring the PL peak at 545 nm.

CONCLUSIONS

The PL peaks in aerogel occur at 318, 428, and 620 nm. The absorption onset appears near 310 nm. All peaks occur well below the bandgap of amorphous silica, indicating the presence of defects or surface states within the aerogel. For example, the non-stoichiometric sub-oxide SiO_x has a smaller bandgap than SiO_2 ($E_g \geq 3\text{--}4$ eV for $x \sim 1.4\text{--}1.6$). The PLE spectra confirm that the contribution to the PL peaks of the doped aerogel are due to the dopant and not to the aerogel. The aerogel spectra are easily distinguishable from and do not interfere with the chromophore spectra.

In the R6G sample, we observed a PL peak at 555 nm. This corresponds to a dimer transition in R6G with emission that is reported to be between 556 - 565 nm.

Innocenzi, et. al.² also show a PL shoulder at 515 nm that has not been assigned. Though we do not see a luminescence peak here, we do observe a strong absorption peak near 515 nm. Our absorption spectrum also shows a shoulder at 490 nm that corresponds to the 500 nm dimer absorption of R6G.

Since the reported peak wavelength of the fluorescence of the fluorescein dimer is located at around 545 or 550 nm³, the PL peak in our spectrum, which is observed at 544 nm, can reasonably be assigned to the dimer fluorescence. The absorption of fluorescein in methanol occurs at 498 nm which corresponds to our absorption peak.

In the Er^{3+} sample, we observe a strong Er^{3+} PL peak at 545 nm and a weaker one at 578 nm. Our absorption spectrum shows peaks at 488, 523, 545, 654, and 796 nm. In comparison, Xu, et. al.⁴ reported PL peaks from Er^{3+} doped sol-gel silica glass at 525, 550, and 660 nm, which likely results from the absorption peaks we observed. The 550 nm PL is ascribed to a $4\text{S}_{3/2} \rightarrow 4\text{I}_{15/2}$ transition in Er^{3+} .

In summary, the optical properties of silica aerogels make them ideal hosts for fluorescent dyes and other luminescent materials for electroluminescent applications. The photoluminescence, absorption, and photoluminescence excitation of chromophores such as rhodamine 6G, fluorescein, and Er^{3+} are not significantly altered when incorporated in an aerogel matrix. Their desirable luminescent properties (visible light emission, and high luminescent quantum efficiency) therefore should remain intact. Nearly any luminescent center can be used, allowing a wide variety in choice of dopant and therefore color. In addition, aerogels can be made into thin films or molded into any shape. Thus, aerogels are a unique, multifunctional host material for a variety of chromophores with applications in the display and imaging fields.

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