



Sol–Gel Encapsulation of Molecules to Generate Functional Optical Materials: A Molecular Programming Approach

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Abstract. The extraordinary opportunities offered by integrating solution chemistry of molecular entities with the solid-state nature of the gel provide the basis for designing a number of novel molecular materials. Herein, we present a strategy based on encapsulation of suitable response active species to impart useful optical properties to sol–gel glasses. The basic concept of this molecular programming approach is based on deliberate incorporation of response-active species in the silica gel framework to elicit specific optical responses. Design of molecular materials for device applications depends on selection of molecules which exhibit well-defined electronic or optical response, and assembly of these molecular components into a geometric structure that retains the rigidity, addressability, and stability necessary for practical applications. The approach is based on using molecules as active species and sol–gel glass as structural matrix in which the molecules are selectively integrated. A designer approach that employs specific molecules for generating optical signals is described. As such the properties of these silica-based glasses can be tuned by varying the composition of encapsulated species. These modified glasses exhibit substantially altered optical properties as compared to pristine silica sol–gels. The optical response of these materials provide initial examples toward designing novel materials whose optical and/or photonic responses can be modulated by structural integration of specific dopant entities.

Keywords: silica sol–gels, optical materials, encapsulation, molecular programming, optical responses

1. Introduction

Design of new materials with precise control and flexibility at a molecular level necessitates regulation of processes that generate photonic and/or optical responses [1]. Development of molecular materials depends on two factors: (a) identification of molecules which exhibit a particular optical response, and (b) assembly of molecular components into a geometric structure that retains the rigidity, addressable, and stability necessary for device applications [2]. An inherent limitation of using molecules is the requirement of a solution phase. A practical approach to use of molecules in device applications requires an active response species and a structural matrix in which the active species is

selectively located. Sol–gel chemistry in combination with suitable optically responsive molecules can be used to provide both the optical responses and the appropriate structural organization necessary for device applications. In this context, encapsulation of suitable molecular entities as active species within a sol–gel-derived host matrix can be used for the design of novel materials using molecular chemistry approaches [3].

The extraordinary opportunities offered by integrating solution chemistry of molecular entities with the solid-state nature of the gel provide the basis for designing a number of novel molecular materials [4–7]. The ease of solution based processing, choice of several precursors, compatibility with both optics and electronics, and the ability to obtain the products in several different configurations and geometries are some of the appealing aspects of sol–gel-derived materials. These

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particular characteristics of sol–gel systems are attractive for design of “smart” devices [8]. While several examples based on use of these materials as sensors have been outlined in literature [9], the potential of these materials for design of advanced functional signal transducing elements that convert an applied stimulus to a response remains largely unexplored.

For design of advanced material and devices, the advantage of using sol–gel-derived glasses is that the pristine SiO_2 material is optically transparent, electrically insulating, functionally inactive, and operationally nonresponsive. Therefore, by selectively integrating specific response-active entities into the glass, it is possible to introduce desired optical, electronic, functional, and operational properties in a modular fashion. This structural/functional modularity allows a sequential modification of the parent material and facilitates rational design of new advanced materials and control of their physical, mechanical, optical, electronic, and functional properties. In this fashion, through a judicious choice of dopants, new properties can be molecularly programmed in the sol–gels. The approach pursued in this work is based on encapsulation/incorporation of molecules in a sol–gel-derived glass to generate useful new photonic and optical properties. The molecular system acts as active species while the sol–gel acts as a structural matrix for rigidity, stability, and addressability. In this paper, we present two different examples of designing optical materials using sol–gel matrices with one example demonstrating the generation of new photonic responses while the other example illustrates programming of new optical responses. The first example is based on using Sb(III) as a dopant to form antimony-silica binary oxides. These materials are characterized by optical properties that are considerably different compared to pristine silica gels in that they exhibit photoluminescence in the visible region. Another example is based on design of an optical memory system based on photoinduced electron transfer between flavin mononucleotide (FMN) and a redox-dye methylene blue (MB). The system shows light dependent optical properties such that under dark conditions the gels are blue-green colored and when irradiated with UV light the gels change their color to light yellow. As such these gels represent examples of an optical memory system. The color changes are reversible and the optical properties of these gels can be modulated by means of an externally applied stimulus in the form of light.

2. Experimental

2.1. Synthesis of Sb-Doped Silica Sol–Gels

The antimony-doped silica sol–gels ($\text{Sb}:\text{SiO}_2$) were synthesized from hydrolysis of SbCl_3 and tetramethyl-orthosilicate (TMOS) precursors. Typical procedure involved mixing 5 g of TMOS, 2 g of SbCl_3 , and 1 mL of deionized water to form a sol. The sol was poured into a polystyrene cuvette to form gels. The gelation times for the sol are on the order of 1–2 min. The freshly prepared gels are light blue-purple in color. Good quality mechanically stable gels can be formed this way. Dried xerogels were obtained by controlled drying of the samples over a period of one month. The xerogels are transparent and dark brown in color.

2.2. Synthesis of FMN:MB:NAD Doped Sol–Gels

TMOS-derived silica sol–gel was used as a matrix for encapsulation. To make the sol 15.27 g TMOS, 3.39 mL deionized water, and 0.22 mL 0.04 M hydrochloric acid were mixed followed by sonication for 20 min. To this 12 volume percent of a buffered mixture of FMN, nicotinamide adenine dinucleotide (NAD) and methylene blue (MB) in 5% TRIS buffer (pH 8.35) was mixed. The sol was poured in a standard cuvette for gel formation. The gelation time is on the order of 1–2 min. The concentrations of the molecular components in the final gel were: MB (0.23 mM); FMN (0.16 mM); NAD (0.27 mM). The gels formed this way are deep blue-green in color.

2.3. Characterization

Optical characterization of the materials was done in using both absorbance and luminescence measurements. Absorption spectra were taken with a UV-VIS Hewlett Packard model 8453 spectrophotometer. The luminescence properties of the sol–gels were monitored with a PTI QM2 spectrofluorometer. The spectra of the samples were obtained in a standard quartz cuvette.

3. Results and Discussion

3.1. Optical Properties of $[\text{Sb}:\text{SiO}_2]$ Sol–Gels

The optical properties of Sb-doped silica sol–gels are significantly different as compared to pristine silica

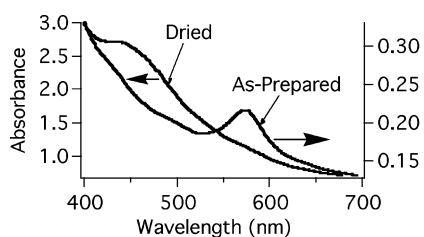


Figure 1. Absorption spectra of Sb:SiO₂ sol-gels.

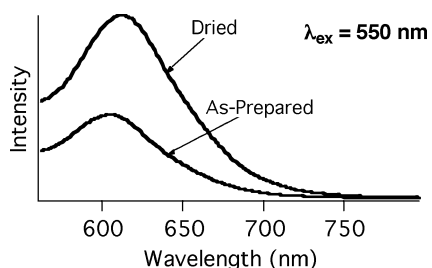


Figure 2. Emission spectra of Sb:SiO₂ sol-gels.

sol-gels (Figs. 1 and 2). These materials show unique optical properties related to absorption as well as emission of light in the visible region. While pristine silica materials are optically transparent in the visible, the

Sb:SiO₂ samples strongly absorb light in the visible region. The as-prepared gels show an absorption band centered at 475 nm which gives them a characteristic light purple-blue color. The color of the gels changes when they are aged or dried with the ambiently-dried xerogels exhibiting essentially an intense peak centered at 440 nm. The xerogels are dark transparent dark-brown colored. The optical properties of these gels are interesting since both antimony oxide and silica are known to be optically transparent in the visible. The Sb-doped sol-gels are also characterized by an emission band in the visible. While conventional silica sol-gels only luminesce in the UV region the red shift of the emission to visible region is rather unique and supports formation of network of binary oxide. The gels exhibit a strong peak in red region around 600 nm when excited with 550 nm light. Although, at present, the exact nature of these transitions remains to be established, it is apparent that these new optical features are due to formation of a binary mixed-metal oxide of antimony and silica with the optical properties arising due to formation of defects sites in the network. The overall network of these gels is characterized by enhanced porosity with very large pores (ca. 10 nm) as shown in TEM images (Fig. 3).

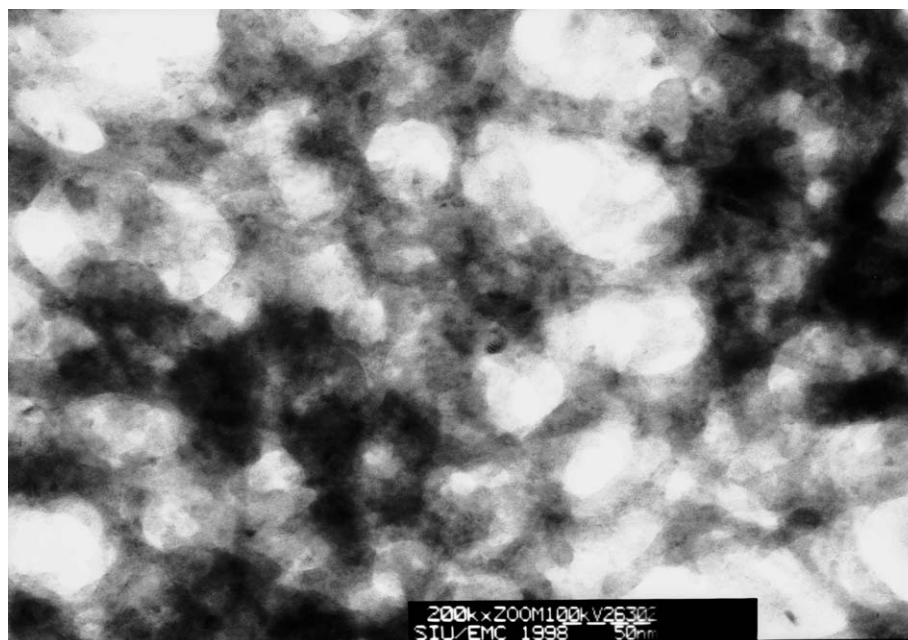


Figure 3. HRTEM image of Sb:SiO₂ sol-gels.

3.2. Optical Properties of FMN:MB:NAD System

The optical properties of this system arise due to the dopants encapsulated in the sol–gels. The gels are blue–green colored in dark and become light yellow colored when irradiated with UV. The color change is due to photoinduced electron transfer from FMN to MB which is blue colored in the oxidized form and colorless in the reduced form. The presence of NAD is not critical, however, its addition makes the response time faster.

The changes in optical features of sol–gels containing the dye methylene blue along with FMN and NAD system are shown in Fig. 4. The strong blue absorption of methylene blue at 665-nm can be made to change by illumination with 365-nm light. The reversible optical response of the system is characterized by light induced color changes such that fading of blue color is observed when the system is illuminated with UV light while color formation accompanies the dark period. The optical response of the system is due to photoinduced reduction of MB which causes fading of blue color followed by subsequently reoxidation under dark condition to regenerate the original color. Figure 4 shows changes in concentration of different components of the FMN:MB:NAD reaction system as it goes through photobleaching and coloration cycles. The change in intensity of absorption band at 665-nm was taken as a measure of methylene blue concentration while the luminescence intensities of FMN and reduced form

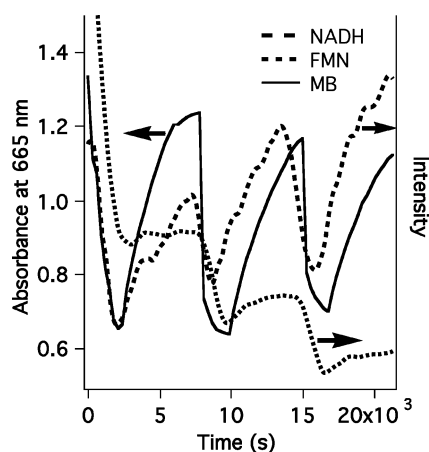


Figure 4. Temporal variations of characteristic optical features of FMN:MB:NAD containing sol–gels. The changes in absorbance maximum at 665 nm band of MB are plotted on the left axis while the changes in intensity of luminescence of FMN (at 535 nm) and NADH (at 470 nm) are plotted on right axis.

of NAD (i.e., NADH) at 535-, and 470-nm, respectively, were used to monitor the concentration variation of these components. The results indicate that the concentration profiles of three molecular components are strongly correlated. Overall, the results indicate coupled redox events between each component when subjected to external stimulus in the form of light. These concentration variations are responsible for the observed changes in optical properties of the sol–gel samples that can be controlled externally by means of UV light. An important aspect of these materials is that they combine all the essential functions of an intelligent system in a one-component monolithic unit such that they are able to sense the external stimulus, translate the stimulus into chemical changes, and generate an active optical response.

4. Conclusions

In summary, this paper reports on two novel doped silica sol–gel systems whose optical properties are dictated by precisely incorporated dopant species. These sol–gels containing the encapsulated species exhibit substantially altered optical properties as compared to pristine or undoped glasses. The strategy of using specific dopant for developing optical responses in sol–gels is illustrated by means of two examples. The first example outlines development of new photonic properties in Sb-doped silica gels while the second example provide an approach to designing novel optical materials whose optical properties can be altered through application of an external stimulus in the form of light. These systems effectively demonstrate the feasibility of molecular programming approach toward design of novel optical and photonic materials using sol–gel process in combination with suitable dopants. The “designer” approach of integrating specific entities enables one to tailor and engineer the properties of a material from a molecular perspective so that a variety of novel materials with predetermined functional responses can be prepared. These materials may find useful applications as photochromic memory and as photonic materials. Finally, the strategy described here offers a potentially powerful approach for designing a diverse range of optical sol–gel materials whose properties may be tailored precisely with systematic control over both the composition of product materials and their properties to ultimately be able to design materials with tunable optical responses.

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