Multiphasic Nanostructured Composites for Photonics: Fullerene-Doped Monolith Glass

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We present the preparation of novel multifunctional nanostructured composite materials using the sol–gel process. We have demonstrated the doping of two optical limiting organic molecules (C_{60} and bisbenzothiazole 3,4-didecyloxythiophene (BBTDOT)) in a single bulk while maintained the optical limiting effect at each of their characteristic wavelengths. A multiphasic composite glass doped with both C_{60} and BBTDOT exhibited effective optical power limiting at 532 and 800 nm due to independent limiting effects at each wavelength generated by each of the two dopants. These composite glasses have excellent optical quality (loss $\approx$ 1 dB/m) and a large bulk size. By using our methodology, it is possible to dope two (or more) different optically responsive materials, each of which will reside in different phases of the matrix to make multifunctional nanostructured bulk materials for photonic applications.

Introduction

The realization of photonics technology rests on the developments of multifunctional materials, which simultaneously satisfy many functional requirements.[1,2] The progress during the past decade in the design of organic systems allows one to prepare new materials with promising lasing and nonlinear optical properties. Examples of such materials are molecules and polymers with π-conjugated electron systems. A major effort has been centered on introducing optically active organic materials into a photostable optically transparent medium such as glass, to allow their use as building blocks for photonic devices. A promising class of materials are the sol–gel processed organic:inorganic hybrid materials which combine the merits of inorganic glass and organic polymers.[3] In this report, we present the preparation of novel multiphase nanocomposite glass monoliths containing fullerene and an organic chromophore as a multifunctional optical power limiting material.

Photonic properties of fullerenes have been a subject of extensive investigation in recent years. Their nonlinear optical properties and optical power limiting behavior have drawn much of the attention.[4–6] In addition, luminescence from C_{60} solutions at room temperature has recently been reported.[7] The past studies have mostly used fullerenes in solution and in a pure solid film form, although fullerene-doped polymers have also been used.[8,9] However, due to limited solubility of fullerenes, it cannot be doped in high concentrations. Furthermore, devices (such as optical power limiters) that require a long interaction length need a high optical quality bulk form. The sol–gel process offers the ability to prepare high optical quality bulks with a long interaction length. Due to the insolubility of fullerenes in solvents used for sol–gel processing, the past approach was based on entrapping a true solution of fullerene in sol–gel-derived films, xerogels,[10] and sonogels.[11] McBranch et al.[11] even demonstrated that the nonlinear optical behavior of fullerene-doped sonogel is similar to that of a liquid solution and not to solid forms of fullerenes, where at high fluences the nonlinear behavior is quenched.[12,13]

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The organic dye we have investigated is bisbenzothiazole 3,4-didecyloxythiophene (BBTDOT) which is fluorescent in the UV-blue region. This dye was synthesized at the Polymer Branch of Air Force Materials Directorate, Wright-Patterson Air Force Base, OH.[14] The linear spectroscopic and third-order nonlinear optical characteristics of BBTDOT in THF solution and composite glasses are discussed elsewhere.[15-17] An important feature of this dye is its high solubility which allows the doping of high concentrations necessary for significant nonlinear effects. BBTDOT shows a strong two-photon nonlinear absorption[18] (TPA) and was previously demonstrated to be capable of optical power limiting at 602 nm.[19,20]

In this paper, we present an approach utilizing sol–gel processing to produce a composite glass that consists of many phases but the phase separation is on the nanometer scale. Using this approach, we prepared a highly porous monolith gel (in the present case, silica) and thermally processed it. The pores in the silica monolith under our processing conditions are in the nanoscale region.[21,22] The pores are then filled with a polymerizable liquid, methyl methacrylate (MMA) in the present case, which is polymerized in situ. This MMA procedure was first pioneered by Pope et al.[23] and has been used by several other groups. The resultant composite is of high optical quality, and one can make large size monolithic bulk forms for various photonics functions such as lasing,[24-26] optical power limiting,[19,20] nonlinear optical response,[27] etc. We have gone further to form a multiphasic nanostructured composite. The concept of a multiphasic nanostructured composite can be used to prepare a wide variety of optical materials. By using a multistep impregnation method, we were able to dope two (or more) different optically responsive materials, each of which resides in different phases of the matrix (the silica phase, the PMMA phase, and the interfacial phase; see Figure 1), to make multifunctional bulk materials for photonics. Here, we present the results on preparation, characterization, and optical power limiting properties of multiphase composite glass monoliths containing fullerene, which is adsorbed at the interfacial phase, and an organic chromophore, BBTDOT in the PMMA phase.

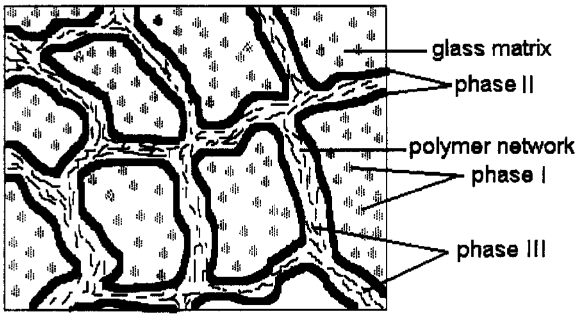

Figure 1. Simplified schematic representation of the multiphasic composite glass.

Experimental Section

Composite Preparation. The procedure used to form highly porous silica-gel bulk glasses, by a two-step hydrolysis sol–gel process, was described previously by Gvishi et al.[15,21,22] The sol–gel glass was prepared from a precursor solution containing tetraethoxysilane (TEOS) (Aldrich 99+% pure) and ethanol in the molar ratio 1:4. After 1 h of prehydrolysis, water (molar ratio 4), and HNO_3 (Aldrich A.C.S. reagent, molar ratio 0.06) were added to complete the hydrolysis. This was followed by the addition of HF (Aldrich 48 wt % in water 99.99+% pure, molar ratio 0.8) to achieve fast gelation. After mixing, the solution was placed into 4.5 mL methacrylate cuvettes and covered with parafilm containing three pinholes on the top. The cuvettes were then placed in an oven (Precision Scientific Freas Mechanical Convection Oven; Model 605) set at 45 °C for 2 weeks. The bulk gels were then removed from the cuvettes and placed in a furnace (Fisher Scientific Isotemp Programmable Furnace; Model 495A) for drying and partial densification to glass by slow heating (50 °C/h) from room temperature to 500 °C. The dimensions of the bulk glasses were 10 mm × 5 mm × 5 mm.

Two identically prepared glasses were then weighed and placed in a saturated C_{60} (Aldrich 99% pure) toluene solution. After the solution was completely adsorbed into the glasses, they were removed and placed on a hot plate at 125 °C for 24 h to remove the toluene and deposit the C_{60} on the walls of the pores. The glasses were then weighed again to determine the amount of C_{60} adsorbed in the glass (0.5 wt/wt % compared to the silica phase).

The impregnation of the organic polymer phase was done as follows. Two bulk glasses (one of which was already doped with C_{60} in the interfacial phase) were immersed in the methyl methacrylate (MMA, Aldrich 99% pure) monomer for 10–15 min. The MMA solution diffused into the sol–gel-derived glass pores and was polymerized therein using benzoyl peroxide (2%) as the catalyst. The MMA bulks were reimmersed in a MMA solution, which at this stage was catalyzed for full polymerization with benzoyl peroxide (0.5%), kept in a sealed container, and placed in the Freas oven at 45 °C until the polymerization process was completed. Using the other identically prepared two glasses (one of which has already been doped with C_{60} in the interfacial phase) the impregnation of the organic polymer phase was done using a MMA solution containing 5% wt/wt BBTDOT. After the polymerization was complete (~3 days) the glasses were removed from the surrounding poly(methyl methacrylate) (PMMA) by a chloroform wash. The glasses were then polished (Buehler Metaserv 200 grinder–polisher) in seven incremental steps, starting with a 180 grit SiC paper and going down to a 0.25 μm diamond paste. The resulting four composite samples (C_{60} + BBTDOT-doped, C_{60}-doped, BBTDOT-doped, and blank) were of high optical quality.

Optical Measurements. The absorption spectra were obtained using a Shimadzu UV–vis 260 spectrophotometer. The spectra were collected by using the blank composite glass as a reference. Fluorescence measurements were performed

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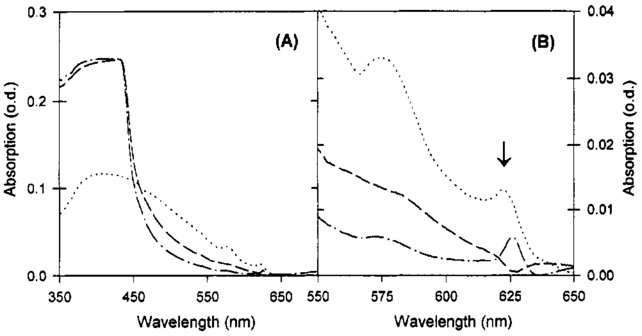

Figure 2. Absorption spectrum of the three composite glasses: the dashed line is for BBTDOT-doped, the dotted line is for C_{60}-doped, and the dashed–dotted line is that for BBTDOT + C_{60}-doped. Panel A: UV–visible absorption spectrum. Panel B: Magnified spectrum of the red region. The arrow indicates the 0 → 0 transition centered at 622 nm.

(90° geometry) with a SLM-Aminco 48000 spectrofluorimeter. An argon-ion laser (Coherent; Innova 90-6) was used as the excitation source with a multiwavelength UV line through a 360 ± 5 nm narrow bandpass (Oriel). The fluorescence was collected through a 420 nm longpass filter (Oriel). The emission spectra were background-subtracted and corrected for detector and monochromator transmission nonlinearities.

The passive losses of light from a blank composite glass were determined by measuring the intensity of the beam incident and the beam transmitted through the bulk. A He–Ne laser (Milles Geriot; class IIIb; 632.8 nm) was used as the light source. The intensity of light before and after transmitting through the bulk was measured using a power meter (Newport; Model 815).

The optical power limiting results were obtained at two wavelengths, 532 and 800 nm. The source of 532 nm was a frequency doubled, Q-switched Nd:YAG laser (Quanta Ray DCR-1A) which delivered 8 ns pulses at a repetition rate of 10 Hz. A dye laser (Quanta Ray PDL-1) with an IR dye (LDS 821) from Exciton was transverse pumped at 532 nm to generate ~5 ns pulses at 800 nm. The beam was focused on the center of the sample by a 30 cm focal length lens. Beyond the sample, the transmitted beam was collected by a short focal length aspheric lens and focused onto the surface of a large area photodiode. This ensured that all the transmitted light was collected and artifacts due to self-focusing or defocusing were eliminated. A beamsplitter placed before the sample directed a part of the beam to a second photodiode which was used to monitor the intensity of the incident beam. The incident laser intensity was controlled by a half-wave plate and polarizer combination. Outputs from both the detectors were processed by a gated integrator and a boxcar averager. An analog-to-digital converter in conjunction with a personal computer was used to acquire and store the data, and each data point was averaged over 30 laser pulses.

The system was calibrated (for power limiting experiment) using the blank composite glass which showed a linear response. Data were collected for the three doped composite glasses by starting at the lowest intensity and gradually increasing until damage occurred in the glass. The transmissivity through the samples at low-intensity incidence beam was also measured. To compare the nonlinearity of the transmitted intensity in the different samples, all the data were normalized to a transmissivity of 1 at a low intensity of the incidence beam.

Results and Discussion

Optical Characterization of the Composite Glasses. Figure 2 presents the absorption spectra of the three composite glasses: the dashed line is for BBTDOT-doped, the dotted line is for C_{60}-doped, and the dashed-dotted line is that for BBTDOT + C_{60}-doped. Panel A presents the absorption spectra at the region between 350 and 700 nm. The two glasses doped with BBTDOT exhibit a strong (saturated) absorption band at ~400 nm which has been shown to be due to a single-photon absorption of BBTDOT.[15] The C_{60}-doped composite glass has minimal absorbance in this region. The two glasses doped with C_{60} show a specific weak absorption band in the region between 550 and 650 nm shown more clearly in panel B. The spectrum exhibits two peaks at ~575 and ~622 nm. The weak peak observed at 626 nm, corresponds to the 0 → 0 transition, was reported previously by Catalán et al.[28] The glass doped only with BBTDOT does not exhibit this feature. The difference in the intensity of the absorption between the two glasses doped with C_{60} in the range 560–630 nm could be a result of fluctuation in concentrations (although they are both prepared in the same manner except for the presence of BBTDOT in one of them). At this stage we are unable to clarify this point further.

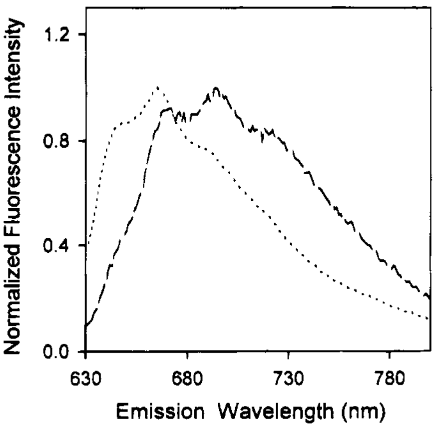

Figure 3. Fluorescence emission spectra of fullerene in toluene solution (dashed curve) and in composite glass (dotted curve), both acquired under ambient conditions (excitation wavelength = 360 nm).

Figure 3 presents the fluorescence emission spectra of fullerene in toluene solution (dashed curve) and in the C_{60}-doped composite glass (dotted curve) at room temperature. The shape of the spectrum which we observed in toluene shows three vibronic peaks (671, 694, and 718 nm) and is similar to the spectrum reported by Kim et al.[7] for C_{60} in toluene. In the composite glass, we observed a similar emission contour with a 30 nm blue shift of the spectrum. The blue shift is attributed to different dielectric constants of the media as suggested before by Reber et al.[29]

The attenuation of light, A, was calculated using the following equation:

$$A = -\frac{10}{L}\log\left(\frac{I_{\text{output}}}{I_{\text{input}}}\right) \qquad (1)$$

where L is the path length through the composite glass, I_{output} is the intensity of the light transmitted through the composite glass, and I_{input} is the incident light intensity. For the blank composite glass, the recovered attenuation loss was approximately 1 dB/m at 632.8 nm. As seen in Figure 2, the doped glasses have a linear

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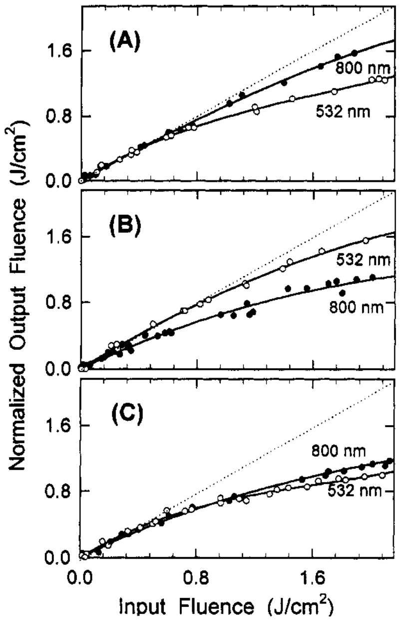

Figure 4. Normalized output fluence as a function of the input fluence for the three composite glasses at 532 (empty circles) and 800 nm (filled circles). Panel A is for C_{60}-doped, panel B is for BBTDOT-doped, and panel C is for C_{60} + BBTDOT-doped composite glasses.

absorption at 632.8 nm, their transmissivity will be discussed with the power limiting results.

Optical Power Limiting in Composite Glasses. Figure 4 presents the normalized output fluence as a function of the input fluence for the three composite glasses at 532 and 800 nm, where panel A is for C_{60}-doped, panel B is for BBTDOT-doped, and panel C is for C_{60} + BBTDOT-doped. It can be seen clearly from Figure 4A that C_{60} is more active as an optical limiter at 532 nm than at 800 nm. Due to a significant linear absorption at 532 nm, this sample, which appears pale brown, shows transmissivity (at a low intensity incidence beam) of 0.40, while at 800 nm it is 0.88. The optical limiting behavior of C_{60} has been suggested to be due to a multitude of mechanisms such as reverse saturable absorption (RSA), nonlinear refraction, and thermal effect which has been discussed elsewhere.[30] At 532 nm, the RSA mechanism is dominant due to a one-photon absorption process.

BBTDOT has a linear absorption maximum at approximately 400 nm and therefore has almost no absorption at either 532 or 800 nm light at low intensity. This was supported by the measured transmissivity (at a low intensity incidence beam) of the pale yellow BBTDOT-doped sample, which was 0.98 at 800 and 0.70 at 532 nm. At higher intensities (>50 MW/cm^2) of the 800 nm beam, a strong TPA induced blue fluorescence was clearly visible in the sample. As expected (Figure 4B), this glass shows a significantly higher nonlinearity at 800 nm than at 532 nm.

On the other hand, the glass doped with C_{60} + BBTDOT had a light brown color and showed transmissivity (at a low intensity incidence beam) of 0.92 at 800 nm and 0.30 at 532 nm. The lower transmissivity at 532 nm is due to linear absorption of the C_{60} molecules. It can be clearly seen from Figure 4C that this sample shows excellent optical power limiting behavior at both 532 and 800 nm. The nonlinear behavior at 532 nm appears to be slightly enhanced compared to the sample doped with only C_{60}. This suggests that there is also a favorable contribution from BBTDOT. On the other hand, at 800 nm, the nonlinearity is slightly less than that due to BBTDOT alone. This is probably due to the fact that the local intensity in the sample decreases due to the presence of C_{60} (some linear absorption), and therefore the nonlinear absorption in BBTDOT, which varies as the square of the incident intensity is reduced.

The damage threshold that we measured in these glasses was in the range 250–300 MW/cm^2 corresponding to a fluence of 2.5–3 J/cm^2. We believe that this value is not the intrinsic damage threshold for the composite glasses but is rather due to particulate contaminants.[31] Processing in a clean-room environment could result in glasses that can withstand much higher fluences without damage.

Conclusions

A novel method to prepare multifunctional nanostructured composites using the sol–gel process has been described in this report. We have demonstrated the doping of two optical limiting materials (C_{60} and BBTDOT) in a single bulk with retained optical limiting effects at each of their characteristic wavelengths. The C_{60}-doped (0.5% wt/wt compared to silica) composite glass exhibited effective optical power limiting at 532 nm due to RSA. The BBTDOT-doped (5% wt/wt compared to polymer) composite glass exhibited effective optical power limiting at 800 nm due to TPA. The multiphasic composite glass doped with both C_{60} and BBTDOT exhibited effective optical power limiting at both wavelengths, independently. The fact that we observed significant optical limiting using nanosecond pulse in the nanostructured composites is further evidence that in the multiphasic nanostructured composites the fullerene mimics its properties in solution but is still phase-separated from the host material and other dopants.

The method described in this article provides excellent optical quality (loss $\approx$ 1 dB/m) in a large size bulk. By using this method, it is possible to dope two (or more) different optically responsive materials, each of which will reside in different phases of the matrix (the silica phase, the PMMA phase, and the interfacial phase), to make multifunctional bulk materials for photonics.

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