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Diazobenzene chromophore-doped silica films with large two-photon absorption cross-section

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ABSTRACT

The diazobenzene chromophore, C.I Direct Red 28 (*Congo Red*) was modified using isocyanatopropyl silane and subsequently incorporated into a silica matrix, which significantly increased the thermal stability of the dye. The third-order nonlinearity of the ensuing hybrid dye–silica film was investigated using Third Harmonic Generation and *Z*-scan measurements at 1064 nm and 400 nm. The observed high, nonlinear refractive index (up to 10^{-8} esu) of the film, as well as the large two-photon absorption cross-section at 1064 nm, was attributed to the enlarged and strengthened conjugated electron system as well as the symmetrical molecular structure of the hybrid material; optical Kerr studies showed that the hybrid films had an ultrafast response time of 0.36 ps at 400 nm.

1. Introduction

Nonlinear optics (NLO) can be expected to continue to play an essential role in photoelectronics and photonics [1–3]. Two-photon absorption (TPA) is a very important third-order NLO effect and can be defined as the simultaneous absorption of two photons via the virtual state at wavelengths far from the molecular linear absorption region. Such nonlinear absorption offers significant potential application in the context of three-dimensional fluorescence imaging, lithographic microfabrication, laser device fabrication, two-photon photodynamic therapy, two-photon pumped up-conversion lasing, optical data storage and optical power limiting [4–12]. Two-photon absorption cross-section is an important parameter used to evaluate the TPA effect and materials with large TPA cross-section are in great demand. Many strategies have been developed to design molecules with large two-photon absorption cross-section; it has been experimentally and theoretically shown that molecular symmetry, strength of donor/acceptor groups, molecular planarity and conjugation length affect TPA cross-section [7,13,14].

Recently, sol–gel derived, organic–inorganic hybrid materials which combine the advantages of both organic chromophores and inorganic matrix have received much attention for both optical and photonic applications because of the inherent properties of the silica matrix, namely high chemical and optical stability as well as ease of modification of processing parameters. Organic molecules with high π-electron delocalization are considered as promising nonlinear optical materials. Active NLO chromophores doped organic–inorganic materials open a new direction for the design and preparation of new types of the applicable NLO materials and devices. In our previous work, disperse red azobenzene chromophore was successfully incorporated into the silica matrix as a side chain, where such side-chain hybrid material shows good third-order optical nonlinearity [15]. However, serious aggregation can be observed among the side-chain chromophores with a long ligand due to the random dispersion in the dense silica matrix, the same as described in other literatures [15–18]. Alternatively, the chromophore would be localized in the inorganic networks separately if being incorporated by two or more covalent linkage points with the matrix, leading to the reduced interaction among the chromophores. Meanwhile, taking into account the significant contribution of delocalization of conjugated electrons to the nonlinear optical properties of hybrid materials, Congo Red (CR; C.I. Direct red 28), containing two amino groups and a diazobenzene chromophore, was chosen as the target NLO chromophore to incorporate within an organic–inorganic hybrid material.

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2. Experimental

2.1. Preparation of hybrid film

CR was modified with 3-isocyanatopropyl trimethoxysilane (ICPTES), and then hydrolyzed with tetraethoxysilane (TEOS) in the presence of 3-glycidyloxypropyl trimethoxysilane as a cross-linker, as shown in Fig. 1. The hydrolyzed sol precursor was aged and then coated on a cleaned glass substrates.

Typically, 0.348 g CR (5×10^{-4} mol) was dissolved in 30 mL DMF under a N_2 atmosphere and 0.247 g ICPTES (10^{-3} mol) as well as several drops of TEA as catalyst, were then added after the CR had completely dissolved. The mixture was stirred at 100 °C for 24 h under a nitrogen atmosphere, after which time, a deep red coloured precursor solution was obtained.

1 mL TEOS, 1 mL GLYMO and 0.05 mL HCl (pH 2) were added to 5 mL of the above CR precursor solution and the ensuing mixture was stirred for 3 days and then aged for 3–4 weeks under ambient conditions. The hybrid films were obtained by spin-coating the sol on a cleaned glass substrate (3000 rpm, 30 min).

2.2. Characterization

UV–vis diffusing reflectance spectra were measured on a Shimadzu UV-3101 equipped with an integrating sphere using $BaSO_4$ as the reference. Fourier transformation infrared (FT-IR) spectra were obtained on Nicolet 7000-C spectrometer with 4 cm^{-1} resolutions using KBr pellets. The samples were scratched from the film and then pressed into pellet with KBr.

Third Harmonic Generation (THG) measurements were performed in a transmission mode. A Nd:YAG laser (Continuum Inc., $\lambda = 1064$ nm, repetition rate = 10 Hz) with a pulse width of 40 ps is used as a fundamental light, which was passed through a narrow band filter and focused with a lens ($f = 200$ mm), finally was incident to the sample. The THG signals were focused by a lens ($f = 50$ mm) and thereafter processed by a spectrometer and detected with an intensified CCD after removing the fundamental light with a narrow band filter at about $\lambda = 355$ nm.

The third-order nonlinear optical properties were measured by using a Z-scan technique. The same fundamental irradiation as that in THG measurements was used to eliminate the accumulative thermal effect. The light intensities transmitted across the samples were measured as a function of the sample position in the Z-direction with respect to the focal plane either through a small aperture (closed-aperture/CA Z-scan) or without an aperture (open-aperture/OA Z-scan), in order to resolve the nonlinear refraction and absorption coefficient. Before measuring, CS_2 was used as a standard reference to calibrate the Z-scan system.

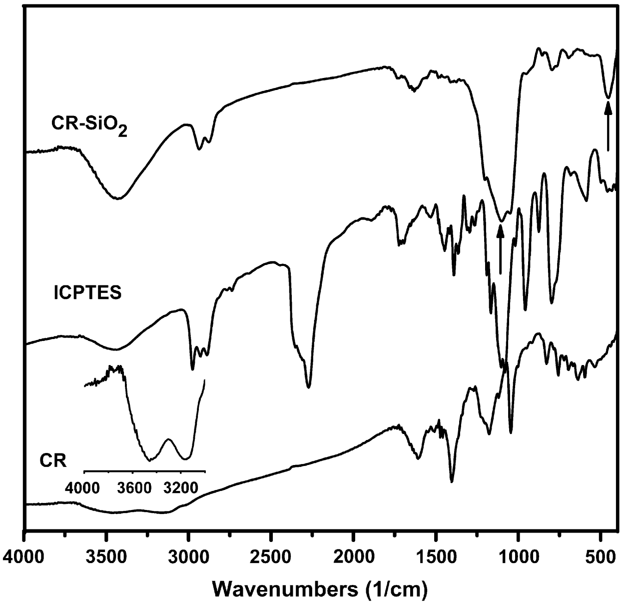

Fig. 2. FT-IR spectra of Congo Red (CR), 3-isocyanatopropyl trimethoxysilane (ICPTES), and CR–SiO_2 hybrid film, respectively. The inset presents the band of amine groups in CR chromophore.

3. Results and discussions

Fig. 2 shows the FT-IR spectra of CR, ICPTES and as-synthesized CR–SiO_2 hybrid film, respectively. The bands of amine groups (3130 cm^{-1}) in CR and the isocyanate group (2270 cm^{-1}) in ICPTES disappeared after the modification, and instead a new band at about 1720 cm^{-1} appears, corresponding to the C=O stretching, indicating the complete reaction between –N=C=O and –NH_2. The successful modification offers the access to the main-chain incorporation of CR into the silica matrix. In the FT-IR spectra of CR–SiO_2 hybrid film, the appearance of the Si–O–Si and O–Si–C bands at

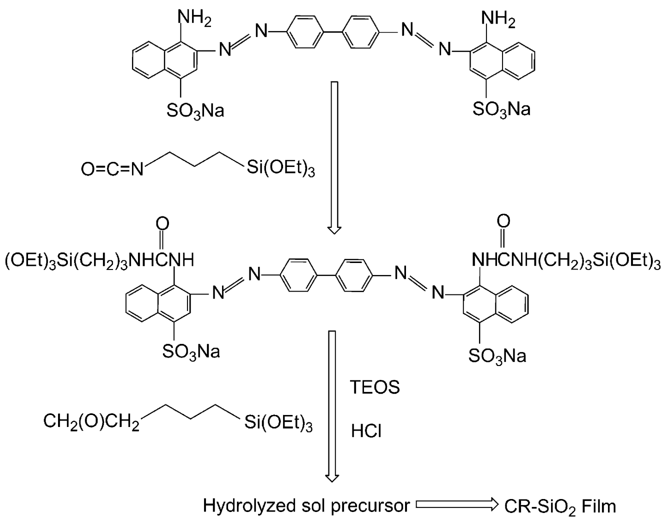

Fig. 1. The presentation scheme for preparing the CR doped main-chain hybrid film.

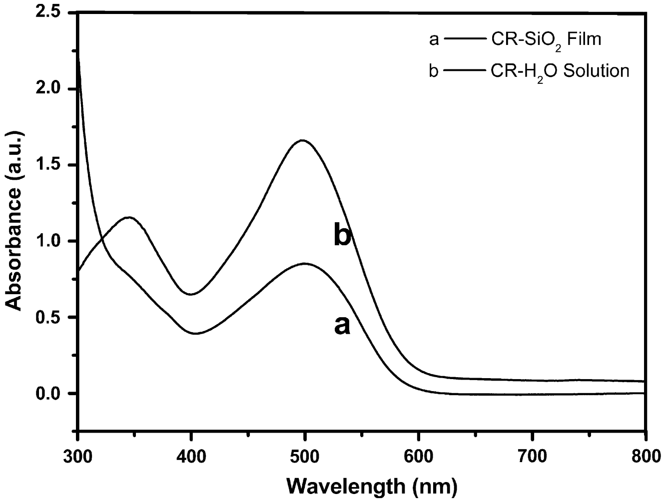

Fig. 3. UV–vis spectra of CR in solution and silica film, respectively.

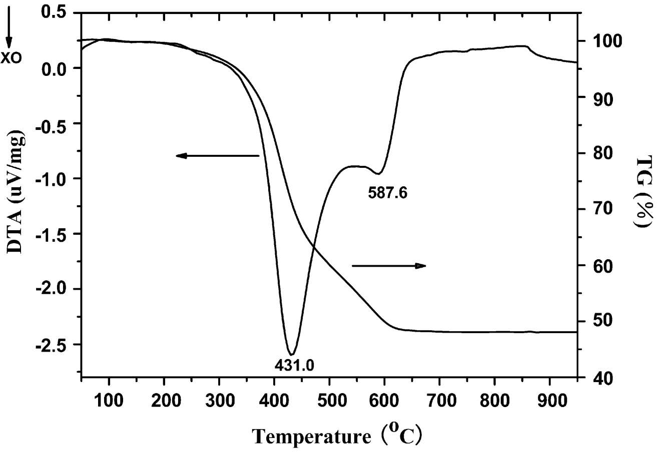

Fig. 4. TG–DTA curves for the CR–SiO_2 hybrid film.

about 480, 800, 1100 cm^{-1} suggests the successful formation of silica networks and covalent bonding between the organics and inorganics. All the results lead to a conclusion that CR chromophore has been covalently linked onto the isocyanate siloxane successfully, and consequently been covalently linked into the silica matrix framework as a main chain.

Fig. 3 shows the UV–vis absorption spectra of CR in solution and SiO_2 film, respectively. The CR solution was prepared by dissolving the CR in deionize water with a molar concentration of about 10^{-5} M, where CR molecules can be considered to exist in a monomer form. CR in solution presents two characteristic absorption bands at 498 nm and 352 nm, corresponding to the π–π^* electron transition in CR molecules. Similarly, main absorption band at 498 nm can be observed in silica film as well as a concealed absorption band at about 352 nm due to the strong absorbance of the silica matrix and substrate in this region, suggesting that the aggregations between azobenzene chromophores are remarkably reduced after being incorporated and localized into the matrix networks as a main chain compared to the side-chain hybrid film. Due to the monomeric dispersion of CR chromophore in silica matrix, the CR concentration in the film can be approximated to satisfy the Beer's law, [19] and according to the absorbance, thickness and the extinction coefficient of CR monomers, it was estimated to be about 0.61 M. Fig. 4 shows the TG–DTA curve for the prepared CR–SiO_2 xerogel material. The organic components account for about 52% of the overall weight. Two exothermal bands can be observed at about 431 °C and 587 °C, corresponding to the decompositions of 3-glycidyloxypropyl trimethoxysilane and main-chain incorporated CR chromophore, respectively, which are significantly higher than that in previous reports where CR was covalently incorporated into the alkyl amide polymer and began to decompose at about 227 °C [20].

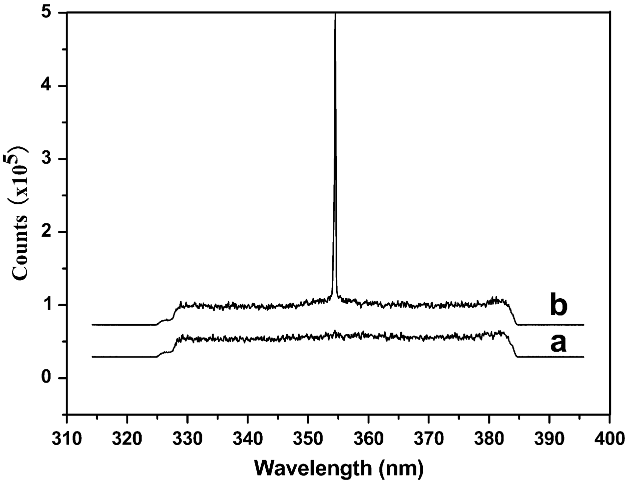

Fig. 5. Third Harmonic Generation (THG) signals of the CR–SiO_2 film and glass substrate, respectively, with a fundamental laser light at 1064 nm.

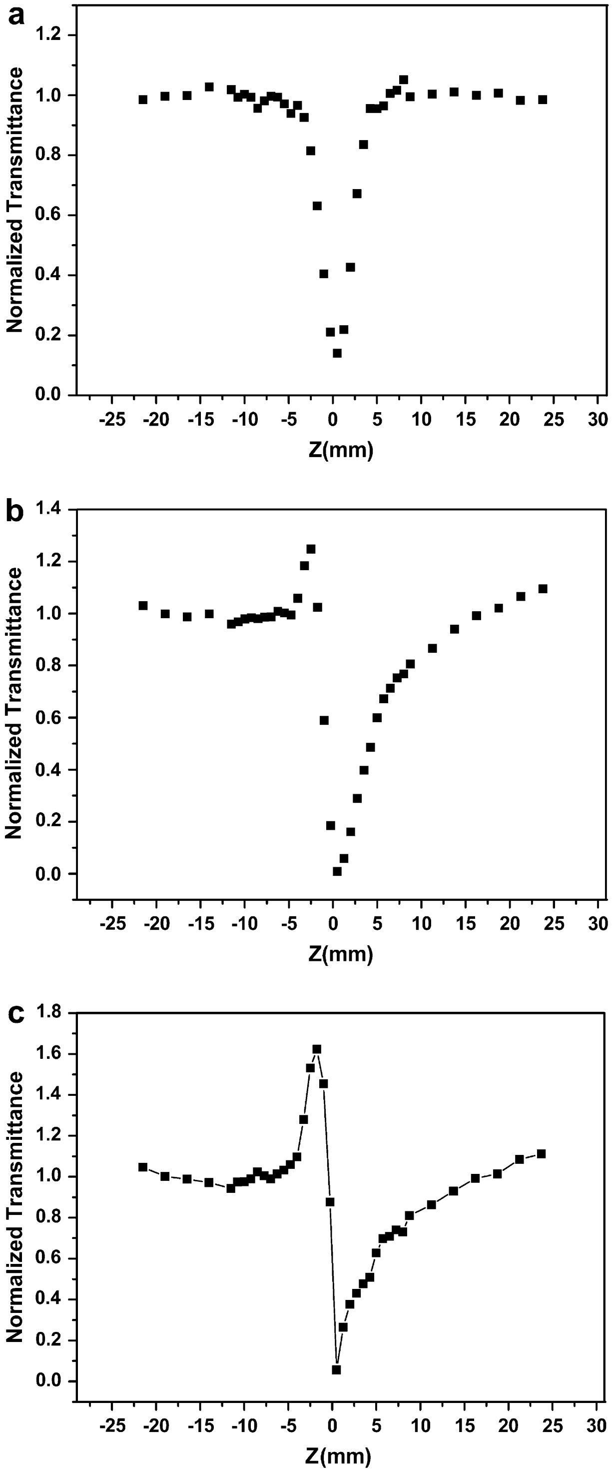

Fig. 6. *Z*-scan results of CR–SiO_2 hybrid film at 1064 nm: (a) open-aperture (OA) curve; (b) original closed-aperture (CA) curve; (c) corrected CA curve.

Third Harmonic Generation (THG) technique has a virtue of being easy to operate and can provide the direct evidence for the presence or absence of third-order optical nonlinearity before the quantitative measurements. Fig. 5 shows the THG signals of CR–SiO_2 hybrid film and the glass substrate, respectively. After the irradiation of a fundamental laser light at 1064 nm, no THG peak can be observed in glass substrate, so the contribution to third-order nonlinearity from glass substrate is negligible under the present measurement condition. However, the CR–SiO_2 hybrid film shows a sharp signal at about 355 nm, indicating the presence of third-order NLO effect in such main-chain hybrid films.

The quantitative measurements of the third-order optical nonlinearity of CR–SiO_2 film at 1064 nm were performed with the *Z*-scan technique using a Nd:YAG laser with a pulse width 40 ps and a repetition rate 10 Hz, which offers simplicity as well as very high sensitivity for measuring both the nonlinear refractive index (n_2) and nonlinear absorption coefficient (β) by the measurement of the normalized transmittance through the closed and open-apertures versus the sample position. The nonlinear absorption of the hybrid film was shown as an open-aperture (OA) curve in Fig. 6a. The transmission is symmetric with respect to the focus where it has minimum transmission, indicating the presence of two-photon absorption. The nonlinear absorption coefficient β can be calculated to be 6.05×10^{-9} m/W according to the equations in Refs. [15,21]. As discussed above, the main-chain doped CR chromophores exist monomerically in the silica networks, the two-photon absorption cross-section δ can be calculated using $\delta = h\upsilon\beta/N$ from the β value, where N is the number of molecules per cm^{-3} and $h\upsilon$ is the photon energy [13,14]. Usually, δ is expressed in Goppert–Mayer units (GM), $1\ GM = 1 \times 10^{-50}\ cm^{-4}$ s/molecules/photon. The TPA cross-section of CR–SiO_2 hybrid film was calculated to be about 3×10^4 GM, considerably higher than that of azobenzene solutions [13,14] and fluorenes and bis(styryl)benzene derivatives [7], which may be mainly attributed to the remarkably higher molar concentration and also much the higher nonlinear absorption coefficient in the film than those in the solution. In addition, the large TPA cross-section also depends on the molecular symmetry, strength of donor/acceptor groups, and conjugation length of CR–SiO_2 hybrid film. Albota and co-workers have shown that large cross-sections can be obtained for molecules possessing symmetric charge transfer from the extremities of a conjugated system to the middle, or vice versa [7]. CR chromophore has an absolutely symmetric molecular structure, the middle diazobenzene chromophore with the electron donors on the opposite sides, which would lead to an enhanced TPA cross-section. It is worthy noting that the enlarged conjugation length, together with the enhanced electron donating capacity from the silica matrix, also plays an important role in the enhancement of the TPA cross-section, because it has been shown that the silane grafting and covalent linkage into silica matrix could enhance the π conjugation of the azobenzene chromophore [15,22].

Fig. 6b shows the *Z*-scan closed-aperture (CA) curve for CR–SiO_2 hybrid film, and the corrected CA curve purely coming from the nonlinear refractive index changes is shown in Fig. 6c due to the presence of the nonlinear absorption. A peak-valley shape presents the negative nonlinear refractive index and a self-defocusing propagation of the laser light in such hybrid film. The nonlinear refractive index n_2 can be estimated to be $-3.05 \times 10^{-15}\ m^2/W$, i.e., -1.13×10^{-8} esu, more than one magnitude higher than that of the disperse red 1 azobenzene chromophore doped side-chain silica hybrid film [15] and other azobenzene chromophore solutions or polymer-based composites at 1064 nm [23–25], which may be attributed to the enlarged π-electron conjugation due to the linked diazobenzene chromophore, as well as the large TPA cross-section.

In addition, the optical nonlinearity of CR–SiO_2 film was also detected by optical Kerr effect (OKE) with laser pulses at wavelength of 400 nm. The response time of the hybrid film is estimated to be 0.36 ps according to the time resolved pump detection response curve, as shown in Fig. 7a, which has the similar value as that of azobenzene chromophores in solutions or matrices [26,27], but it is shorter than that of DR azobenzene doped side-chain hybrid film [15] (about 0.6 ps, also as shown in Supporting information) attributed to the photoisomerization between the *trans* and *cis* configurations of azobenzene chromophore. However, taking into account the complicated and giant CR molecule together with the main-chain structure fixed in the rigid silica matrix (Fig. 7b), such a photoisomerization between the *trans* and *cis* configurations is believed to be non-effective, therefore the ultrafast response can be attributed to the electronic nonlinearity due to the delocalization of the conjugated electrons rather than the photoisomerization effect of CR molecules. This ultrafast NLO response has great potential for applications in ultrafast communication and signal processing systems.

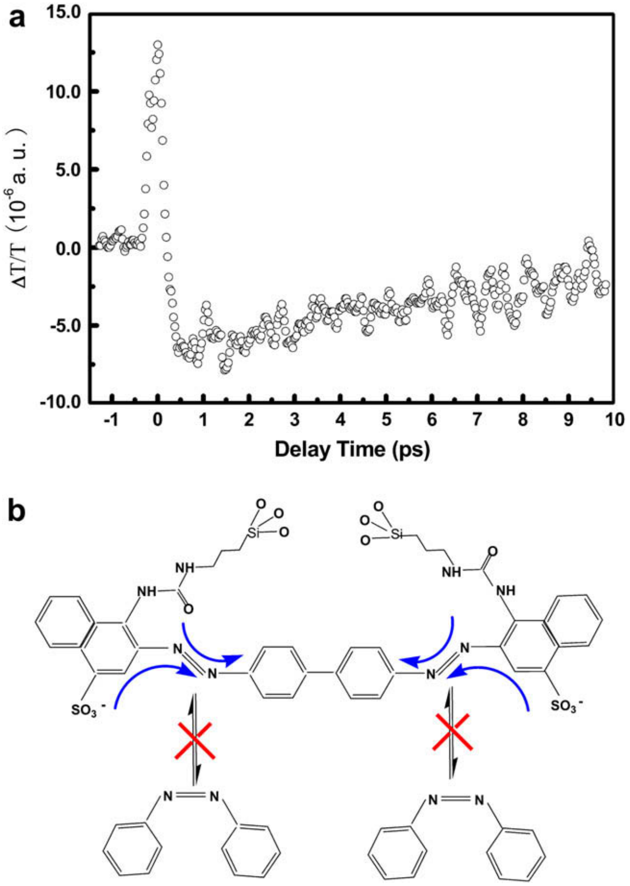

Fig. 7. (a) Time resolved OKE response curve of CR–SiO_2 hybrid films with laser pulses at wavelength of 400 nm; and (b) schematic representation for time responses due to electron nonlinearity.

4. Conclusions

C.I. Direct Red 28 was successfully incorporated into a silica matrix such that chromophore aggregation is minimised and the thermal stability of the dye is increased. The CR–SiO_2 film displays a very large TPA cross-section and enhanced third-order optical nonlinearity owing to the symmetrical molecular structure of the hybrid material and increased extent of conjugation at 1064 nm; furthermore, the hybrid film exhibits ultrafast response time (0.36 ps at 400 nm).

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Appendix. Supporting information

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.dyepig.2009.01.002

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