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Abstract. The ultrafast third-order nonlinear optical properties of C_{60} + vinyltriethoxysilane $H_2C{=}CHSi(OC_2H_5)_3$ (C_{60} + VTES) sol-gel were investigated by the femtosecond optical Kerr gate (OKG) technique at 800 nm. The third-order optical susceptibility was measured to be 5.42×10^{-14} esu for C_{60} + VTES at a weight concentration of 0.06 wt.%. Using C_{60} + VTES as the OKG material, we acquired a series of narrow bandwidth and symmetric gated spectra continuously from the chirped white light continuum generated in water with femtosecond laser pulses. The gated spectra obtained using the C_{60} + VTES OKG have distinct superiorities compared with CS_2. [DOI: 10.1117/1.3644555]

Subject terms: fullerene; optical Kerr gate; femtosecond; nonlinear optical properties.

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1 Introduction

The materials with large nonlinear optical susceptibilities and ultrafast response time have attracted much attention in the past two decades.[1–4] They were properties essential for various photonic devices such as ultrafast all-optical switches, optical modulators, and optical limiting.[5–8] Among the numerous materials investigated, fullerene (C_{60}) and its derivatives were explored with great interest.[9–11] Due to the larger activity of C_{60} molecule with plenty of delocalized π electrons, C_{60} showed excellent optical properties, especially relatively large third-order nonlinear optical (NLO) susceptibility and fast response time. This was due to the break of the highly symmetric electronic structure of C_{60} by the introducing charge transfer process. A good number of works on the nonlinearity of C_{60} were reported, and they were focused mostly on liquid solution of C_{60} and C_{60}-doped bulk material.[12–17] Compared with the solution $C_{60,}$ the bulk materials containing C_{60} have obvious advantages due to favorable physical–chemical stability and are easily formed into desired shapes. Therefore, new C_{60}-doped bulk materials with a large optical nonlinearity and a fast response time were crucial for practical application. Sol-gel processing was a significant technique for developing the organic–inorganic hybrid nanocomposites at low temperatures, at which organic molecules may not be decomposed. Thus, the nonresonant-type bulk materials with C_{60} synthesized by the sol–gel method were expected to have large NLO susceptibilities, low optical absorption, ultrafast response time, long interaction length, and compact-sized optical elements. In addition, although many C_{60}-doped bulk materials with excellent NLO properties have been reported,[13,17] the research results using C_{60}-doped bulk materials as optical Kerr gate (OKG) medium to investigate ultrafast phenomena were not really mentioned.

In the present work, we applied the ultrafast OKG of C_{60} + vinyltriethoxysilane $H_2C{=}CHSi(OC_2H_5)_3$ (C_{60} + VTES) to arbitrarily choose a slice of the chirped white light continuum (WLC) generated in water with femtosecond laser pulses. Experimental results showed that the gated spectra intercepted using OKG of the C_{60} + VTES have much narrower bandwidth and better symmetrical profile than that of CS_2. Moreover, we reported the measurement of the NLO properties of the C_{60} + VTES bulk material using femtosecond the OKG technique at 800 nm. The third-order optical susceptibility was obtained at about 5.42×10^{-14} esu for C_{60} + VTES.

2 Experimental Set-Up

The C_{60}-doped bulk material was synthesized by hydrolysis condensation of the organically modified precursors vinyltriethoxysilane (VTES) in ethanol under acid (HCl)-catalyzed hydrolysis and basic-catalyzed condensation. Details of preparation processing were described in the literature.[18] C_{60} was dissolved in *N*,*N*-dimethyl formamide/ethanol mixed solvent and sonicated for about 1 h and then introduced into the sol-gel precursor solution. The weight concentration of C_{60} + VTES employed in our experiments was 0.06 wt.%.

For the measurement of the NLO properties of medium, other technologies, such as degenerate four-wave mixing,[19] nonlinear interferometry,[20] and *Z*-scan,[21] have been proposed and used. However, the first two methods all required relatively complex experimental apparatus. On the other hand, although *Z*-scan was a simplistic and highly sensitive technique, the main deficiency of *Z*-scan was that it cannot provide information about fast response time of a medium. In view of the above, we employed the femtosecond OKG method to study the NLO properties of C_{60} + VTES.

The experimental setup is shown in Fig. 1. A chirped-pulse-amplified Ti:sapphire laser system was employed, which delivered pulses of 30 fs duration at 800 nm with a 1-kHz repetition rate. The output beam was split into two

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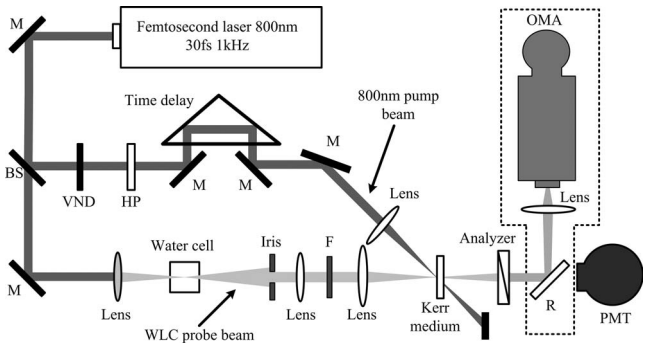

Fig. 1 Experimental setup for the OKG measurement. M: mirror; BS, beam splitter; HP: half-wave plate; PMT: photomultiplier tube; VND: variable neutral-density filter; F: low-pass filter; OMA: optical multichannel analysis spectrometer system; R: folding reflector.

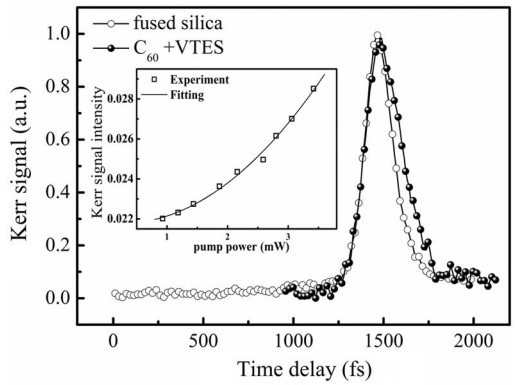

Fig. 2 The OKG experimental results of $C_{60}+$VTES and fused silica under the same conditions. The inset is the pump power dependence of OKG signals in $C_{60}+$VTES when the delay time was kept at 0 fs.

parts. The intense one acted as the pump beam which passed through an optical delay line driven by a step motor for introducing the delay time of the pump beam to the probe beam. A half-wave plate and a variable neutral-density filter were inserted into the optical path of the pump beam to change the polarization angle and energy of the pump beam, respectively. The WLC was generated by focusing the weak beam into a 1-cm thick quartz cell containing water as the probe beam. An iris was placed close to the back surface of the cell to eliminate the outer conical emissions from white-light filaments. A low-pass filter was used to remove the strong infrared part of the WLC spectrum. After recollimation, the WLC and pump beams were cross incident into the Kerr material by two achromatic lens with focus length 20 and 10 cm, respectively. The polarization of the pump and WLC beams were adjusted to be $\pi/4$ to each other. After transmitting through the Kerr material, the WLC beam passed through an analyzer, the transmission axis of which was strictly perpendicular to that of the WLC beam. The analyzer allowed only Kerr signals to pass through it, when the pump and probe beams overlapped spatially and temporally on the Kerr material. A photomultiplier tube was employed as a detector. When the gated spectra were measured, the slice of WLC transmitted through the analyzer was reflected by a folding reflector behind the analyzer and then completely focused onto an optical multichannel analysis (OMA) spectrometer system.

3 Results and Discussion

Using the typical cross OKG setup, the nonlinear response time of $C_{60}+$VTES was measured at a wavelength of 800 nm. The thickness of $C_{60}+$VTES was 0.7 mm. Fused silica was selected as a reference sample because it has an instantaneous (about 1 fs) response.[22] As shown in Fig. 2, the response time of $C_{60}+$VTES is about 242 fs full width at half maximum (FWHM). The duration of the time-resolved Kerr signal for fused silica is about 185 fs. The broadening of the 800 nm pulse was caused by group velocity dispersion effect when it transmitted through the nonreflective optical elements in the OKG setup.

The OKG signals of fused silica and $C_{60}+$VTES were measured under the same conditions. The circles in Fig. 2 show the experimental results. The magnitude of $\chi^{(3)}$ of the $C_{60}+$VTES sample can be calculated with the following equations:[13,23]

$$\chi_S^{(3)} = \chi_R^{(3)} \left(\frac{I_S}{I_R}\right)^{1/2} \left(\frac{n_S}{n_R}\right)^2, \tag{1}$$

where the subscripts S and R stand for sample and fused silica, respectively, I is the OKG signal intensity of the sample at zero delay time, and n is the linear refractive index. The nonlinear refractive index n_2 and n of fused silica are 2.4×10^{-16} cm^2/W and 1.45, respectively.[24] The nonlinear refractive index was related to the third-order optical susceptibilities by[25]

$$n_2 \left(\frac{\text{cm}^2}{\text{W}}\right) = \frac{0.0395}{n^2} \chi^{(3)}(\text{esu}). \tag{2}$$

The corresponding $\chi^{(3)}$ of fused silica is 1.28×10^{-14} esu. The linear index of the sample is 1.55. The value of $\chi^{(3)}$ for $C_{60}+$VTES is obtained to be 5.42×10^{-14} esu by Eq. (1). The third-order optical susceptibility measured is smaller than that of other C_{60}-doped bulk materials reported in Ref. 13, which is probably due to the low concentration of C_{60} in the bulk material.

In the OKG measurements, the probe transmittance of the sample was given by[26]

$$T = T_0 \left(\frac{24\pi L_{\text{eff}} \chi^{(3)}}{n_S^2 a^3 C \lambda_p}\right)^2 I_{\text{pump}}^2, \tag{3}$$

where a is the beam radius at the focal point; L_{eff} is the absorption coefficient; C is the velocity of light; λ_p is the wavelength of probe beam; and I_{pump}^2 is the pump intensity. The inset of Fig. 2 gives the probe transmittance as a function of the pump intensity at 800 nm when the delay time between the pump and probe pulses was kept at 0 fs. From the inset, below the pump power of 3.5 mW, the measured values of the transmittance increased in proportion to the square of pump intensity as expected from Eq. (2). This result confirms that the system is in the OKG operation.

To validate the practical application of $C_{60}+$VTES in a broadband spectrum, it was employed as the medium of ultrafast OKG to arbitrarily choose a slice of the WLC generated in water with 800 nm femtosecond laser pulses. Figure 3 shows the absorption spectra of the medium. From the figure, it is noted that no obvious linear absorption from 400 to 800 nm was observed in $C_{60}+$VTES. So this material was suitable as the Kerr gating material to select the WLC. The strong infrared part of WLC was filtered. The spectral

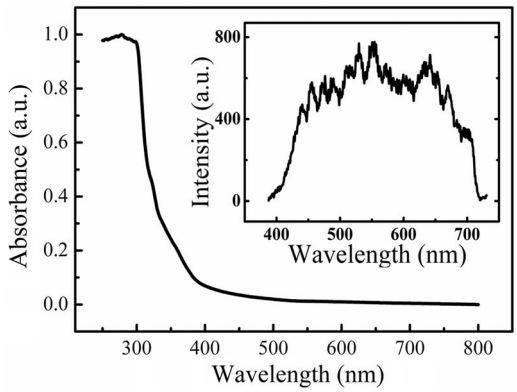

Fig. 3 Absorption spectra of $C_{60}+$VTES and the spectra of WLC (inset).

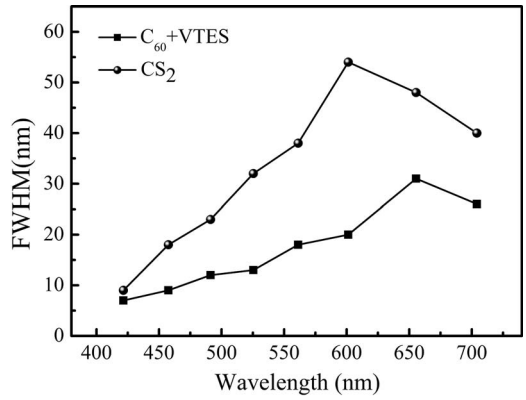

Fig. 5 Variation of FWHM of the Kerr-gated spectra as a function of the wavelength.

characteristic of WLC generated was measured by using an OMA spectrometer system. As shown in the inset of Fig. 3, the WLC spectrum ranged from 400 to 700 nm.

Figures 4(a) and 4(b) show the obtained gated spectra of WLC when $C_{60}+$VTES and CS_2 are used as Kerr media, respectively. By varying the delay time between pump and WLC probe beams, the slices with different center-wavelengths in WLC were intercepted arbitrarily. Compared with CS_2, the gated spectra using $C_{60}+$VTES have much narrower bandwidth and a better symmetrical profile. This was because the nonlinear response time of $C_{60}+$VTES was much faster than that of CS_2. This signified that the OKG with $C_{60}+$VTES had a higher time resolution for its potential practical application. In addition, the experimental results show that OKG with $C_{60}+$VTES has a higher ability to intercept WLC than CS_2 in the short-wavelength region. Particularly, in the wavelength range from 408 to 457 nm, the gated spectra selected by CS_2 can hardly be distinguished, while the gated spectra selected by $C_{60}+$VTES were clear.

The Kerr-gated spectra of the WLC pulse were characterized with OKG measurements. Figure 4 presents the relative spectral width versus the various center-wavelengths of the gated spectra. As can be seen from the figure, the bandwidth of the gated spectrum first increases and reduces afterward when the center-wavelength of the gated spectrum moves from 408 to 700 nm. This is attributed to the chirp of the WLC pulse. However, due to the ultrafast response time of $C_{60}+$VTES, the bandwidths of all gated spectra acquired by

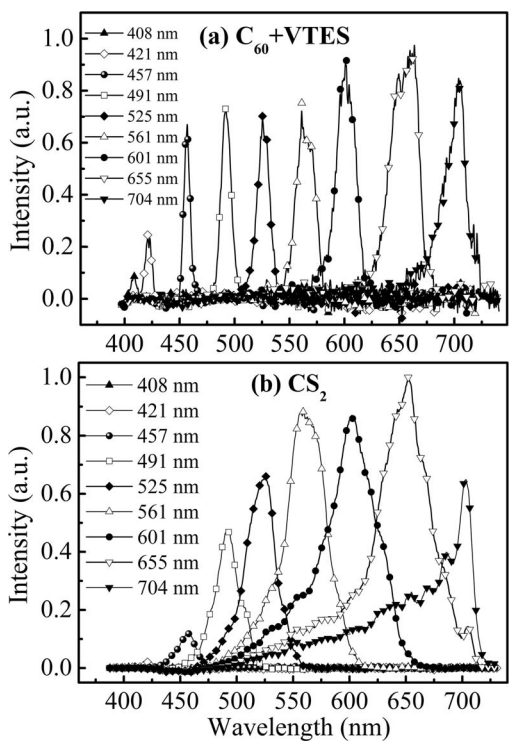

Fig. 4 A series of Kerr gated spectra of WLC probed at different time delay. (a) $C_{60}+$VTES as Kerr material; (b) CS_2 as Kerr material.

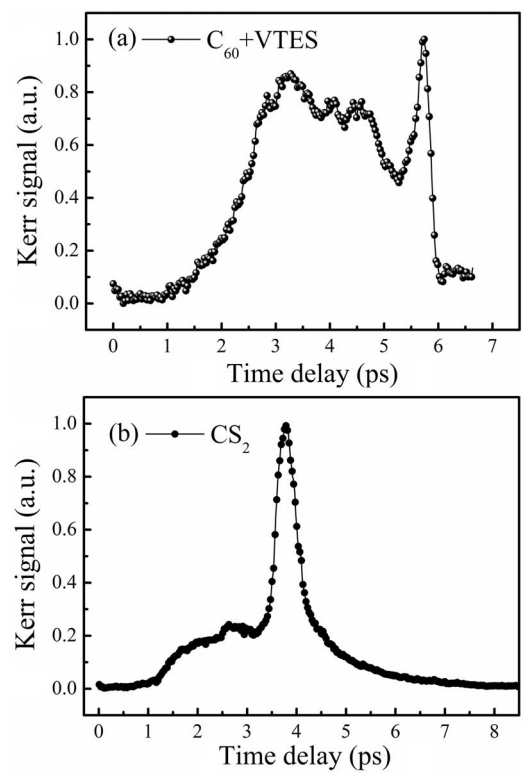

Fig. 6 Time-resolved measurements for the WLC using OKG with different Kerr materials. (a) $C_{60}+$VTES; (b) CS_2.

the C_{60} + VTES gate are narrower than that acquired by CS_2, as shown in Fig. 5.

The time evolution of the WLC pulse was also measured by using the time-resolved optical Kerr gate with C_{60} + VTES and CS_2, and the results are shown in Fig. 6. Here, the 800 nm filter has been moved. As shown in Fig. 6(a), the duration of the time-resolved signal of C_{60} + VTES with WLC probed was estimated to be about 3.3 ps (FWHM). The temporal broadening of the WLC pulse was mainly acquired during the generation and propagation in the water cell and optical elements before the sample. The WLC pulse presented positive chirps. This means that the leading edge of the WLC pulse comprised the red spectral component while the trailing edge comprised the blue component. The most energy of the WLC pulse will be in the red spectral region which gives rise to the tailing edges of the time-resolved Kerr signals of C_{60} + VTES and CS_2 are higher than the leading edges. Furthermore, the tailing edge of the time-resolved Kerr signal of C_{60} + VTES is steep because the third-order optical nonlinearity in this material originated from mainly electronic polarization. The time-resolved Kerr signal of CS_2 with WLC probed has a long trailing edge, which is attributed to the slow response time from molecular orientation relaxation.[27,28]

4 Conclusions

In conclusion, the optical nonlinearity of C_{60} + VTES has been measured by OKG techniques with femtosecond laser pulses. Third-order susceptibility of 5.42×10^{-14} esu was obtained at a weight concentration of 0.06 wt.%. The nonlinearity response time of that was 242 fs. Compared with CS_2, C_{60} + VTES had a distinct advantage when it acted as the Kerr gate material. The gated spectra obtained using C_{60} + VTES have a narrower bandwidth and better symmetry with respect to CS_2. The experiments in this investigation confirmed that C_{60} + VTES has both relatively large nonlinearity and an ultrafast response time. These advantages promised this medium to find potential applications in femtosecond OKG measurement and other optical devices.

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