

Third-order nonlinear optical responses of colloidal Ag nanoparticles dispersed in BMI.BF₄ ionic liquid

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Abstract: The third-order nonlinear optical responses of tetrafluoroborate 1-*n*-butyl-methylimidazolium (BMI.BF₄) and colloidal Ag nanoparticles dispersed in this medium were investigated. Hybrid organic-metallic colloids consisting of silver nanoparticles dispersed in BMI.BF₄ were synthesized. Using the thermally managed Z-scan technique, the electronic contribution to the nonlinear refractive indexes of the BMI.BF₄ and colloids with two different nanoparticles filling factors were measured, as well as the media's nonlinear absorption. The performance of these systems for all-optical switching was also evaluated. The obtained results indicate that these are promising candidates for the development of nonlinear optical applications.

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OCIS codes: (160.4330) Nonlinear optical materials; (190.4400) Nonlinear optics, materials; (160.4236) Nanomaterials.

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1. Introduction

Hybrid nanostructured organic-metallic colloidal systems are among the most promising systems for the development of optical and photonic devices due to the fact that they can

present improved physical and chemical characteristics in comparison with the separated organic or metallic constituents. For instance, the presence of metallic nanoparticles enhances significantly optical nonlinear responses [1–9], the thermo-optical effect [6, 10, 11], Raman [12, 13] and luminescent [14, 15] emissions of composite systems. However, the optimal choice of the dispersant, stabilizer and particles is still a matter of research in order to obtain more stable hybrid materials with suitable optical properties.

Among the myriad of organic materials, ionic liquids (ILs) are a class of molten salts consisting only of ions that melt at temperatures below 100 °C. In particular those derived from imidazolium cation possess various interesting physico-chemical properties [16–18]. These properties include high chemical and thermal stability, low inflammability, a negligible vapor pressure, being liquid over a wide temperature range, wide electrochemical windows, excellent ionic conductivity, easy recycling, and tunable miscibility with water and organic solvents. The ILs are used in several areas, such as electrolytes for battery [19, 20], electrochemical sensors [16], solvents for organic synthesis and catalysis [21] and optical applications [22–24]. Moreover, ionic liquids provide an excellent medium for the formation and stabilization of transition-metal nanoparticles and no extra stabilizing molecules are needed [18, 25–27].

Although there is huge potential for the improvement of the ILs optical properties aided by the presence of metallic nanoparticles, no investigation on the optical properties of hybrid colloids of such media has been reported yet, nor any optical application exploiting this kind of material has been proposed up to this moment. In this work, we report on the investigation of the third-order optical nonlinearities of 1-*n*-butyl-3-methylimidazolium tetrafluoroborate (BMI.BF₄) and colloids of Ag nanoparticles (AgNP) dispersed in this IL. Using the Z-scan technique with thermal management [28–32], the electronic contribution to the nonlinear refraction of these media was measured and the potentiality of this colloidal system for all-optical switching applications analyzed. The obtained results demonstrate that hybrid systems composed by metallic nanoparticles and ionic liquids are promising materials for nonlinear optical applications.

2. Experiment

The BMI.BF₄ with silver nanoparticles dispersed in (Ag-BMI.BF₄) were synthesized as previously described in the literature [26, 33, 34]. In a Fischer-Porter bottle containing BMI.BF₄ (1 mL), a mixture of Ag₂O (34.0 mg, 0.15 mmol) and *n*-butylimidazole (80 mL, 0.61 mmol) was stirred at room temperature for 15 min yielding a black dispersion. The system was then heated to 85 °C and hydrogen (4.0 bar) was admitted to the system. After stirring for 2 h a brown ‘solution’ was obtained. The reactor was evacuated for 1 h at 100 °C to remove excess hydrogen and *n*-butylimidazole [35]. Highly stable colloidal system, hereafter called mother solution (MS), was obtained with a 1.52×10^{-3} Ag particles filling factor.

The analysis of the morphology and the electron diffraction (ED) of the AgNP obtained were carried out on a JEOL microscope (JEM-2010) equipped with an energy-dispersive X-ray spectroscopy (EDS) system and a JEOL JEM-1200 EXII electron microscope operating at accelerating voltages of 120 kV. The samples for TEM were prepared by dispersion of the Ag-BMI.BF₄ nanoparticles at room temperature and then collected on a carbon-coated copper grid. UV-VIS-NIR absorption spectroscopy was performed in order to identify the surface plasmon resonance due to the AgNP and measure the linear absorption coefficient of the colloid at the laser wavelength.

The investigation of the media's nonlinear refractive index was performed using a tunable mode-locked Ti:Sapphire laser as excitation source. This system was tuned at 793 nm and delivered 200 fs pulses at a 76 MHz repetition rate. The light beam was modulated at 14 Hz, with 0.09 duty cycle, by a chopper with an opening rise time equal to 24 μs. The modulated beam was focused by a convergent lens with 7.5 cm focal length. The colloidal sample was placed within a 1 mm width quartz cuvette. This cell was attached to a linear translation stage which was put along the beam path. Using a computer-controlled motorized step motor

system, the sample position relative to the lens focal plane was modified. The light transmitted through the nonlinear medium was spatially filtered by an iris and monitored by a photodetector as a function of the sample position.

Owing to the laser high repetition rate, electronic and thermal contributions to the nonlinear refraction phenomena are present. However, these effects can be discriminated due to the distinct dynamics they exhibit [29–32]. While the nonlinear refraction of electronic origin displays an instantaneous response, the formation of a thermal lens is slow. Therefore, defining $t = 0$ as the instant that the chopper begins to unblock the laser beam, only the electronic nonlinearity contributes to the measured transmittance at times instants near to $t = 0$. On the other hand, the thermal effect overcomes the electronic at longer times, and the spatial profile of the transmitted light is thermally modified in this case.

However, the direct transmittance measurement at $t = 0$ is not feasible. Indeed, between $t = 0$ and the chopper rise time (τ_{risetime}), the laser beams is partially blocked. Due to this fact, the laser beam spatial profile on the sample surface is not Gaussian. Therefore, a Z-scan curve cannot be obtained accurately in the temporal range $0 < t < \tau_{\text{risetime}}$. This problem could be avoided by following the procedure proposed by Gnoli et al [31]. During the Z-scan measurement, at each sample position, the temporal evolution of the normalized transmittance was acquired. The measured data between $t = 0$ and τ_{risetime} were disregarded. Then, the remaining temporal curve of the normalized transmittance was extrapolated until $t = 0$ s, using a single exponential decay function. From the obtained values for the normalized transmittance at $t = 0$, the Z-scan curve at this time instant was rebuild. The material nonlinear refractive index of electronic origin can be obtained fitting this curve with the equation [28]

$$Tr(z) \cong 1 + \frac{4\Delta\Phi_0(z/z_0)}{\left[(z/z_0)^2 + 9\right]\left[(z/z_0)^2 + 1\right]}, \quad (1)$$

where z is the sample position relative to the lens focal plane ($z = 0$), $\Delta\Phi_0 = k n_2 I_0 L_{\text{eff}} / \sqrt{2}$ is the nonlinear phase shift, k is the modulus of the wavevector, n_2 is the medium nonlinear refractive index, I_0 is the light intensity at the focus, $L_{\text{eff}} = (1 - e^{-\alpha_0 L}) / \alpha_0$ is the sample effective length, α_0 is the linear absorption coefficient of the colloid, L is the sample length, $z_0 = \pi w_0^2 / \lambda$ is the beam Rayleigh length, w_0 is the minimum beam waist and λ is the laser wavelength. This procedure was tested using CS₂ as a reference nonlinear medium, and the obtained result presented a very good agreement with previous works reported in literature [28, 30–32].

The material nonlinear absorption can be investigated using the Z-scan technique without the iris. In this case, we employed the same focalization lens, photodetector and Ti:Sapphire laser tuned at 793 nm, but its repetition rate was reduced to 1 kHz by means of a pulse picker, and no chopper was employed. The intensity of the light transmitted through the sample was measured as a function of its position. The transmittance normalized by the transmitted intensity when the sample was positioned far away from the lens focal plane can be expressed as [28]

$$Tr(z) = \sum_{m=0}^{\infty} \frac{[-q_0(z, 0)]^m}{(m+1)^{3/2}}, \quad (2)$$

where $q_0(z, t) = \alpha_2 I_0(t) L_{\text{eff}} / (1 + z^2/z_0^2)$ and α_2 is the sample's nonlinear absorption coefficient.

3. Results and discussions

The Ag(0) nanoparticles were prepared by simple reduction of Ag₂O in BMI.BF₄ using the procedure described by Janiak and associates [34]. In this procedure the sole by-product is water and generates silver nanoparticles of different diameters, but with roughly spherical shapes, in the ionic liquid. To investigate the optical properties of this hybrid system, the filling factor of the colloid was reduced by diluting the MS using BMI.BF₄. Two colloids with different concentrations were produced using this approach, namely AG1 and AG2, with 0.76×10^{-3} and 0.38×10^{-3} filling factors respectively.

In Fig. 1 are presented a typical TEM image of the produced particles and the absorption spectra of the MS and the neat BMI.BF₄. As can be observed, mostly particles with less than 10 nm diameters are produced using this approach. However, larger particles are also produced [34] and can be visualized in the image. The absorbance presents a broad peak, centered at 452 nm. This result indicates that Ag nanoparticles with distinct sizes are present in the colloid, as observed at the TEM images. Indeed, although the majority of the produced particles are smaller than 10 nm, the larger particles give a strong contribution to the colloid optical properties, as they occupy a significant sample volume despite their small amount. Similar results were observed in previous investigated colloidal systems consisted of Ag particles in BMI.BF₄, produced by an alternative method [12]. It was also verified that samples' linear absorption coefficient, at 793 nm, increases as the particles' filling factor is raised, as shown in Table 1.

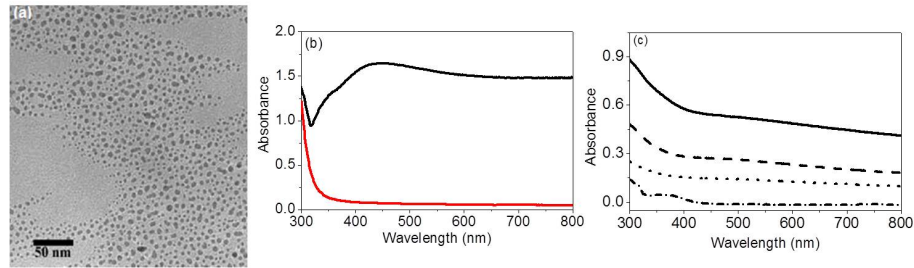


Fig. 1. (a) TEM micrograph of Ag-BMI.BF₄. (b) UV-VIS-NIR absorption spectra of the mother solution (black line), as prepared, and pure BMI.BF₄ (red line), measured within a 5 mm quartz cell. (c) UV-VIS-NIR absorption spectra of MS (solid line), AG1 (dash line), AG2 (dot line) colloids and pure BMI.BF₄ (dash-dot line), measured within a 1 mm quartz cuvette.

Table 1. Optical properties of the investigated samples

Sample	Filling factor	α_0 (cm ⁻¹)	n_2 (cm ² /W)	a_2 (cm/W)	T	W
AG1	0.00076	4.16	-6.3×10^{-14}	-1.4×10^{-10}	0.4	> 0.06
AG2	0.00038	2.27	-4.4×10^{-14}	$< 5 \times 10^{-11}$	< 0.2	> 0.07
BMI-BF ₄	0	0.014	$< 1.0 \times 10^{-15}$	$< 5 \times 10^{-11}$	< 7.6	> 2.2

The reconstructed closed aperture Z-scan curves at $t = 0$ for the investigated colloids and the neat BMI.BF₄ are shown in Fig. 2. The respective fitting curves using Eq. (1) are also displayed. As can be observed, the colloids presented a typical negative nonlinear refraction, however no signal could be detected for the neat IL. Moreover, as the particles filling factor was increased, the nonlinear refractive index was also raised up to two orders of magnitude. A summary of the obtained values for the nonlinear refractive index of those materials are presented in Table 1.

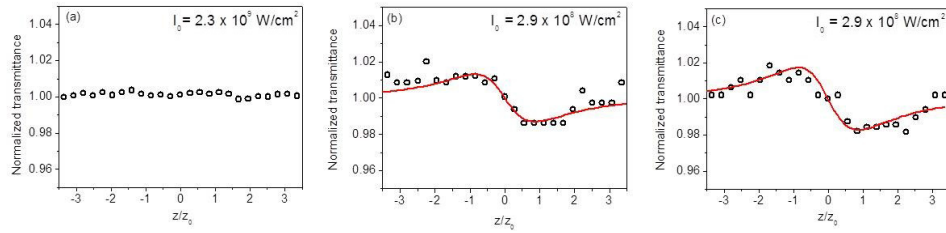


Fig. 2. Closed aperture Z-scan curves at $t = 0$ of (a) pure BMI.BF₄, (b) AG2 and (c) AG1 samples. Open circles correspond to the experimental data and the red lines are the fitting curves obtained with Eq. (1).

It is worth mentioning that even the neat BMI.BF₄ presents a negligible negative nonlinear refractive response. Indeed, it is inferior to the experimental resolution of our Z-scan system, which was very small in modulus, about one order of magnitude smaller than the CS₂ [30–32] at 800 nm. However, with the addition of the silver particles, this negative nonlinearity could be enhanced about two orders of magnitude, and the colloid displayed a strong third-order response comparable or superior to others nonlinear media, such as CS₂ and colloidal metallic nanoparticles in distinct liquids [3–9].

Z-scan measurements with the MS were also carried out. However, we could not get a clear and symmetric Z-scan curve at any excitation power used in this work. Indeed, reducing the average laser power below 20 mW, there was a significant reduction of the signal to noise ratio and the Z-scan curves could not be accurately obtained. On the other hand, no better results were achieved by increasing the laser power. We believe that these distortions could be attributed to the stronger light scattering observed for colloids with high particles concentration. This result indicates that, in this particular system, it is not always possible to increase the colloid nonlinear optical response by raising the Ag particles concentration only. At higher particles filling factor, light scattering can be an issue, and the medium might not be useful for nonlinear optical applications.

Open aperture Z-scan measurements were also carried out. In Fig. 3 it is presented the obtained curves for the AG1 and AG2 samples. A very weak saturated absorption behavior could be observed for the AG1 sample, while nonlinear absorption was not detected for the sample with AgNP's lower filling factor, neither to the pure IL. The value of the measured nonlinear absorption coefficient is also provided in Table 1. It must be stressed that, even at relatively large nanoparticles filling factor, the nonlinear absorption displayed by AG1 sample was very low in comparison with other systems containing metallic nanoparticles [3–5, 9].

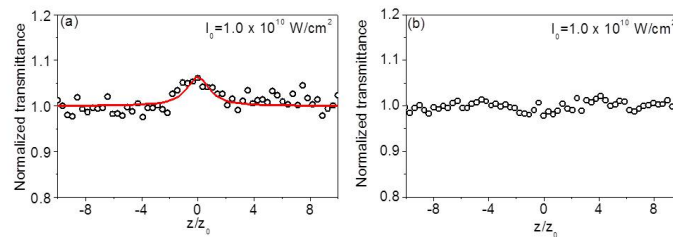


Fig. 3. Open aperture Z-scan curves of (a) AG1 and (b) AG2 samples. Open circles correspond to the experimental data and the red line is the fitting curve obtained with Eq. (2).

The potential use of this colloidal system for all-optical switching application was also investigated. As demonstrated previously, a good material for this end must fulfill the conditions $|W| = |\Delta n_{\max}/\lambda\alpha_0| > 0.27$ and $|T| = |2\alpha_2\lambda/n_2| < 1$, where $\Delta n_{\max} = n_2 I_{\max}$ is the maximum refractive index change achievable, limited by saturation [35]. In the present study, we employed as $I_{\max}$ the value of I_0 used during the Z-scan measurements for each medium. The modulus of resolution limit of our experimental system for the α_2 measurements, 5 x

10^{-11} cm/W, was used as a limit value for the BMI.BF₄ and AG2 samples' nonlinear absorption coefficients. Hence, the calculated values shown in Table 1 are merely the inferior (superior) limits to the samples' figure of merit $W(T)$.

It was observed that the colloids exhibit an improved performance for the T parameter, but an inferior value for the W figure of merit in comparison to the neat IL. In these systems, the increase on the linear absorption overcomes the enhancement of the nonlinear refraction, due to the presence of particles with larger size. Nevertheless, as we calculated only the W inferior limits, the results suggest this colloidal system has a good potential for the development of all-optical switching applications.

It must be emphasized that here we are measuring either the nonlinear response of the BMI.BF₄ (neat IL) or the overall nonlinear refraction and absorption of the composite medium. As demonstrated previously, the third-order nonlinear optical response of composite media containing a small amount of nanometallic inclusions depends strongly on the linear and nonlinear dielectric functions of the host and metal, as well as on the particles' filling factor [36–38]. Hence, even if the host presented a negligible nonlinear refractive index, the measured value of n_2 does not reflect only the nonlinear response of the inclusions, but also depends on the local field enhancement factor, which is related to the particles' and host's dielectric functions. For instance, if the colloid contains a narrow size distribution of spherical nanoparticles, the composite nonlinear refraction index and absorption coefficient varies linearly with the particles filling factor but, nevertheless, this value still depends on local field enhancement factor as well [6, 37, 38]. However, in the present paper, as the colloids present a broad size distribution, the models developed previously could not be directly applied to describe the obtained results.

4. Conclusions

In summary, the nonlinear optical properties of colloidal silver nanoparticles dispersed in BMI.BF₄ ionic liquid were investigated. Large enhancements to the electronic contribution to the nonlinear refraction, as well as to the linear absorption of this colloid were observed. A very weak saturated nonlinear absorption was also characterized for the colloid with highest Ag filling factor. Moreover, the figures of merit for all-optical switching of the pure BMI.BF₄ and the colloids were also evaluated. Our results suggest that the presence of Ag particles improve the performance of the IL and that this hybrid system is a good candidate for the development of ultrafast nonlinear devices.

Acknowledgments

The authors thank the financial support from CAPES, CNPq/MCT, FAPITEC/SE, Nanofoton Network, INCT-FOTÔNICA.