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Incorporation of Gold Nanoparticles in Single-Atomic Layered Materials and Their Plasmonic Absorption Characteristics as Highly-Efficient Nonlinear Optical Media

Shahid S. Kamar, Hussein V. Amirov, Hamid R. Hashimi, Mansour H. Arsatov

Department of Chemistry, College of Applied Sciences, Azerbaijan Technology University, Ganja, AZERBAIJAN

Abstract

In this work, gold nanoparticles were incorporated in single-atomic layered materials by cold press at room temperature. These nanoparticles were dispersed in different solvents in order to introduce the effect of solvent type on their characteristics. The linear and nonlinear optical properties of the gold nanoparticles and prepared composite samples as well as their structural characteristics were determined. The linear optical activity of gold nanoparticles incorporated in the single-atomic layered material was highly damped while their nonlinear optical activity was affected but still observed. These results can be successfully used for the employment of precious metal nanoparticles in biomedical applications.

Keywords: Nonlinear optics; Gold nanoparticles; Atomic layered materials; Nanotechnology

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1. Introduction

Nanotechnology has been rapidly growing and finding various applications in different fields of science and technology over the last decades. Different kinds of nanomaterials have been synthesized and characterized for their potential use in electrical, optical and medical devices and etc. The carbon allotropes discovered in recent decades, are the most outstanding examples of nanomaterials with distinct types of morphologies and applications. Fullerenes, carbon nanotubes, graphene and carbon nanoparticles are respectively 0, 1, 2 and 3 dimensional structures of carbon with their own characteristic physical properties. These carbon allotropes have been extensively studied for their mechanical, electrical, optical and nonlinear optical (NLO) properties. Concerning their NLO properties, it is shown that fullerenes have reverse saturable absorption at certain wavelengths [1,2], carbon nanotubes show ultrafast third-order nonlinearities and saturable absorption [3] and graphene shows ultrabroadband resonant NLO response [4,5]. Furthermore, it is shown that the recently discovered graphene oxide (GO) has reverse saturable absorption [6] and optical limiting properties [7-10].

A variety of techniques are being used for measuring the NLO properties of materials. Among them, the z-scan technique introduced by Sheik-Bahae et al. [11,12] is considered as one of the simplest methods for measuring the real and imaginary parts of the complex nonlinear refractive index of materials. Despite its simplicity, in many cases, the original z-scan theory [12] is not completely accurate, i.e. when the nonlinear medium response to laser radiation is nonlocal in space. Whenever the laser induced nonlinear response at a certain point of the medium is not solely determined by the laser intensity at that point, but also depends on the laser intensity in the surrounding regions, it will be called a nonlocal nonlinear optical response [13]. Generally, a variety of mechanisms may contribute to the nonlinearity, some of which may be nonlocal [14]. For instance, when the nonlinear medium is dispersed inside a dielectric solution, reorientation of the dipoles (permanent or induced molecular dipoles) as a result of the optical field action is nonlocal in space and changes the electric

field experienced by the nonlinear medium. Recently, the z-scan theory has been generalized to consider the possibility of the sample nonlocal response in case of pure nonlinear refraction [15] and nonlinear refraction at the presence of nonlinear absorption [16]. It is shown that nanostructures can exhibit nonlocal responses due to the laser beam scattering by nanoparticles [17]. However, a variety of other mechanisms may produce the nonlocal nonlinear response of nanostructures, such as the dipolar response of the induced or permanent polarized molecules of the material that contains the nano-objects. The nonlocal z-scan theory [15,16], can be used for systematically analyzing the role of various mechanisms in producing the nonlocal nonlinear response of different materials.

Recently, we have reported a new method for synthesizing GO supported Au nanoparticles [18]. In this paper, we describe the preparation of GO/Au dispersions in three different solvents, i.e. water, DMF (N,N-Dimethylformamide) and NMP (N-Methyl-2-pyrrolidone). Nonlinear optical properties of the resultant dispersions have been measured using the z-scan technique. The nonlocal z-scan theory [16] has been used for analyzing the measured data and to obtain the nonlinear refractive index, nonlinear absorption coefficient and order of nonlocality of the dispersions.

2. Experimental Part

Preparation of Au nanoparticles and synthesis of GO and GO/Au powders was explained in our previous work in detail [18]. Preparation of GO/Au suspensions in different solvents will be described. The method of measuring the nonlinear optical properties of materials will be explained thereafter.

The GO/Au suspensions were prepared in three different solvents: water, DMF (N,N-Dimethylformamide) and NMP (N-Methyl-2-pyrrolidone) with a concentration of 2 mg/mL. The dispersions in each solvent were prepared by a 1 h sonication. The dispersions were further centrifuged at 5000 rpm for 20 min. GO suspensions were also prepared in the three mentioned solvents without the Au nanoparticles to study the role of nanoparticles addition on their optical properties.

The z-scan technique was used for measuring the complex nonlinear indices of refractions of the GO/Au suspensions. Scheme of the used z-scan experimental setup is shown in Fig. (1).

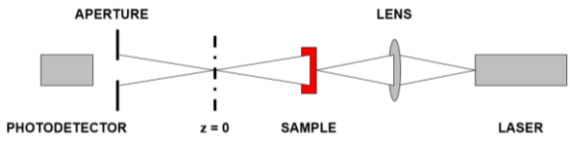

Fig. (1) Schematic illustration of the z-scan setup

In this setup, the laser beam (CW He-Cd, λ=442nm, P= 12 mW) is focused to a spot size of 1.6 μm by an f= 25 cm convex lens. The beam spot size is first measured on the focusing lens by a CCD camera (SAMSUNG SDC415PH) and then calculated at the focal position using the well-known thin lens conversion formulas [19]. In order to avoid the CCD saturation or damage, the laser beam intensity is reduced by a variable beam attenuator consisting of a half-wave plate and a polarizing beam splitter cube. A 1 mm thickness quartz cell containing the suspension is moved along the optical axis (the z axis) from one to the other side of the lens focal point. Before measurements, suspensions were ultrasonicated for 20 minutes to prevent their precipitation. For measuring the real part of the nonlinear refractive index, the z-scan setup is used in its closed-aperture form which is shown in Fig. (1). In this form, since the nonlinear material reacts like a weak z-dependent lens [20], the far-field aperture makes it possible to detect the small beam distortions in the original beam. Since the focusing power of this weak nonlinear lens depends on the nonlinear refractive index [20], it would be possible to extract its value by analyzing the z-dependent data acquired by the detector and by cautiously interpreting them using an appropriate theory [16]. To measure the imaginary part of the nonlinear refractive index, or the nonlinear absorption coefficient, the z-scan setup is used in its open-aperture form. In open-aperture measurements, the far-field aperture is removed and the whole signal is measured by the detector. By measuring the whole signal, the beam small distortions become insignificant and the z-dependent signal variation is due to the nonlinear absorption entirely. Using the z-scan theory [12,16], one can find the value of the nonlinear absorption coefficient.

3. Results and Discussion

The resulting solution of Au-NPs was characterized by UV-Visible spectroscopy. Figure (2) shows the UV-Vis absorption spectrum of Au nanoparticles solution. In this work, All the UV-Visible measurements were performed at room temperature by a Perkin Elmer 550ES from 300 to 750 nm with a resolution of 1 nm. The resonance at 531 nm is clearly seen and arises due to the excitation of surface plasmon vibrations in the Au nanoparticles [21]. The presence of this plasmonic absorption peak is clear evidence in support of the formation of Au nanoparticles.

In Fig. (3), the Transmission Electron Microscopy (TEM) image of the Au nanoparticles is shown. TEM images were taken by Philips CM120 transmission electron microscope. The estimated mean particle size of Au nanoparticles is about 27 nm. The mean particle size was obtained by measuring the diameter

of over 100 particles in all the TEM images to ensure good statistics.

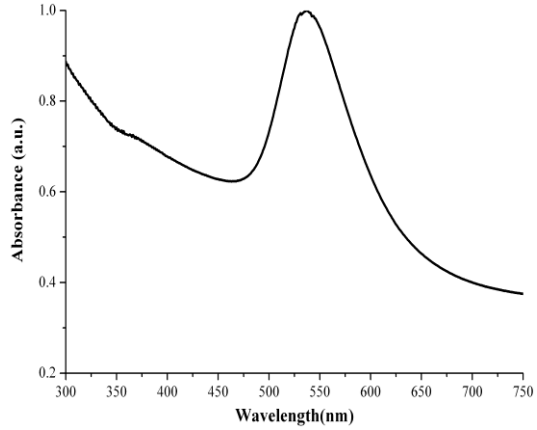

Fig. (2) Absorption spectrum of Au nanoparticles solution

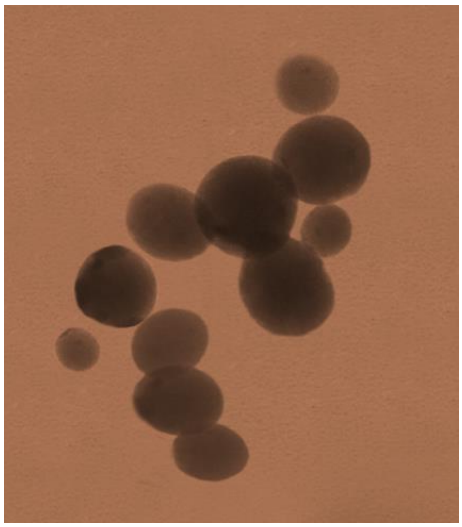

Fig. (3) TEM image of Au nanoparticles

Figure (4) shows the TEM images of GO/Au nanocomposite powder. It can be seen that Au nanoparticles are distributed between the GO layers.

Figure (5) shows the optical absorption spectra of the GO suspensions in three solvents with and without the presence of Au nanoparticles. For simplicity, we have named GO suspensions in DMF (N,N-Dimethylformamide), water and NMP (N-Methyl-2-pyrrolidone) as the G-D, G-W and G-N, respectively. Furthermore, GO/Au suspensions in DMF, water and NMP are also respectively named as G-A-D, G-A-W and G-A-N. It can be seen that by addition of Au nanoparticles to G-D, G-W and G-N, Au plasmonic absorption peak appears on the G-A-D, G-A-W and G-A-N absorption spectra. The plasmonic absorption peak of the Au nanoparticles at 531 nm is a little red-shifted in DMF and shifted more toward the blue end of the visible spectrum by changing their surrounding medium from water to NMP. In order to more clearly see these features, the measured wavelengths at which plasmonic resonances have occurred are listed in table (1).

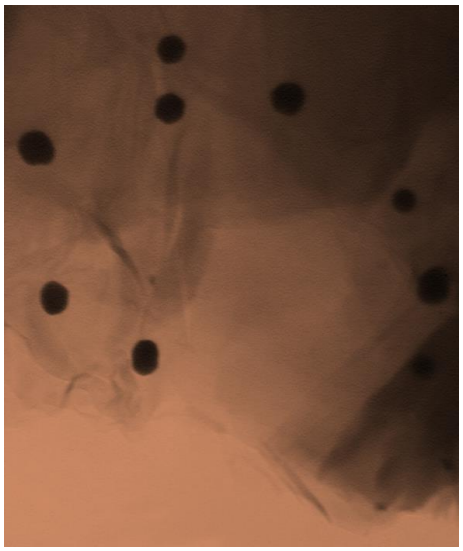

Fig. (4) TEM image of GO/Au nanocomposite powder

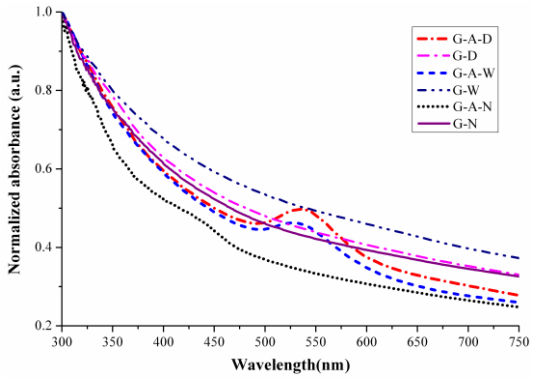

Fig. (5) Optical absorption spectra of GO and GO/Au dispersions in different solvents. Acronyms: G-A-D (GO/Au in DMF), G-D (GO in DMF), G-A-W (GO/Au in water), G-W (GO in water), G-A-N (GO/Au in NMP) and G-N (GO in NMP)

Inspecting Fig. (5), one can also see that the plasmonic peak is less predominant in NMP solution. Since G-A-D, G-A-W and G-A-N have GO/Au in common, variation of their linear optical properties can be attributed to their different solvents that surround the Au nanoparticles. Indeed, according to the Mie theory, the wavelength at which plasmon resonance occurs depends on optical characteristics of the medium which surrounds the nanoparticles [22]. It would be of no surprise if the surrounding medium can also play an influential role in determining the nonlinear optical response of nanoparticles.

If the surrounding medium has a dielectric nature, it can change the induced nonlinear phase shift in the impinging laser beam on the sample surface in z-scan experiments due to its nonlocal action [14,15].

The complex nonlinear refractive index of all the specimens was measured using the z-scan technique. To this end, z-scan technique was used in both closed and open aperture configurations. For G-D, G-W, G-N and Au nanoparticles suspensions, no detectable signal could be detected by the far-field detector which means that these samples do not produce a detectable nonlinear response for the used experimental conditions. Indeed, in the first order of approximation, the intensity dependent nonlinear refractive index and absorption coefficient can be written as:

$$n = n_0 + n_2 I \quad (1)$$

$$\alpha = \alpha_0 + \beta I \quad (2)$$

where n_0 and α_0 and n_2 and β are the linear refractive index and absorption coefficient and nonlinear refractive index and absorption coefficient, respectively. Since the intensity itself is proportional to the laser power, we have chosen the laser power as low as possible (12 mW) to be able to study the sole effect of Au nanoparticles addition to G-D, G-W and G-N. Indeed, these samples had nonlinear responses for higher laser powers. We have deliberately decreased the laser power to a level that no detectable signal could be measured for these samples. This would make the final conclusions more obvious and one can easily evaluate the role of Au nanoparticles addition in changing the nonlinear responses of G-D, G-W and G-N. Furthermore, if the exciting laser source has a wavelength (i.e., 442 nm in our case) far from the surface plasmonic absorption peak of nanoparticles (537 nm for Au nanoparticles), one can avoid the plasmonic resonance contribution in the nonlinear response of the samples. This would also reduce the thermal effect contribution in the nonlocal response of the samples and make it possible to concentrate on the role of the dielectric nature of the solvents itself.

Table (1) The measured plasmonic absorption peak wavelengths of Au nanoparticles suspension as well as GO/Au dispersions in deferent solvents

Absorption Peak (nm)			
Au	G-A-D	G-A-W	G-A-N
537	534	527	435

The open aperture z-scan data of G-A-D, G-A-N and G-A-W are represented in figures 6(a-c). Furthermore. The reverse saturable absorption behavior in Fig. (6) are shown to be characteristics of the GO [6,7,23]. The nonlocal z-scan theory [16] is used for finding the nonlinear refractive index and nonlinear absorption coefficient of the samples. In short, in this theory the nonlinear absorption coefficient and refractive index can be found using a two-step procedure. Using the open aperture z-scan data, the nonlinear absorption coefficient β can be deduced by performing a one parameter fit using the following equation:

$$T_o(z) = \frac{\ln(1 + q_0(z))}{q_0(z)} \quad (3)$$

with

$$q_0(z) = \frac{\beta I_0 L_{eff}}{1 + (z/z_0)^2} \quad (4)$$

where $L_{eff} = (1 - \exp(-\alpha_0 L))/\alpha_0$ is the sample effective thickness and is defined using the sample real thickness L. I_0 being the on-axis intensity at focus and z_0 is the laser beam Rayleigh length. In the second step and with β known, the nonlinear index of refraction n_2 and the nonlinear parameter m can be obtained with a two parameter fit on the closed-aperture z-scan data using the next equation:

$$T_c(z) = 1 - \frac{\left(4mkn_2 x + \beta\left(x^2 + (2m+1)\right)\right) I_0 L_{eff}}{(x^2 + (2m+1)^2)(x^2+1)} \quad (5)$$

where $x=z/z_0$ and k is the wave number. The nonlinear least squares fitting is used to fit Eq. (5) to the measured closed aperture z-scan data. The trust-region algorithm of the MATLAB software is implemented for this purpose. The phenomenological parameter m is the order of nonlocality and can be any real positive number. This parameter shows the nonlocality amount in the sample response to the electric field of the irradiating laser beam [15,16].

In this study, the dipolar response of the induced or permanent polarized molecules of the materials that surround the Au nanoparticles can produce the nonlocality. Since all the samples have GO in common, their different nonlocal responses can be attributed to their different kinds of solvents. The fitting results according to equations (3) and (5) are also respectively shown by solid lines in Fig. (6). The measured nonlinear optical properties of the samples are summarized in table (2). G-A-N exhibits superior nonlinear optical properties in comparison with G-A-D and G-A-W.

Note that although the linear absorption coefficient of G-A-N is less than 2 times than that of the G-A-D, the nonlinear refraction of the former is around 200 times larger than the latter. We are of the opinion that the different nonlocal responses of their corresponding solvents, NMP in the former and DMF in the latter, is the major reason for this difference. One must note that nonlinear scattering by Au nanoparticles and heat distribution or the thermal effect may also contribute in the nonlocal response of the samples. However, two points seem in order. First, all the samples have been prepared in the same way and we expect nearly equal amounts of Au nanoparticles in the same volumes of them. Therefore, it is also expected that Au nanopaticles

contribution in the observed nonlocality, be nearly the same for all the samples. Second, since the linear absorption coefficients of the samples have the same order of magnitudes (see table 2), and this coefficient mainly determines the amount of deposited heat inside the samples, we expect the amount of nonlocality due to the resulted temperature gradient be also at the same order of magnitudes for all of them. Therefore, one can conclude that this is the dielectric nature of the surrounding media that dominates the nonlocality and results in the considerable difference between the nonlinear responses of G-A-D, G-A-N and G-A-W. Unfortunately, the nonlocal z-scan theory [15,16] is unable to distinguish between the various nonlocal mechanisms in z-scan experiments in its current form, and more work should be done to further develop it.

The most noteworthy point about table (2) is that the nonlocal parameter of G-A-N is relatively larger than those of the G-A-D and G-A-W. This may indicates the more polarizability of the G-A-N compared with G-A-N and G-A-W. Since *m* is a phenomenological parameter and is included in the sample nonlinear response just for considering the difference between the spatial distribution of the induced nonlinear phase shift and the laser beam intensity distribution [15], much more studies are needed to approve this conclusion. Indeed, the nonlocal z-scan theory should be further developed to quantify the role of various physical phenomena that may change the sample nonlinear response. Another important point that should be noted is that by addition of Au nanoparticles, the nonlinear optical properties of GO in different solvents have been improved considerably. The enhanced nonlinear optical behaviors may arise due to the enhanced nonlinear scattering by the incorporated Au nanoparticles. Indeed, as we have pointed out previously, nonlocality arises when the laser induced nonlinear response at a certain point of the medium depends also on the laser intensity in the surrounding regions. The nonlinear scattering of Au nanoparticles, which depends on the laser intensity at their positions, can change the nonlinear response at other positions and hence can contribute in the nonlocal response of the media. The improved nonlinear optical properties of GO can broaden its application in various fields. Its larger nonlinear refractive index can find a possible application in optical switches and its enhanced reverse saturable absorption, which can be seen in figure 6, can bring it into application in optical limiters.

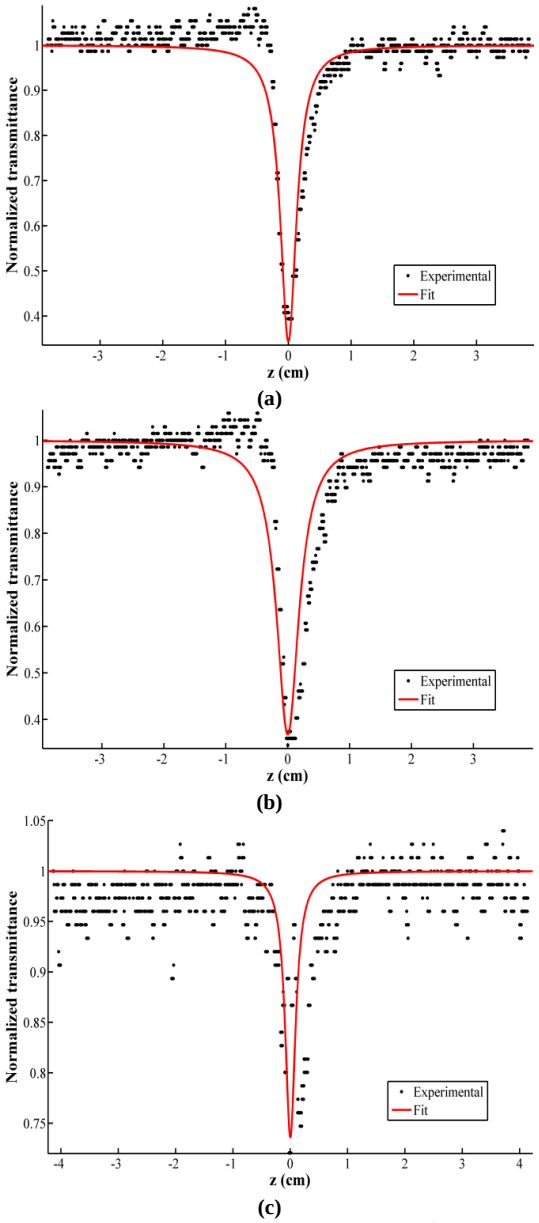

Fig. (6) Open aperture z-scan data (dots) and fitting results (solid lines) of a) G-A-D, b) G-A-N and c) G-A-W. All the three samples exhibit reverse saturable absorption for the used laser wavelength

Table (2) Nonlinear optical properties of G-A-D, G-A-N and G-A-W. The linear optical absorption coefficients at 442 nm are also given in the last column

sample	n_2 (cm^2/W)	β (cm/W)	m	α (cm^{-1})
G-A-D	2.3×10^{-7}	4.4×10^{-3}	5.2	1.31
G-A-N	4.5×10^{-5}	6.2×10^{-3}	422	2.16
G-A-W	6.2×10^{-12}	1.2×10^{-3}	1.4	1.09

4. Conclusion

GO, Au nanoparticles and GO/Au nanodispersions in different solvents have been prepared and their optical, structural and nonlinear optical properties have been studied in this work. It is

shown that the solvent material can change the optical and nonlinear optical properties of GO/Au. It is proposed that the nonlocal action of the solvent material may be the source of variation of the nonlinear optical properties of the samples. This proposal is confirmed by applying the nonlocal z-scan theory [15,16] for analyzing the z-scan measurement data. Previously, it was also shown that the light scattering by nanoparticles may be the source of nonlocality in the sample response in z-scan measurements [17]. We are of the opinion that whenever one expects the sample nonlocal response in z-scan experiments, the nonlocal z-scan theory should be used to measure the more accurate values of the nonlinear refractive and absorption coefficients. More future studies can be conducted to examine the role of other nonlocal mechanisms in z-scan experiments. The nonlocal z-scan theory should also be further developed to for quantifying the role of various nonlocal mechanisms. In this way, it would be possible to extract the values of other constants, like the sample polarizability or heat diffusion coefficient, from the measured nonlocal parameter.

It is also shown that the incorporation of Au nanoparticles can enhance the nonlinear optical behavior of the GO. The improved nonlinear optical properties of GO can open new avenues for its application in various fields. Other metallic nanoparticles may also improve the nonlinear optical properties of the GO and many more experiments can be performed to investigate how they can do this. Such works are in progress and will be reported in near future.

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