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Enhancement mechanism of the saturable absorption effect in reduced graphene oxide decorated with silver nanoparticles

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Abstract: Reduced graphene oxide (rGO) decorated with silver nanoparticles exhibits an enhanced nonlinear absorption effect compared with pure rGO. Using femtosecond time-resolved transient absorption spectroscopy, the enhancement mechanism and carrier dynamics of the composites are experimentally demonstrated. When the material is excited by laser pulses, the excited carriers in the conduction band of graphene will transfer to the d-band of silver before returning to the valence band. As the decay process (~210 ps) is much longer than that of the relaxation time in pure graphene (~fs), the bleaching effect of valence band is prolonged, resulting in enhanced saturable absorption effect.

1. Introduction

Graphene and its derivatives have found extensive applications in many fields due to their excellent properties such as high surface area, excellent electrical conductivity, strong mechanical strength, and remarkable biocompatibility [1–4]. Graphene also showed important applications in the optical and nonlinear optical (NLO) fields, benefiting from its unique property of zero bandgap and broadband absorption in the whole visible and infrared range [5]. When graphene is irradiated by an intense ultrashort laser pulse, electrons could be excited from the top of the valence band (VB) to the bottom of the conduction band (CB). If the relaxation lifetime of the electrons is long enough, further absorption of the incident laser pulse will be limited, and saturable absorption (SA) effect takes place. Because of this special optical property, graphene can be used as a saturable absorber in mode-locked lasers [6,7].

In the recent years, many efforts have been devoted to improve the NLO properties of graphene [8–12]. Due to presence of various oxygen such as functional groups like epoxy (-COO), hydroxyl (OH-) and carboxyl groups (-COO-), graphene oxide (GO) is easily to interact with varied organic and inorganic materials. By attaching various functional groups or decoration of metals onto GO, the composites showed interesting NLO absorption effect. Studies have shown that the combination of graphene with noble metals nanoparticles (NPs), may improve the SA properties comparing to the single components [8–10]. In our previous report, we fabricated rGO decorated with silver NPs and observed the enhanced nonlinear absorption and refraction effect, however, the enhancement mechanism was not clear [13]. Although previous theories have shown that the interaction through molecular charge-transfer and surface plasmon resonance may be the main factors in enhancing the nonlinear properties of the hybrids [14], the enhancement mechanism especially the carrier dynamics in the nonlinear response still needs to be verified experimentally.

Femtosecond time-resolved transient absorption (TA) spectroscopy is a practical tool to study the transient dynamics inside materials, which has been widely used to study some photophysical and photochemical processes [14–16]. Herein, studied the NLO response of reduced graphene

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oxide decorated by silver NPs (AgNPs/rGO) via femtosecond laser Z-scan measurements, and enhanced SA effect in the hybrids is observed compared with pure rGO. Using the femtosecond TA measurements, the enhancement mechanism and carrier dynamics of the materials are experimentally demonstrated. When the composites are excited by laser pulses, the carriers in the CB of graphene would transfer to the d-band of Ag, and then the VB of graphene. As a result, the bleaching effect of the VB of graphene is prolonged and an enhanced SA effect of the rGO is induced.

2. Experimental section

GO used in our work was purchased from Nanjing XFNano Materials Tech Co., Ltd., (Nanjing, China). The AgNPs/rGO was synthesized by femtosecond laser ablation in solution method using GO and $AgNO_3$ as raw materials [13]. When femtosecond laser irradiates on GO aqueous solution containing metal ions, multi-photon absorption and ionization of GO and the solvent might take place, generating extreme conditions with high temperature and pressure. In this process, Ag ions and GO in the solution react with the generated electrons forming metal atoms and rGO, respectively. These metal atoms can be attached to the dispersed GO or rGO and nucleate quickly, and large quantities of the simultaneously formed nuclei finally result in the AgNPs decorated on the rGO. In our experiments, the procedures are as follows: 6 mg of GO was dispersed in 30 ml of distilled water by ultrasonication to obtain a uniform yellow solution. 0.03 mmol $AgNO_3$ was added into the solution and irradiated by a focused femtosecond laser (100 fs pulses width, 800 nm central wavelength. and 1 kHz repetition rate). In the laser ablation process, fs laser beam with 300 mW power was focused into the solution for 1 h using a lens with 100 mm focal length. During this process, a magnetic stirrer was used to keep the solution irradiated homogeneously.

The morphology of the AgNPs/rGO composites were characterized by transmission electron microscopy (TEM, JEM-2100 UHR STEM/EDS, JEOL) and high resolution TEM (HRTEM). Chemical structures were studied by X-ray photoelectron spectroscopy (XPS) with an ESCALAB Xi + XPS spectrometer. Raman spectra were obtained using a Raman spectrometer with excitation wavelength of 633 nm. The UV-Vis absorption spectra were measured using a UV-2600 spectrophotometer by filling the liquid samples into cuvettes with 10 mm optical path.

The samples were dropped on 1 mm thick glass substrates and dried at room temperature for NLO measurements. The NLO properties of the products were investigated by an OA Z-scan system using femtosecond laser emitted from the same laser system [17]. Laser pulses were focused by a converging lens (f = 200 mm). The averaged thickness of the samples was measured to be about 100 nm, and the radius of the Gaussian beam waist were estimated to be 34 μm. As the drop-casted films are inhomogeneous, several measurements are taken at 5-10 different areas in the same sample, and the averaged results was obtained.

Femtosecond time-resolved transient absorption (TA) spectroscopy were used to analyze the ultrafast dynamics in the materials. In the TA measurement, the femtosecond laser output was divided into two parts: pump light and probe light. The pump pulses irradiated on the sample for excitation and the probe pulse was used to detect the TA in the sample. In our experiments, the probe light was irradiated on a white sapphire crystal to generate a broadband white-light continuum ranging from 450 nm to 750 nm. The signal was recorded by a fiber-coupled spectrometer and analyzed by a computer.

3. Results and discussions

The optical properties, morphology, and chemical structures of the prepared AgNPs/rGO are firstly studied. Figure 1(a) shows the absorption spectra of the GO, rGO and AgNPs/rGO samples. The characteristic absorption shoulder around 305 nm in GO is due to the n→π* transitions of C = O bonds [18]. After laser reduction, enhanced absorption in the whole visible light range is

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observed in rGO. When the rGO is decorated with Ag NPs, a distinct absorption peak located at about 410 nm attributed to the localized surface plasmon resonance (SPR) of Ag NPs appears [19]. Figure 1(b) shows the TEM image of the composite, in which Ag NPs are well distributed on rGO sheets. The inset on the top-left shows HRTEM image of Ag NPs, and crystal lattice fringes with 0.23 nm spacing are observed, according with the (111) plane of Ag crystallite. The statistic size distribution of Ag NPs indicates an average size of 20 nm ranging from 10 nm to 38 nm.

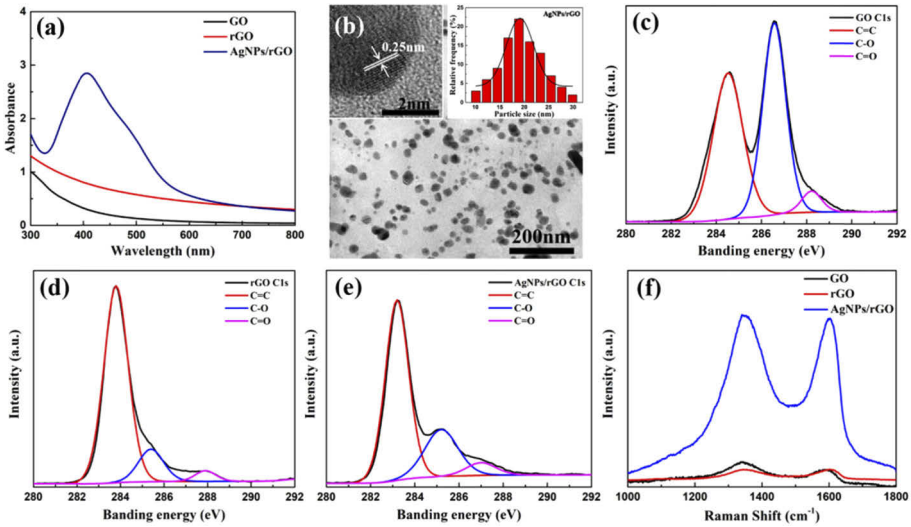

Fig. 1. (a) Absorption spectra of the GO, rGO, and AgNPs/rGO, (b) TEM image of AgNPs/rGO, the insets show the HRTEM image and size distribution, (c)-(e) XPS spectra and (f) Raman spectra of GO, rGO, and AgNPs/rGO.

Figure 1(c)-(e) show the XPS spectra of C1s in GO, rGO and AgNPs/rGO, respectively. The banding energy peak at 283.8 eV, 285.4 eV and 287.9 eV in each sample are assigned to C = C, C-O and C = O groups, respectively. The percentage of C-O and C = O deceases significantly when the GO is reduced to rGO, indicating the reduction of oxygen functional groups. In the Raman spectra (Fig. 1(f)), the characteristic D band and G band located at 1350 cm^{-1} and 1600 cm^{-1} are observed in the samples. The G peak is caused by the in-plane vibration of the sp^2 carbon atoms, and the D peak corresponds to the defects in carbon materials which is inexistent in integral structure [20,21]. These two peaks in rGO change slightly compared with those in GO, indicating that very few defects are induced in the laser ablation process. Besides, the Raman spectra in AgNPs/rGO composites are obviously enhanced due to the Surface-Enhanced Raman Scattering (SERS) effect caused by the decorated Ag NPs [20–23]. All the characterizations given above suggest that GO nanosheets are reduced after femtosecond laser irradiation and Ag NPs are well decorated on rGO.

It should be noted that, the experimental parameters, such as laser power, ablation time and reactant concentration could affect the optical properties and morphology of products. Figure 2 summarizes the influence of Ag ion concentration on the products. From Fig. 2(a) we can see that, the characteristic absorption peak of Ag NPs increases with increasing the Ag ion concentration, indicating that more Ag NPs are formed and decorated on the surface of rGO. The TEM images given in Fig. 2(b) also shows the change of Ag NPs concentration with Ag ion concentration. While more Ag NPs are decorated on the graphene, the characteristic Raman peaks of graphene are enhanced (as shown in Fig. 2(c)).

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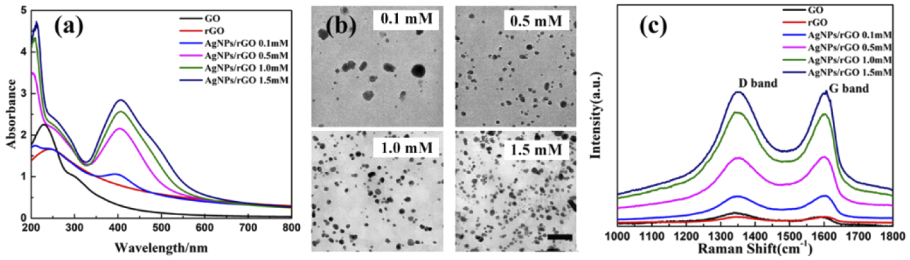

Fig. 2. (a) Absorption spectra, (b) TEM images, and (c) Raman spectra of samples with different Ag ion concentrations. The scale bar in the lower right corner indicates 200 nm.

Femtosecond laser Z-scan technique is used to measure the nonlinear absorption effect in the samples. To rule out the influence of glass substrate, the Z-scan curve was also measured under the same conditions, and the nonlinear transmittance change of the rGO and AgNPs/rGO as functions of Z position was obtained through dividing the nonlinear transmittance curve of the sample by that of the substrate (as given in Fig. 3(a)). The normalized transmittances of both materials increase obviously as the power density increases near the focus, suggesting a strong nonlinear SA effect in the materials. The solid lines in the figure show the fitting results using SA equations [24,25]. Compared with rGO, the AgNPs/rGO samples show obviously stronger SA effect, which is enhanced with increasing the Ag NPs concentration. The enhancement of the SA effect in the hybrids may be resulted from the interaction between graphene and Ag NPs. In the previous reports, some theoretical depiction has been promoted to explain the optical nonlinearity enhancement of AgNPs/rGO hybrids. When irradiated by laser pulses, electrons in graphene are easily excited from the valence band (VB) to conduction band (CB). The bleaching of VB in graphene will block the further absorption of incident laser, causing SA effect of the material. By decoration of Ag NPs, the excited carriers would transfer to the d-band of silver atoms instead of returning to the valence band (VB) directly (as shown by the Process (2-3) in Fig. 3(b)), causing the prolonging of the bleaching effect and the enhancement of the SA effect of the hybrids [26,27].

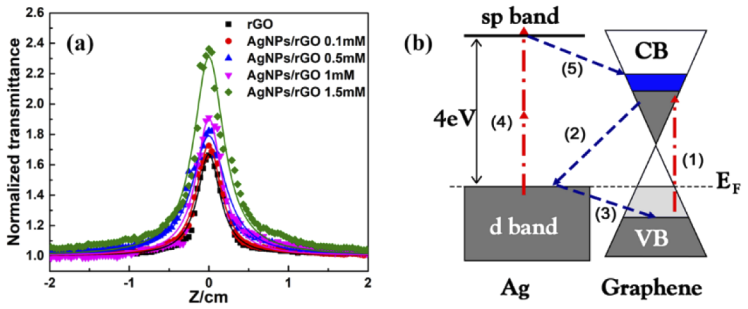

Fig. 3. (a) OA Z-scan results of rGO and AgNPs/rGO. The solid lines show the fitting curves of the results. (b) The energy band diagram of the AgNPs/rGO interface.

Although the interaction and carriers transfer between Ag NPs and graphene in the hybrids have been predicted theoretically, direct experimental proof is still lacking for the carrier dynamics in the material. In this work, we studied the ultrafast dynamic processes in AgNPs/rGO using femtosecond time-resolved TA spectroscopy. Figure 4(a) shows the TA spectra of the composites as a function of the pump and probe delay. In the TA spectra, a negative absorption peak centered at 580nm is observed, as shown in Fig. 4(b). Figure 4(c) depicts the temporal behavior of the

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TA signal at 580 nm. By fitting the results, an establishing process (~20 ps) and a slow decay process containing two time constants (~300 ps and 2.9 ns) are obtained.

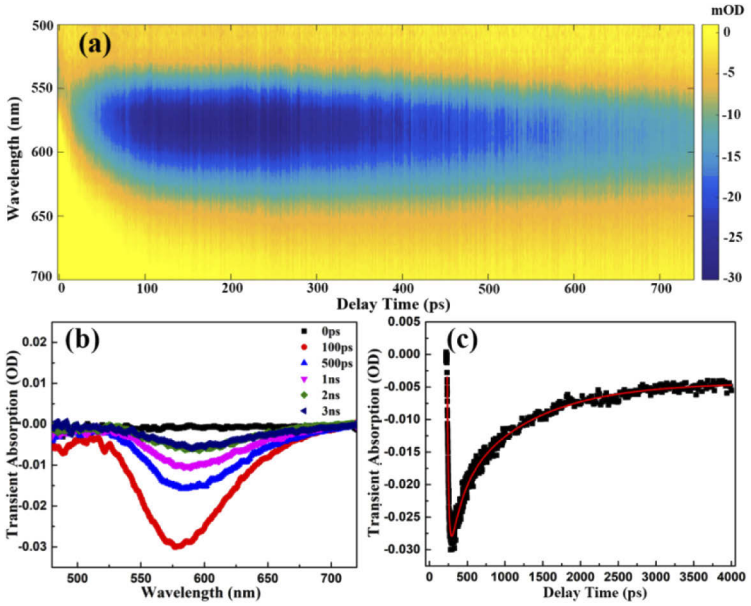

Fig. 4. (a) TA spectra of the composites as a function of the pump and probe delay. (b) The TA of AgNPs/rGO as a function of probe wavelength at different delay times with a pump power of 10 mW; (c) TA at the wavelength of 580 nm of AgNPs/rGO as a function of probe delay time with a pump power of 10mW

As shown by the energy level scheme given in Fig. 3(b), when rGO is decorated with silver-nanoparticles, electrons transfer from graphene to the Ag NPs via the interface to achieve a common Fermi level [11]. When the sample is irradiated by 800 nm femtosecond laser, graphene could be easily excited, causing the filling of the CB and bleaching of VB. Meanwhile, electrons in Ag NPs could also be excited from d-band to sp-band through two-photon absorption. The excited electrons could transfer from the sp-band of Ag to the CB of graphene, and the highest filled energy level in CB goes up. With the further filling of CB in graphene, absorption of the probe light with shorter wavelength was limited, resulting in a negative absorption around 580 nm as shown in Fig. 4(b). The electron transfer process (Process (5) in Fig. 3(b)) is accordance to the establishing time mentioned above, which takes place in about 20 ps, corresponding to the lifetime of the carriers in sp-band. The relaxation process of absorption at 580 nm is corresponding to the transfer of the carriers from CB of graphene to the d-band of Ag atoms (Process (2) in Fig. 3(b)), which is measured to be about 300 ps. The longer decay process of 2.9 ns could be attributed to the interaction between AgNPs/rGO composites and surrounding solvent.

To further understand the carriers transfer in the hybrids, TA spectra under different pump power excitation are recorded. Figure 5(a) shows the TA spectra with the pump power changing from 4mW to 10mW and the pump-probe delay fixed at 100 ps. The negative absorption peak shows an obvious blue-shift with increasing the pump power, as summarized by Fig. 5(b). When the pump power irradiated on the AgNPs/rGO is increased, more electrons are excited to the sp-band of Ag atoms, resulting in the increment of filling degree of the CB in graphene. As a result, light absorption with higher energy (lower wavelength) could be blocked, causing the blue

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shift of the transient negative absorption peak of the material. This result accords well to the energy band diagram of the AgNPs/rGO composites.

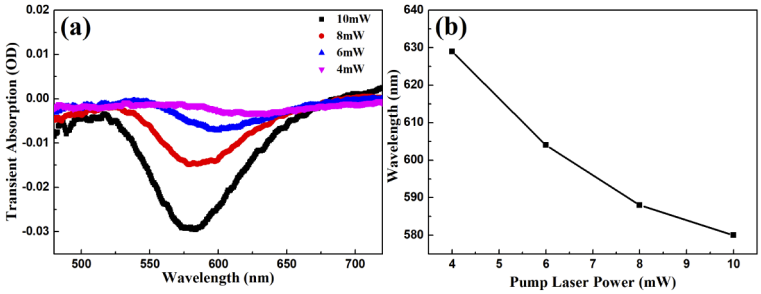

Fig. 5. (a) TA of AgNPs/rGO with the pump laser power changing from 4 mW to 10 mW and a probe delay time of 100 ps. (b) The negative absorption peaks as a function of the pump laser power.

4. Conclusion

In conclusion, enhancement mechanisms of NLO absorption in rGO decorated by Ag NPs is studied using femtosecond TA technique. In pure graphene, the electrons in graphene are easily excited from VB to CB by light excitation. The bleaching of VB in graphene will block the further absorption of incident light, causing SA effect of the material. As the relaxation of excited electrons in the CB of graphene is very fast (~fs), the bleaching effect of VB could vanish in the duration of the incident light pulse, resulting in a weak SA effect of the material. In this work, we demonstrate that both the rGO and Ag NPs could be excited when AgNPs/rGO composites are irradiated by laser pulses. The electrons transfer from the CB of graphene to the d-band of Ag would cause the prolonging of the bleaching effect of the VB of graphene, and finally induce an enhanced SA effect of the rGO.

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Disclosures

The authors declare no conflicts of interest.

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