All-optical control in metal nanocomposites due to a reversible transition between local field enhancement and local field depression upon irradiation by ultrashort control-pulses of light

Song-Jin Im and Gum-Song Ho

Department of Physics, Kim Il Sung University, Daesong District, Pyongyang, North Korea

E-mail: elib.rns@hotmail.com

Received 4 February 2014
Accepted for publication 19 February 2014
Published 17 March 2014

Abstract
We theoretically study the non-perturbative effective nonlinear responses of metal nanocomposites based on the intrinsic third-order nonlinear response of metal nanoparticles. The large intrinsic third-order nonlinear susceptibility of metal nanoparticles and irradiation by an ultrashort control pulse of light with a sufficiently high peak intensity and moderate fluence can induce a local field depression and saturated plasmon bleaching in the metal nanoparticles. If the control pulse is on, the metal nanocomposites behave like a dielectric due to the local field depression, while if the control pulse is off, they behave like a metal, showing a high absorption due to the local field enhancement at the plasmon resonance. This phenomenon can be applied to the ultrafast and remote control of light in metal nanocomposites.

Keywords: nonlinear optical properties, nanocomposites, surface plasmon resonance

1. Introduction
The nonlinear properties of metal nanoparticles have been extensively studied for applications in optics, medicine and biology [1]. Metal nanocomposites have great potential as nonlinear optical materials because of the large intrinsic nonlinearities of metal nanoparticles [2–5] and the local field enhancement near the plasmon resonance [6], resulting in significantly enhanced effective nonlinearities.

Negative nonlinear absorptions, which are called saturated absorptions in metal nanoparticles, have been experimentally observed [7–16] and interpreted by the plasmon bleaching related to the intrinsic electron dynamics in the metal nanoparticles [12, 13, 17]. For higher intensities, positive nonlinear absorptions, which are called reverse-saturated absorptions, have been observed [9, 11, 12, 16, 17] and attributed to different processes such as the electron-ejection [12, 19] and multiphoton absorption connected with interband transition [10, 12, 18] in metal nanoparticles. Some studies reported a decrease in the negative nonlinear absorption coefficient for higher intensities and attributed it to the reverse-saturated absorption effects starting to play an important role in the overall nonlinear response [10, 12]. However, the reverse-saturated absorption effects overlap with other effects and are strongly dependent on laser characteristics such as fluence, pulse width and repetition rate, making the quantitative consideration of individually extracted effects very difficult and complicated. Different experimental results were observed even at the same intensities and wavelengths, and the interpretation of the experimental results are controversial [12, 18].

In theoretical works, the third-order and fifth-order effective nonlinear responses of metal nanocomposites have
been studied by approaches such as the generalized Maxwell–Garnett model [20] and $T$-matrix method [21], respectively, which are valid for relatively low intensities below 1 MW cm$^{-2}$. In [22], the intensity-dependent change in the permittivity of the metal nanoparticles was taken into account in a self-consistent way mainly for intensities about the saturation intensity (defined as the intensity at which the linear loss is reduced by a factor of two), for which the local field factor was reduced but still larger than unity, showing local field enhancement. It was predicted that metal nanocomposites could be used as saturable absorbers with low saturation intensities in the MW cm$^{-2}$ range. Although some calculations for intensities in the GW cm$^{-2}$ range [22] were obtained, the results were not interpreted in detail.

In this paper, we theoretically study in more detail the non-perturbative effective nonlinear responses of metal nanocomposites for higher intensities in the GW cm$^{-2}$ ranges for which the local fields can be depressed rather than enhanced and the plasmon bleaching, which causes the saturated absorptions, can be saturated. Based on the Maxwell–Garnett formalism and the intrinsic third-order nonlinear response of metal nanoparticles, disregarding the reverse-saturated absorption effects, we predict that the negative nonlinear absorption coefficient decreases for higher intensities. We predict a transition between the local field enhancement and the local field depression upon irradiation by ultrashort control pulses of light, which can be used for the remote control of light in metal nanocomposites with a control light.

2. The non-perturbative effective nonlinear response of metal nanocomposites

The effects of the morphologies and compositions of nanocomposites on their effective linear optical properties can be described by Maxwell–Garnett formalism. Based on the intrinsic third-order nonlinear response of metal nanoparticles, the generalized Maxwell–Garnett (GMG) model gives the expression for the third-order effective nonlinear response of metal nanocomposites [20]:

$$\epsilon_{\text{eff}} \approx \epsilon_{\text{GMG}} = \epsilon_0 + f \chi_3^{(m)} \frac{3\epsilon_d}{\epsilon_m + 2\epsilon_d} \left( \frac{\epsilon_d}{\epsilon_m + 2\epsilon_d} \right)^2 |E_0|^2. \quad (1)$$

Here, $\epsilon_0$ represents the effective linear permittivity of the nanocomposites and $\epsilon_m$ and $\epsilon_d$ the permittivity of the metal nanoparticles and the dielectric host medium, respectively. $f$ represents the fill factor, $\chi_3^{(m)}$ the intrinsic third-order nonlinear susceptibility of the metal nanoparticles, and $E_0$ the incident electric field strength. The expression in parentheses corresponds to the local field factor $x$. The GMG model gives an insight into the enhanced effective nonlinearity and saturated absorption of the nanocomposites at the plasmon resonance. However, for a sufficiently high peak intensity of light, the GMG model would become unreasonable because the local field factor can have a large change due to a significant nonlinear shift of the permittivity of the metal nanoparticles at the plasmon resonance. Although higher order models have been suggested [21], they also cannot describe the non-perturbative effective nonlinear responses of the nanocomposites for a high peak intensity of light.

Combining the intrinsic third-order nonlinear response of the metal nanoparticles and the Maxwell–Garnett formalism describing the effects of the morphology and the composition of the nanocomposites, the effective permittivity of the nanocomposites can be expressed by

$$\epsilon_{\text{eff}} = \epsilon_d \frac{1 + 2(1-x)f}{1-(1-x)}$$

$$\epsilon_0 = \epsilon_{\text{eff}} + \chi_3^{(m)} |x E_0|^2, \quad (2)$$

$$x = \frac{3\epsilon_d}{\epsilon_m + 2\epsilon_d}.$$

The first equation of the expression (2), which is the Maxwell–Garnett equation expressed by the local field factor $x$, is intuitive because the local field factor is the most important parameter determining the effect of the morphology and the composition of the nanocomposites on their effective optical properties. $\epsilon_0$ is the linear permittivity of the metal nanoparticles. Note that in the limit of low light intensity and of small fill factor, equation (2) gives the GMG model. We solve the equations in a self-consistent way.

Figure 1 shows the non-perturbative effective nonlinear responses of the fused silica doped with silver nanoparticles with the fill factor $f = 0.05$ at the wavelength $\lambda = 450$ nm versus the incident intensity of light. The size of the silver nanoparticles is assumed to be about 10 nm, which is between the mean-free path of the electrons and the skin depth. Electromagnetic interaction between the metal nanoparticles can be ignored by taking the small fill factor below 0.1 [23]. We use the experimental data of the permittivity of silver [24] and take the intrinsic third-order nonlinear susceptibility $\chi_3^{(m)} = (-6.3 + 1.9i) \times 10^{-16}$ m$^2$ V$^{-2}$ [25]. In figure 1(a), the imaginary part of the effective permittivity of the nanocomposites calculated by the GMG model deviates from that calculated by equation (2) for intensities higher than 10 MW cm$^{-2}$, and even has negative values showing a non-physical amplification. Thus we know that the effective nonlinear response of the nanocomposite becomes non-perturbative for the high intensities. In figure 1(b), the nonlinear absorption coefficient $\beta(I) = \Delta \alpha(I)/\Delta I$ has negative values, showing the saturated absorption due to plasmon bleaching, and decreases for higher intensities, showing saturated plasmon bleaching. In [10, 12] the decrease in the negative nonlinear absorption coefficient was experimentally observed and attributed to positive nonlinear absorption effects such as the electron ejection in metal nanoparticles. We note that the intrinsic third-order nonlinear response of metal nanoparticles, disregarding the positive nonlinear absorption effects and the effect of the morphology and the composition of the nanocomposite, can also cause a decrease in the negative nonlinear absorption coefficient.

Figure 2 shows the local field factor $|x|$ versus the wavelength for different incident intensities in the silver-doped fused silica with the fill factor $f = 0.01$, calculated by equation (2). In the cases of the low incident intensities, one can see the plasmon resonance and the local field enhancement.
3. All-optical control in metal nanocomposites

Figure 3 shows the real and imaginary parts of the effective refractive index of the fused silica doped with silver nanoparticles with a fill factor of \( f = 0.01 \) versus the wavelength for different incident intensities calculated by equation (2). One can see the low imaginary parts of the effective refractive indices for the high incident intensities showing a low absorption in the nanocomposite, as predicted above. The real part of the effective refractive index for the high incident intensities is close to the refractive index of the host dielectric medium. In the ideal case of a very high incident intensity, the effective permittivity of the metal nanocomposite converges to a value determined by the kind of host dielectric medium, and the fill factor and is independent of the property of the metal:

\[
\varepsilon_{\text{eff,ideal}} = \varepsilon_d \left\{ 1 + \frac{2f}{1 - f} \right\}.
\]

The effective optical properties of nanocomposites can be remotely controlled with a control light utilizing the cross-nonlinearity in the metal nanoparticles. The cross-nonlinear susceptibility of metal nanoparticles \( \chi_m^{(3)}(\omega_3; \omega_1, -\omega_2, \omega_3) \) is predicted to be large like the self-nonlinear susceptibility \( \chi_m^{(3)}(\omega_1, -\omega_2, \omega_3) \), while \( \chi_m^{(3)}(3\omega_3; \omega_1, \omega_2, \omega_3) \) for the third-harmonic generation is depressed and smaller by several orders of magnitude than that of the self-nonlinear susceptibility \([10, 26]\). Based on the intrinsic third-order nonlinear response of metal nanoparticles and the Maxwell–Garnett formalism, the effective permittivity of metal nanocomposites irradiated by both the signal light at the frequency \( \omega_s \) and the control light at \( \omega_c \) can be expressed by

\[
\begin{align*}
\varepsilon_{\text{eff}}(\omega_s) &= \varepsilon_d \left\{ 1 + \frac{2(1 - x_s)f}{1 - (1 - x_s)f} \right\}, \\
\varepsilon_{\text{eff}}(\omega_c) &= \varepsilon_d \left\{ 1 + \frac{2(1 - x_c)f}{1 - (1 - x_c)f} \right\},
\end{align*}
\]

\[
\begin{align*}
\varepsilon_m(\omega_s) &= \varepsilon_m^{(3)}(\omega_s; \omega_c, -\omega_s, \omega_3) |x_s E_0(\omega_s)|^2 + \chi_m^{(3)}(\omega_s; \omega_c, -\omega_s, \omega_3) |x_c E_0(\omega_c)|^2, \\
\varepsilon_m(\omega_c) &= \varepsilon_m^{(3)}(\omega_c; \omega_s, -\omega_2, \omega_3) |x_s E_0(\omega_s)|^2 + \chi_m^{(3)}(\omega_c; \omega_s, -\omega_2, \omega_3) |x_c E_0(\omega_c)|^2, \\
x_s &= \frac{3\varepsilon_d}{\varepsilon_m(\omega_s) + 2\varepsilon_d}, \quad x_c = \frac{3\varepsilon_d}{\varepsilon_m(\omega_c) + 2\varepsilon_d}.
\end{align*}
\]
Figure 3. The real and imaginary parts of the effective refractive index of the fused silica doped with silver nanoparticles with a fill factor of \( f = 0.01 \) versus the wavelength for different incident intensities calculated by equation (2).

Figure 4. The real and imaginary parts of the effective refractive index of the fused silica doped with silver nanoparticles with a fill factor of \( f = 0.01 \) versus the wavelength of the signal light for different incident intensities of the control light at a wavelength of \( \lambda_c = 500 \) nm calculated by equation (4). Here we assume that the control-light is far more intensive than the signal light. We take the cross-nonlinear susceptibility \( \chi_m^{(3)}(\omega_s; \omega_c, -\omega_c, \omega_s) \) and the self-nonlinear susceptibility \( \chi_m^{(3)}(\omega_s; \omega_s, -\omega_s, \omega_s) \) to be the same as the intrinsic third-order nonlinear susceptibility used in figure 1. One can see that the effective optical properties of the nanocomposite can be controlled with an intensive control-light. The nanocomposite irradiated by the control light can behave like a dielectric, showing a low absorption, while in the absence of the control light it can behave like a metal, showing a high absorption at the plasmon resonance.

Figure 5. The transmittance of the 70 nm layer of the fused silica doped with silver nanoparticles with a fill factor \( f = 0.05 \) at the linear plasmon resonance \( \lambda_s = 414 \) nm versus the peak intensity of the control light at the wavelength \( \lambda_c = 500 \) nm. By sending a control pulse with the high peak intensity, the transmittance can be controlled.
4. Conclusion

We theoretically predict that the intrinsic third-order nonlinear response of metal nanoparticles and the effects of the morphology and composition of nanocomposites can result in the non-perturbative effective nonlinear response of the nanocomposites, such as saturated plasmon bleaching and local field depression, and suggest that all-optical control in nanocomposites is due to the transition between the local field enhancement and local field depression. However, the intensities needed in the GW cm$^{-2}$ range can cause positive nonlinear absorption effects, resulting in significant changes in the intrinsic third-order nonlinear response of the metal nanoparticles. We assume that sub-picosecond control pulses of light with moderate fluence and repetition rate will keep the metal nanocomposites from effects such as electron-ejection, cumulative heating and optically induced irreversible damage. The switching time in such a device will be limited by the inherent cooling time, which is of the order of 1 ps [26].

References

[1] Pelton M, Aizpurura J and Bryant G 2008 Metal nanoparticle plasmonics Laser Photon. Rev. 2 136–59
[2] Hache F, Ricard D, Flytzanis C and Kreibig U 1988 The optical Kerr effect in small metal particles and metal colloids: the case of gold Appl. Phys. 47 347–57
[3] Falcao-Filho E L, de Araujo C B and Rodrigues J J 2007 High-order nonlinearities of aqueous colloids containing silver nanoparticles J. Opt. Soc. Am. B 24 2948–56
[4] Gomez L A, de Araujo C B, Brito-Silva A and Galembeck A 2008 Solvent effects on the linear and nonlinear optical response of silver nanoparticles Appl. Phys. B 92 61–6
[5] Rativa D, de Araujo R E and Gomes A S 2008 One photon nonresonant high-order nonlinear optical properties of silver nanoparticles in aqueous solution Opt. Express 16 19244–52
[6] Okada N, Hamanaka Y, Nakamura A, Pastoriza-Santos I and Liz-Marzan L M 2004 Linear and nonlinear optical response of silver nanoprism: local electric fields of dipole and quadrupole plasmon resonances J. Phys. Chem. B 108 8751–5
[7] Kyong M and Lee M 1999 Nonlinear absorption and refractive index measurements of silver nanorods by the Z-scan technique Opt. Commun. 171 145–8
[8] Wundke K, Poetting S, Auxier J, Schuelzgen A, Peyghambarian N and Borrelli N F 2000 PB8 quantum-dot-doped glasses for ultrashort-pulse generation Appl. Phys. Lett. 76 10–2
[9] Ganeev R A, Rasysnansky A I, Stepanov A L and Usmanov T 2003 Nonlinear absorption at visible light in silicate glasses doped with copper nanoparticles Quantum Electron. 33 1081–4
[10] Ganeev R A, Rasysnansky A I, Stepanov A L and Usmanov T 2004 Saturated absorption and nonlinear refraction of silicate glasses doped with silver nanoparticles at 532 nm Opt. Quantum Electron. 36 949–60
[11] Elim H I, Yang J, Lee J-Y, Mi J and Ji W 2006 Observation of saturable and reverse-saturable absorption at longitudinal surface plasmon resonance in gold nanorods Appl. Phys. Lett. 88 083107
[12] Gurudas U, Brooks E, Heiroth D M, Lippert T and Wokaun A 2008 Saturable and reverse saturable absorption in silver nanodots at 532 nm using picosecond laser pulses J. Appl. Phys. 104 073107
[13] Seo J T et al. 2009 Optical nonlinearities of Au nanoparticles and Au/Ag coreshells Opt. Lett. 34 307–9
[14] Rangel-Rojo R et al. 2009 Anisotropy in the nonlinear absorption of elongated silver nanoparticles in silica, probed by femtosecond pulses Opt. Commun. 282 1909–12
[15] Boni L D, Wood E L, Toro C and Hernandez F E 2008 Optical saturable absorption in gold nanoparticles Plasmonics 3 171–6
[16] Zheng C, Ye X Y, Cai S G, Wang M J and Xiao Q X 2010 Observation of nonlinear saturable and reverse-saturable absorption in silver nanowires and their silica gel glass composite Appl. Phys. B 101 835–40
[17] Philip R, Kumar G R, Sandhyarani N and Pradep T 2000 Picosecond optical nonlinearity in monolayer-protected gold, silver, and gold-silver alloy nanoclusters Phys. Rev. B 62 13160
[18] Qu S, Zhang Y, Li H, Qiu J and Zhu C 2006 Opt. Mater. 28 259
[19] Grua P, Morreeuw J P and Bercegol H 2003 Electron kinetics and emission for metal nanoparticles exposed to intense laser pulses Phys. Rev. B 68 035424
[20] Sipe J E and Boyd R W 1992 Nonlinear susceptibility of composite optical materials in the Maxwell–Garnett model Phys. Rev. A 46 1614–29
[21] Kothari N C 1990 Effective-medium theory of a nonlinear composite medium using the $T$-matrix approach: Exact results for spherical grains Phys. Rev. A 41 4486–92
[22] Kim K H, Husakou A and Herrmann J 2010 Saturable absorption in composites doped with metal nanoparticles Opt. Express 18 21918–25
[23] Hamanaka Y, Fukuta K, Nakamura A, Liz-Marzn L M and Mulvaney P 2004 Enhancement of third-order nonlinear optical susceptibilities in silica-capped Au nanoparticle films with very high concentrations Appl. Phys. Lett. 84 49384940
[24] Tanabe K 2008 Field enhancement around metal nanoparticles and nanoshells: a systematic investigation J. Phys. Chem. C 112 15721–8
[25] Falcao-Filho E L, de Araujo C B, Galembeck A, Oliveira M M and Zarbin A J 2005 Nonlinear susceptibility of colloids consisting of silver nanoparticles in carbon disulfide J. Opt. Soc. Am. B 22 2444–9
[26] Kim K-H 2013 Nondegenerate nonlinear optical susceptibility of dielectric composite materials containing metal nanoparticles Laser Phys. 23 115401