Carbon 120 (2017) 203–208

Contents lists available at ScienceDirect

Carbon

journal homepage: www.elsevier.com/locate/carbon

Induced chirality in micron wave through electromagnetic coupling between chiral molecules and graphene nanostructures

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ARTICLE INFO

Article history:
Received 20 January 2017
Received in revised form
14 April 2017
Accepted 10 May 2017
Available online 13 May 2017

ABSTRACT

The intricate mechanisms of plasmon-induced circular dichroism (CD) in a visible region are considered based on chemical and physical influences, in which a simple model and formulations are required. Here, we demonstrate theoretically that plasmon-induced CD is approximately contributed by the cross-interaction between equivalent electric and magnetic dipole moments for chiral molecules and plasmon nanostructures. To prove electromagnetic couplings, we introduce graphene into plasmon nanostructures and design asymmetrically inscribed graphene dual-rings arrays (IGDAs) with high-order hybrid modes. Results show that ultrahigh-order plasmon-induced CD signals are achieved in micron wave, which is easily detected by mature microwave technology. The maximum enhancement factor of induced CD could reach up to four orders of magnitude. In addition, an induced CD signal could be tuned only by varying the Fermi energy of IGDAs rather than by varying geometric dimensions. For different molecules, the electromagnetic couplings still hold. The results could be used to dynamically design chiral sensors in biology and chemistry.

1. Introduction

Chiral structures cannot be made to coincide with their mirror images. In 1969, Sherman demonstrated the optical property of chiral chlorophyll-a, which presents different optical responses to right circularly polarized (RCP, +) and left circularly polarized (LCP, -) light [1], i.e., circular dichroism (CD) [2–4]. CD spectroscopic techniques probe the molecular conformation, but suffer from poor sensitivity [5,6]. Meanwhile, surface plasmon-based near-field enhancement delivered through specifically designed substrates is highly successful for ultrasensitive optical biosensor applications [7,8], such as surface-enhanced Raman spectroscopy (SERS) [9]. However, SERS lack conformational information about the molecules, such as information about molecular chirality.

Recently, experimental [10–13] and theoretical [14–16] research has reported on the interaction between chiral molecules and metal nanostructures for inducing chiral signals of molecules from UV spectral to visible regions. The CD enhancement factors of chiral molecules and metal nanostructures reach up to 1000 [17]. The reason for this finding is attributed to physical reasons, such as the plasmon-generated superchiral near fields [18–20] or induced optical activity due to near fields, both at isolated plasmonic nanostructures and at hotspots between the gap of nanostructures [21,22]. In the experiment, the reason for this finding is attributed to chemical reasons, such as the charge transfer to a plasmonic nanostructure through bonds formed by chemisorbed analyses [23]. Interband-absorption-enhanced unusual CD band can originate from conformational changes of the chemisorbed molecules [24].

The abovementioned phenomenon opens novel opportunities in ultrasensitive probing of chiral molecules and for novel optical nanomaterials based on chiral elements. However, the mechanism of induced CD signals is complex and ambiguous. Therefore, a simple model and formulations are required to understand the reasons for induced CD. In addition, all the induced CD signals reported above are present around visible regions. If the CD signals were induced around micron wave regions, chiral molecules could be detected more easily than at around visible regions. These results stem from mature microwave technologies that have been applied in electronics systems. The graphene has successfully applied in micron wave [25]. We can use graphene to replace metallic material in nanophotonics. Asymmetric placed rings can show many high-order hybrid modes when they interact with each other, which can be selective detected in a long region.

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http://dx.doi.org/10.1016/j.carbon.2017.05.042
0008-6223/

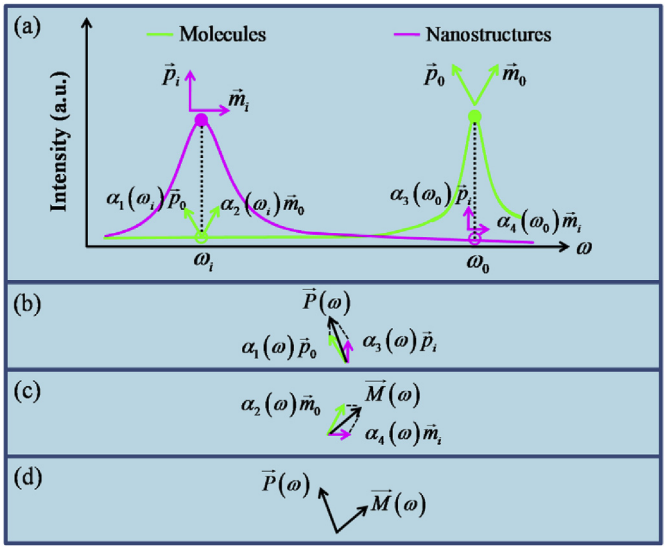

Fig. 1. Schematic of electromagnetic coupling between chiral molecules (green line) and plasmon nanostructures (magenta line): (a) the normalized intensities of equivalent electric and magnetic dipole moments, the vector resultant of electric (b) and magnetic (c) dipole moments, (d) the total electric and magnetic dipole moments. (A colour version of this figure can be viewed online.)

In this study, we demonstrate theoretically that plasmon-induced CD approximately contributes to the cross-interaction between equivalent electric and magnetic dipole moments for chiral molecules and plasmon nanostructures. To prove the electromagnetic couplings, we introduce graphene into plasmon nanostructures and design asymmetrical inscribed graphene dual-ring arrays (IGDAs) with high-order hybrid modes. Results show that ultrahigh-order plasmon-induced CD signals are achieved in the micron wave, which is easily detected by mature microwave technology. The maximum enhancement factor of induced CD could reach up to four orders of magnitude. In addition, the induced CD signal could be tuned only by varying the Fermi energy of IGDAs rather than by varying geometric dimensions. For different molecules, the electromagnetic couplings still hold.

2. Theory

Fig. 1(a) shows the normalized intensities of equivalent electric and magnetic dipole moments for chiral molecules (green line) and plasmon nanostructures (magenta line) and are described as two functions of ω, which is the angular frequency of incident light. The resonant absorptions of chiral molecules and plasmon nanostructures are ω_0 and ω_i, respectively. For chiral molecules at ω_0, the resonant electric and magnetic dipole moments of chiral molecules are labeled as $\vec{p}_0$ and $\vec{m}_0$, respectively. Given the chirality of molecules, $\vec{p}_0 \cdot \vec{m}_0 \neq 0$, which do not form a right angle between $\vec{p}_0$ and $\vec{m}_0$. For plasmon nanostructures at ω_i, the resonant electric and magnetic dipole moments of plasmon nanostructures are labeled as $\vec{p}_i$ and $\vec{m}_i$, respectively. As a result of the achirality of plasmon nanostructures, $\vec{p}_i \cdot \vec{m}_i = 0$, which forms a right angle between $\vec{p}_i$ and $\vec{m}_i$.

The normalized intensities of electric and magnetic dipole moments decay from resonant angular frequencies to non-resonant angular frequencies. The decayed coefficient is defined as $\alpha(\omega) \propto 1/(\omega - \omega_0)^2$ [16]. The coefficient will reach infinity at $\omega = \omega_0$, which is not a reality in physical systems. In this study, decay coefficients with the form $e^{-(\omega-\omega_0)^2/\sigma}$ is proposed and proved in the Results and Discussion section. Decayed coefficients of electric dipole moments of chiral molecules are defined as $\alpha_1(\omega) = e^{-(\omega-\omega_0)^2/\sigma_1}$, $\alpha_2(\omega) = e^{-(\omega-\omega_0)^2/\sigma_2}$ for magnetic dipole moments of chiral molecules, $\alpha_3(\omega) = e^{-(\omega-\omega_0)^2/\sigma_3}$ for electric dipole moments of plasmon nanostructures, and $\alpha_4(\omega) = e^{-(\omega-\omega_0)^2/\sigma_4}$ for magnetic dipole moments of plasmon nanostructures. At ω_i, $\vec{p}_0$ and $\vec{m}_0$ decay into $\alpha_1(\omega_i)\vec{p}_0$ and $\alpha_2(\omega_i)\vec{m}_0$, respectively. At ω_0, $\vec{p}_i$ and $\vec{m}_i$ decay into $\alpha_3(\omega_0)\vec{p}_i$ and $\alpha_4(\omega_0)\vec{m}_i$, respectively.

The quantum theory of the CD effect of chiral molecules is described as a ω function [26,27].

$$\mathrm{CD}_{\mathrm{molecules}}(\omega) \propto \mathrm{Im}\,[\alpha_1(\omega)\vec{p}_0 \cdot \alpha_2(\omega)\vec{m}_0]. \tag{1}$$

When plasmon nanostructures are introduced into chiral molecules, the total electric dipole moments $\vec{P}(\omega)$ can be composited by $\alpha_1(\omega)\vec{p}_0$ and $\alpha_3(\omega)\vec{p}_i$, as shown in Fig. 1(b). The total magnetic dipole moments $\vec{M}(\omega)$ can be composited by $\alpha_2(\omega)\vec{m}_0$ and $\alpha_4(\omega)\vec{m}_i$, as shown in Fig. 1(c). Therefore, as shown in Fig. 1(d), the CD effect of chiral molecules and plasmon nanostructures is described as a general equation

$$\mathrm{CD}_{molecule+\mathrm{plasmon}}(\omega) \propto \mathrm{Im}\left[\vec{P}(\omega)\cdot\vec{M}(\omega)\right] \propto \mathrm{Im}\left[(\alpha_1(\omega)\vec{p}_0 + \alpha_3(\omega)\vec{p}_i)\cdot(\alpha_2(\omega)\vec{m}_0 + \alpha_4(\omega)\vec{m}_i)\right] \tag{2}$$

Taking α_1 and α_2 into Eq. (2), the CD effect of chiral molecules and plasmon nanostructures is described as

$$\begin{aligned}\mathrm{CD}_{molecule+\mathrm{plasmon}}(\omega) &\propto \mathrm{Im}\left[\left(e^{-(\omega-\omega_0)^2/\sigma_1}\vec{p}_0 + e^{-(\omega-\omega_i)^2/\sigma_3}\vec{p}_i\right)\cdot\left(e^{-(\omega-\omega_0)^2/\sigma_2}\vec{m}_0 + e^{-(\omega-\omega_i)^2/\sigma_4}\vec{m}_i\right)\right] \\ &\propto \mathrm{Im}\left[e^{-(\omega-\omega_0)^2(1/\sigma_1+1/\sigma_2)}\vec{p}_0\cdot\vec{m}_0 + e^{-(\omega-\omega_0)^2/\sigma_1-(\omega-\omega_i)^2/\sigma_4}\vec{p}_0\cdot\vec{m}_i + e^{-(\omega-\omega_0)^2/\sigma_2-(\omega-\omega_i)^2/\sigma_3}\vec{m}_0\cdot\vec{p}_i\right],\end{aligned} \tag{3}$$

where $e^{-(\omega-\omega_i)^2/\sigma_3-(\omega-\omega_i)^2/\sigma_4}\vec{p}_i\cdot\vec{m}_i = 0$ because of $\vec{p}_i\cdot\vec{m}_i = 0$ for achiral plasmon nanostructures. When $\omega = \omega_0$, Eq. (3) is reduced into

$$\mathrm{CD}_{molecule+\mathrm{plasmon}}(\omega_0) \propto \mathrm{Im}\left[\vec{p}_0\cdot\vec{m}_0 + e^{-(\omega_0-\omega_i)^2/\sigma_4}\vec{p}_0\cdot\vec{m}_i + e^{-(\omega_0-\omega_i)^2/\sigma_3}\vec{m}_0\cdot\vec{p}_i\right]. \tag{4}$$

Given CD lines of chiral molecules in the UV region and plasmon bands of nanostructures in the visible or infrared regions, then $(\omega_i - \omega_0)^2 >> 0$. Therefore, $e^{-(\omega_0-\omega_i)^2/\sigma_4}\vec{p}_0\cdot\vec{m}_i$ and $e^{-(\omega_0-\omega_i)^2/\sigma_3}\vec{m}_0\cdot\vec{p}_i$ could be ignored because they are of a higher order infinitesimal with respect to $\vec{p}_0\cdot\vec{m}_0$. Therefore, Eq. (3) could be approximated as