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Second-harmonic generation from bimetal composites doped with metal nanoparticles

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HIGHLIGHTS

- Second harmonic generation from bimetal composites using the nonlinear Mie theory and the effective medium theory is presented.
- The effect of temperature on the second harmonic generation is studied.
- Influence of interparticle plasmon coupling on the second harmonic generation is investigated.
- The contribution of dipolar, quadrupolar and octuolar modes is considered and discussed.

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ABSTRACT

In the present paper, we study the nonlinear optical response of the bimetal composites doped with metal nanoparticles in the framework of nonlinear Mie theory combined with the Maxwell–Garnett model. We concentrate on the second-order harmonic generation from bimetal nanocomposites including silver and gold particles, since sometimes the nonlinear optical response is sensitive to the more accurate of material structure than linear optical response. We show that optical second harmonic generation is strongly sensitive to temperature as an environmental parameter, interparticle plasmon coupling between Au and Ag nanoparticles (the filling factor of inclusions), the particle size and the surrounding medium. However, this work shows good potential of bimetal composites for nonlinear optics at the nanoscale.

1. Introduction

The study of linear and nonlinear optical response of nanosized metal particles is very important for development of various applications such as plasmonics and ultrafast switching [1,2]. In addition, metal nanoparticles and their nanocomposites are essential tools for biomedical research and nanophotonics [3,4]. One of the most studied nonlinear optical processes in plasmonic nanomaterials is optical second harmonic (SH) generation, which is often used in surface probes and spectroscopic studies of molecules adsorbed on surfaces [5]. Optical SH generation is a second-order nonlinear phenomenon which requires the breakdown of inversion symmetry and has been found to be strongly enhanced at metal interfaces and metal nanostructures [6,7]. On this basis, the generation of optical signals by plasmonic nanoparticles as metal and composite nanoparticles, which are very good candidates for the enhancement of nonlinear optical effects, opens new fields for studies at nanometer scales in the area of nanoscience and nanotechnology [8–10].

The generation of SH radiation is the most common technique for generating different wavelengths of light. It is also a powerful spectroscopic tool in determining the properties of metallic nanostructures [11]. The linear and nonlinear optical response of metal nanoparticles is specified by collective excitations of their conduction electrons which lead to unique optical properties [12,13]. Since the SH intensity is related to the local field enhancement and the surface plasmon resonance (SPR) frequency, the generation of second-order harmonic from metal nanoparticles exhibits a strong surface enhancement [14,15]. It is important to note, however, that metallic nanoparticles have a large nonlinear optical response and therefore study of nonlinear processes in metal nanostructures is called nonlinear plasmonics [16]. Moreover, the nonlinear optical properties of nanostructures attracted significant attention in recent years and these studies laid the foundation of nonlinear plasmonics.

Nonlinear optical effects such as the generation of SH radiation in metal nanoparticles has been studied and investigated by several researchers during the last years. For example, Dadap et al.

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studied the SH generation from small spherical particles of centrosymmetric material in the Rayleigh–Gans approximation and showed that the surface SH polarization gives rise to two radiation modes, the electric dipole and electric quadrupole [17]. Nappa et al. investigated the SH light scattered from a liquid suspension of small gold metallic particles [18]. The core-shell nanoparticles with γ-Fe_2O_3 core and gold shell were fabricated, and their nonlinear optical properties were studied by Kolmychek et al. [19]. Beer and Roke developed a method for the second-harmonic and sum-frequency scattering using nonlinear Mie theory for spherical particles [20]. Bachelier et al. investigated experimentally and theoretically nonlinear optical properties of spherical gold nanoparticles in a specific scattering and polarization configuration. They showed that the interference effects between dipolar and octupolar plasmons can be used as a fingerprint to discriminate the local surface and nonlocal bulk contributions to SH generation [21]. However, the SH generation of optical radiation by metal nanoparticles and nanoshells has been discussed in several papers [22–26].

But, with advances in nanoscience and nanotechnology, it has become possible to fabricate nanomaterials with particular structures and unique features in order to investigate optical processes. One type of nanostructure for nonlinear plasmonics is composite nanomaterials, which can be potentially applied to nonlinear optics and optoelectronics. They are formed by homogeneous mixing of constituent elements in a dielectric host matrix that is generally composed of two (or more) different metal particles dispersed in a dielectric matrix and can enhance the nonlinear optical properties through plasmonic interactions [27]. In particular, a new type of composite nanomaterial is called bimetal composite nanoparticle (BCN) with two metal inclusions [28]. BCNs consist of metallic inclusion particles exhibiting electronic/optical properties than monometallic nanoparticles, due to their unique tunable spectral and optical properties. An important privilege of BCNs is their continuously tunable surface plasmon band because of the possibility of composition changes in contrast to monometal composites [29]. The nonlinear optical response of BCNs depends on the electromagnetic and plasmonic interactions between particles. When a metal nanoparticle is placed in close contact to another, electromagnetic coupling between the particles may further improve the optical responses. Therefore, an increased effective nonlinear optical response can be achieved through plasmonic effects. On the other hand, plasmonic excitations can significantly increase nonlinear optical effects in addition to the local electromagnetic fields [30]. Hence, the role of surface plasmon modes in the enhancement of nonlinear optical processes due to the local fields, is a key factor in the development of promising applications such as nonlinear optical sensing and plasmonic sensors [12,31].

In this work, we will investigate the second-order optical nonlinearity from BCNs based on the Maxwell–Garnett approximation and the nonlinear Mie theory. We present a theoretical model which allows one to generate nanoscale SH by bimetallic composites, because sometimes the linear optical response is insensitive to the more accurate material structure. It is shown that multipolar electrical moments excited in the particle provide the main contribution to the SH radiation. Influence of the plasmon coupling between two metal particles (plasmon–plasmon interaction) on the second-harmonic radiation is studied. In addition, the temperature dependence of second-order nonlinear optical response is discussed by considering the electron–phonon and surface scattering.

2. Modeling: the second harmonic scattering cross section and temperature dependence

In our model, a bimetal composite consists of a set of equally

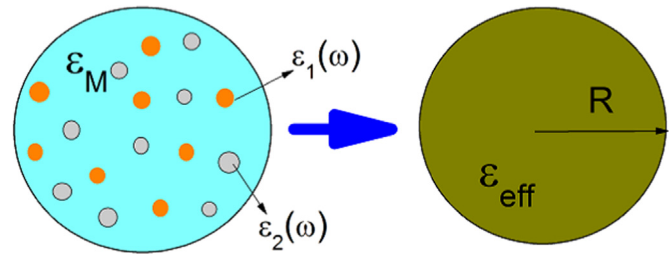

Fig. 1. Schematic representation of BCN containing Au and Ag particles dispersed in a host homogeneous matrix with the dielectric permittivity ε_M. The effective dielectric permittivity of the system is ε_{eff}.

sized Au and Ag nanoparticles with dielectric functions $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ and filling factors $f_1(=f_{Au})$ and $f_2(=f_{Ag})$, respectively. In other words, we consider a random mixture of two types of grains denoted by Au and Ag particles with different dielectric functions. The gold and silver nanoparticles are randomly dispersed in a host homogeneous matrix with the dielectric function ε_M as shown in Fig. 1. It is assumed that the filling factor is so small that the particles are separately included in the host matrix. The nanocomposite as a whole behaves like a homogeneous medium with an effective dielectric constant, ε_{eff}. Also, the dielectric permittivity of the surrounding space of system is ε_h. We assume that the gold and silver particles have the same spherical shape and they are very small compared to the wavelength of light.

2.1. Nonlinear Mie theory and the SH scattering cross section

Nonlinear optical response of metal nanoparticles can be modelled by using many methods such as the nonlinear Mie theory and the quasi-static approximation. Nonlinear Mie scattering theory is a combination of light scattering and nonlinear optics, and it gives a basic understanding of harmonic generation from nanoparticles [20]. Here, we will theoretically study the second-order nonlinear response of BCNs by applying the Mie scattering theory and the Maxwell–Garnett (MG) effective medium formalism. It is important to note that the generation of SH is useful and important for generating different wavelengths of light for many applications as a probe for studying surface phenomena and nonlinear optical switching at the nanoscale [8,32]. Furthermore, the MG model is particularly important from the viewpoint of new types of nonlinear nanomaterials [10].

As mentioned above, our theoretical formulation is based on the nonlinear Mie scattering theory and the effective medium approach introduced by the MG model. On the other hand, we perform our model to calculate of the SH scattering cross section for spherical BCNs. Consider a BCN containing gold and silver nanoparticles illuminated by an electromagnetic wave. The size of BCN is much smaller than the wavelength of incident light. Without going into the full details of calculations for Mie theory that can be found in Refs. [6,9], the scattered intensity for second-order harmonic can be determined by the following formula:

$$Q_{sca}^{(2)} = \frac{1}{\pi(kR)^2}\sum_{l,m}|A_E^{(2)}(l,m)|^2, \tag{1}$$

where $l=1$, 2 and 3 denotes the contribution of the electric dipole, quadrupole and octupole in the SH scattering cross section, respectively. Also, the coefficient of $A_E^{(2)}(l,m)$ has the form

$$A_E^{(2)}(l,m) = \frac{\pi kR}{\sqrt{l(l+1)}}\frac{\frac{\partial}{\partial r}[rj_l(k_1r)]}{\varepsilon_{eff}(2\omega)j_l(k_1r)D_H - h_l^{(1)}(kr)D_J}a_{l,m}^{(2)}, \tag{2}$$

where $D_h = \frac{\partial}{\partial r}[rh_l^{(1)}(kr)]$, $D_J = \frac{\partial}{\partial r}[rj_l(k_1r)]$ and $k_1 = \sqrt{\varepsilon_{eff}(2\omega)}\,k$ with $k(=k_{2\omega}) = 2\omega/c$ [9], in which R is the radius of spherical