Gradiation-controlled electric field distribution in multilayered colloidal crystals

L. F. Zhang,1,a) J. P. Huang,1,b) and K. W. Yu2,3,c)

1Surface Science Laboratory (National Key Laboratory) and Department of Physics, Fudan University, Shanghai 200433, China
2Department of Physics, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong
3Institute of Theoretical Physics, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong

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We exploit theoretically nonlinear optical materials by graded multilayered colloidal crystals, whose basic layer is made of metallo-dielectric nanoparticles immersed periodically in a host fluid. In the crystals, either the volume fraction of nanoparticles or the dielectric constant of host fluid can vary gradually within layers. The electric field distribution can be shown to exhibit a peak in a certain layer, and that the position of the peak can change by tuning the incident angular frequency. Such a gradation-controlled electric field distribution serves as a physical mechanism for understanding the enhanced nonlinear optical responses with a broad plasmon band. © 2008 American Institute of Physics.

Colloidal crystals have been extensively studied in nanomaterials engineering and their potential applications range from nanophotonics to chemistry and biomedicine.1−5 They also possess flexible structures and can be prepared via templated sedimentation, methods based on capillary forces, and electric fields. One important aspect in the engineering of nanophotonic materials is the realization of graded heterostructure by colloidal crystals, where the composition (or other properties) is varied continuously in space. The origins and types of the gradient have led to embodiment of complex and tunable physical properties of graded composites.6−10 Many artificially graded-index optical metamaterials and elements have been fabricated nowadays.11

We shall describe multilayer (or layer-graded) colloidal crystalline materials whose features vary continuously with the layers. Each layer can be seen as a single homogeneous colloidal nanocrystal with a homogeneous host. Here, we shall investigate two cases of multilayered colloidal crystalline materials, namely, either the nanoparticles or host in each layer change continuously with the layers.

Let us start by considering a tetragonal unit cell which has a basis of two colloidal nanoparticles, each of which is fixed with an induced point dipole at its center. One of the two nanoparticles is located at a corner and the other one at the body center of the cell. Its lattice constants are denoted by \( c_1 = lq^{-1/2} \) and \( c_2 = lq \) along \( x(y) \) and \( z \) axes, respectively. In this case, the uniaxial anisotropic axis is directed along the \( z \) axis. The degree of anisotropy of the periodic lattice is measured by how \( q \) deviates from unity. In particular, \( q = 0.8735, 1.0, \) and \( 2^{1/3} \) represent the bct, bcc, and fcc lattice, respectively. In general, the individual colloidal nanoparticles should be touching. Due to recent advancements in the fabrication of nanoshells,12,13 a colloidal crystal without the nanoparticles touching can also be achieved if one adds a dielectric surface shell on metallic cores. In this case, the dielectric constant of the surface shell may be set to be the same as that of the host, so that the multipolar interaction between the metallic nanoparticles (cores) might be small enough to be neglected. When an external electric field is applied along the \( x \) axis, the induced dipole moment \( \mathbf{P} \) is perpendicular to the uniaxial anisotropic \( z \) axis. Then, the local field \( \mathbf{E}_L \) at the lattice point \( \mathbf{R} = 0 \) can be determined by using the Ewald–Kornfeld formulation14 calculated over a three-dimensional periodic lattice of grains,

\[
E_L = P \sum_{j=1}^{2} \sum_{\mathbf{R} \neq 0} \left[ -\gamma(R_j) + x_j^2 q^2 \gamma_2(R_j) \right] \frac{-4\pi P}{V_c} \prod_{G \neq 0} \left( \frac{G^2}{G_0^2} \right)^{1/2} \exp \left( -\frac{G^2}{4\pi^2 q^2} \right) + 4\pi \frac{P q^3}{3\sqrt{\pi}},
\]

where \( \gamma(r) = \left[ \text{erfc}(\sqrt{\pi} r) / r^3 \right] + 2 r \sqrt{\pi} \exp(-\sqrt{\pi} r^2), \quad \gamma_2(r) = \left[ 3 \text{erfc}(\sqrt{\pi} r) / r^3 \right] + 4 \sqrt{\pi} \exp(-\sqrt{\pi} r^2) \), and \( \text{erfc}(\sqrt{\pi} r) \) is the complementary error function. Here, \( n \) is an adjustable parameter making the summation converge rapidly, and \( R \) and \( G \) respectively denote the lattice vector and reciprocal lattice vector. \( \mathbf{R} = (l q^{1/2} m x + q^{1/2} m y + q^{1/2} m z), \) and \( \mathbf{G} = (2 \pi / l)(l q^{1/2} m x + q^{1/2} m y + q^{1/2} m z), \) where \( l, m, n, u, v, \) and \( w \) are integers. In Eq. (1), \( x_j \) and \( R_j \) are respectively given by \( x_j = l - (j - 1)/2 \) and \( R_j = |R - [(j - 1)/2]a_x + a_y + c_z| \), and the structure factor \( \Pi(G) \) is \( \Pi(G) = 1 + \exp[iu(v + w)/\pi] \). The local electric field can be obtained by summing over all integer indices \((u,v,w) \neq (0,0,0)\) for the summation in the reciprocal lattice and \((j,l,m,n) \neq (1,0,0,0)\) for that in the real lattice. In our calculation, because of the exponential factors, we may impose an upper limit to the indices, that is, all indices ranging from \(-L \) to \( L \), where \( L \) is a positive integer. Now we define a local field factor \( \alpha_L \) in transverse field cases, \( \alpha_L = 3 V E_z / (8 n q P) \). It is worth noting that \( \alpha_L \) is a function of a single variable \( q \). In the mean time, there is \( \alpha_L = 3 - 2 \alpha_T \) (Refs. 14 and 15) which denotes the local field factor in longitudinal field cases, here, the longitudinal (or transverse) field cases correspond to the fact that the \( E \) field of the incident light is parallel (or perpendicular) to the uniaxial anisotropic \( z \) axis. For the bct, bcc, and fcc lattices, we obtain \( \alpha_T = 0.953 51, 1.0, \) and \( 1.0 \) (or alternatively \( \alpha_T = 1.092 98, 1.0, \) and \( 1.0 \)), respectively. Next, for cal-

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a)Electronic mail: zhanglf@fudan.edu.cn.

b)Author to whom correspondence should be addressed. Electronic mail: jphuang@fudan.edu.cn.

c)Author to whom correspondence should be addressed. Electronic mail: kwyu@phy.cuhk.edu.hk.
calculating the effective dielectric constant \( \varepsilon(i, \omega) \) (\( \omega \): angular frequency of an incident light) of the colloidal crystal in the \( i \)th layer along the \( z \) axis, we resort to the anisotropic Maxwell–Garnett formula \(^{16} \) with a high degree of accuracy due to the explicit determination of \( \alpha_L \),

\[
\frac{\varepsilon(i, \omega) - \varepsilon_2}{\varepsilon_2 + (\alpha_L^2/3)[\varepsilon(i, \omega) - \varepsilon_2]} = p(i) \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_2 + (1/3)(\varepsilon_1 - \varepsilon_2)},
\]

where \( \varepsilon_1 \) stands for the dielectric constant of the spherical metallic core, \( \varepsilon_2 \) represents that of the host fluid (or surface shell), and \( p(i) \) is the volume fraction of the metallic core in the \( i \)th layer, see Eq. (6) below. Next, the effective third-order nonlinear susceptibility \( \chi(i, \omega) \) for the colloidal crystal in the \( i \)th layer is given by\(^ {17} \)

\[
\chi(i, \omega) = p(i) \frac{\langle \Delta E_{\text{lin}}^2 \rangle^2 \langle \Delta E_{\text{lin}} \rangle^2}{\langle E_0^2 \rangle^2} \chi_1,
\]

where \( \chi_1 \) is the (intrinsic) third-order nonlinear susceptibility of the metallic core, \( E_0 \) the external electric field along \( z \) axis, \( E_{\text{lin}} \) the linear local electric field inside the metallic core, and \( \langle \cdots \rangle \) the volume average of \( \cdots \) over the layer. Both \( \langle \Delta E_{\text{lin}}^2 \rangle \) and \( \langle \Delta E_{\text{lin}} \rangle^2 \) can be expressed in the spectral representation.\(^ {17,18} \) Here the third-order nonlinear susceptibility \( \chi(i, \omega) \) satisfies the local constitutive relation between the displacement \( \mathbf{D}(i, \omega) \) and the electric field \( E(i, \omega) \) inside the \( i \)th layer, \( \mathbf{D}(i, \omega) = \varepsilon(i, \omega) \mathbf{E}(i, \omega) + \chi(i, \omega) \mathbf{E}(i, \omega)^2 \mathbf{E}(i, \omega) \), where nonlinear responses [namely, \( \chi(i, \omega) \mathbf{E}(i, \omega)^2 \mathbf{E}(i, \omega) \)] are much smaller than linear responses [i.e., \( \varepsilon(i, \omega) \mathbf{E}(i, \omega) \)], satisfying the requirement of weak nonlinearity.

For multilayered colloidal crystalline materials, we can use the equivalent capacitance of a series combination to calculate the linear response (optical absorption) \( \overline{\varepsilon}(\omega) \),

\[
\frac{1}{\overline{\varepsilon}(\omega)} = \frac{1}{N} \sum_{i=1}^{N} \frac{1}{\varepsilon(i, \omega)}.
\]

By virtue of the continuity of electric displacement, we have the relation \( \varepsilon(i, \omega) E(i) = \overline{\varepsilon}(\omega) E_0 \). Next, we take one step forward to obtain the effective third-order nonlinear susceptibility \( \overline{\chi}(\omega) \) as an integral over the whole crystal\(^ {19} \)

\[
\overline{\chi}(\omega) = \frac{1}{N} \sum_{i=1}^{N} \chi(i, \omega) \left[ \frac{\overline{\varepsilon}(\omega)}{\varepsilon(i, \omega)} \right]^2 \left[ \frac{\overline{\varepsilon}(\omega)}{\varepsilon(i, \omega)} \right]^2.
\]

For model calculations, the dielectric constant \( \varepsilon_1(\omega) \) of the metallic core is given by the Drude model, \( \varepsilon_1(\omega) = 1 - \omega_p^2 / (\omega^2 + i \omega \gamma) \), where \( \omega_p \) (or \( \gamma \)) is the plasmon frequency (or relaxation rate). Here we consider a bct (\( \rho = 0.873 \, \text{S} \)) lattice for the longitudinal field case. The principal axis of the bct lattice (\( z \) axis) is the same as the axis of the gradient of the dielectric function of the host dielectric. Figure 1 shows in the logarithmic scale (a) the linear optical absorption \( \text{Im}[\overline{\varepsilon}(\omega)] \) and (b) nonlinearity enhancement as a function of the reduced frequency \( \omega / \omega_p \). In Figs. 1(a) and 1(b), the multilayered colloidal crystal with a graded volume fraction is studied, which means that the packing density gradually increases or decreases between two consecutive layers. In general, for achieving the gradation profile of volume fractions, the nanoparticles may get larger, or they may get closer together within a layer. We use \( N \) to denote the total number of layers, and \( R_c \) for the ratio between the radii of the core and dielectric shell. For the system in our discussion.

![FIG. 1. For the bct lattice, the linear optical absorption Im[\varepsilon(\omega)] and the enhancement of the third-order optical nonlinearity |\varepsilon(\omega)|/\chi_1 vs the normalized incident angular frequency \omega/\omega_p. (a) and (b). Multilayered colloidal crystals with the volume fraction with gradation profile \rho(i)=(i/N)\Phi_0, which consist of five layers (dotted line) and 25 layers (solid line), at \( \epsilon_2 = 2.25 \). The dashed lines in (a) and (b) show the case of a homogeneous colloidal crystal (in which identical metallic cores with dielectric shells are immersed in a homogeneous host fluid) with volume fraction of metallic component \( p=0.363 \, \text{S} \) (which corresponds to \( R_c=0.804 \, \text{S} \)), a value obtained by averaging over the crystal containing 25 layers with \( \rho(i)=(i/N)\Phi_0 \). Parameter: \( \gamma=0.02\omega_p \).](http://apl.aip.org/apl/copyright.jsp)
of multilayered colloidal crystals changes with the photon frequency. On the other hand, for multilayered colloidal crystals with the same graded volume fraction as already used in Figs. 1(a) and 1(b), as a function of the number of layers \( N \) at different incident photon energy \( \hbar \omega \), for (a) \( \hbar \omega = 2.13 \text{ eV} \) ( ), 2.26 eV ( ), 2.38 eV ( ), and 2.50 eV ( ) and (b) \( \hbar \omega = 2.01 \text{ eV} \) ( ), 2.13 eV ( ), 2.26 eV ( ), and 2.38 eV ( ).

![FIG. 2. Electric field distribution of multilayered colloidal crystals with the same graded volume fraction as already used in Figs. 1(a) and 1(b), as a function of the number of layers \( N \) at different incident photon energy \( \hbar \omega \), for (a) \( \hbar \omega = 2.13 \text{ eV} \) ( ), 2.26 eV ( ), 2.38 eV ( ), and 2.50 eV ( ) and (b) \( \hbar \omega = 2.01 \text{ eV} \) ( ), 2.13 eV ( ), 2.26 eV ( ), and 2.38 eV ( ).](image)

profile, the graded-index host can exhibit the characters (Figures being similar but, not shown here) similar to those displayed in Fig 1.

To show the validity of our results, we use the experiment data extracted from Table 1 in Ref. 21 instead of Drude dielectric model, where the optical constants of gold were investigated and its dielectric constant \( \varepsilon_i = n^2 = (n + ik)^2 \) ( \( n \) =n +ik: complex index of refraction) was shown as a function of incident photon energy in units of eV. Figure 2 shows the corresponding results, where the electric field distribution of multilayered colloidal crystals changes with the photon energy \( \hbar \omega \). Same as the results predicted in Drude model (figures being similar, but not shown here), the peak of the electric field can emerge and change from one layer to the other at different photon energy \( \hbar \omega \), both for five layers [Fig. 2(a)] and 25 layers [Fig. 2(b)]. This also shows that the position of peaks can be tuned by photon energy (or incident angular frequency \( \omega \)). Thus, it becomes a promising way for one to adjust the electric field distributed by controlling the frequency. On the other hand, for multilayered colloidal crystals with the graded-index host, the peak of electric field can also be controlled by \( \omega \) (no figures shown here).

It is known that the surface plasmon mode of individual metallic nanoparticles can couple to each other through strong dipole-dipole interactions. In a dilute system, the surface plasmon resonance frequency of an individual nanoparticle in a graded medium must have a wide distribution forming a broad resonant band due to gradation in the materials parameters. However, the local electric field should still be sharply peaked around the nanoparticles, causing significant absorption. While at higher concentration (as in our examples), the strong dipole-dipole interactions between metallic nanoparticles in different layers tend to broaden the electric field distribution, leading to a broad peak. That also means that the electric field in layers was influenced by the electric field in the neighboring layers due to the strong dipole-dipole interactions between metallic nanoparticles in different layers, thus, the sharp peak (strong electric field is almost distributed in one layer) becomes a broad peak (strong electric fields are distributed in many layers). Such a broad peak leads to redistribution of the absorption over many layers and hence increase the figure of merit (namely, the ratio between the nonlinear response and corresponding linear absorption) in the band.

Related with the phenomena shown in Fig. 1, the dependence of the position of a peak on the incident angular frequency also gives an easy way for understanding the enhancement of third-order nonlinearity. Compared with the homogeneous colloidal crystals, each layer in multilayered colloidal crystals with a graded volume fraction or a graded-index host has a different frequency region for achieving the peak distribution, so the multilayered colloidal crystals have more chances for the existence of the peak distribution (when the frequency changes), and a gradual transition comes to appear from sharp peaks to a broad continuous band as the number of the layers increases.

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