Plasmonic enhancement by metallic spherical nanoparticles

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Abstract
In this work we study the enhancement of the electromagnetic field in the free space surrounding metallic nanoparticles due to the effect of their localized plasmon resonance. We start from a review of the known results in the case of a simple metallic spherical nanoparticle and then extend these results to the general case of any network of many identical spherical metallic nanoparticles. For illustration, some typical lattices of identical spherical metallic nanoparticles will be investigated. Analytical expressions and algebraic equations determining the electromagnetic field in the free space surrounding these typical networks will be derived.

Keywords: plasmonic, plasma frequency, localized plasmon resonance LPR, dipole moment

1. Introduction

Since the appearance of the celebrated article of Fujishima and Honda [1] on pure water splitting in a photoelectrochemical cell with a titania photoanode, many research works on utilizing the visible light responsive titania-based nanostructures for the fabrication of the photoanodes of the photocatalytic, photoelectrochemical and photovoltaic cells have been performed (see, for example, a recent review [2] and references therein). Besides anion- and cation-doping titania to create the materials with energy band gaps narrower than that of pure titania, as well as sensitizing titania by dyes or quantum dots, it was also proposed to enhance the photocatalytic activity of titania under the action of visible light by loading nanoparticles of noble metals Au and Ag on pure titania and profiting from the localized plasmon resonance (LPR) effect of these metallic nanoparticles [3–24]. In this work we present the basics of the theory of the light enhancement due to the LPR effect in the metallic nanoparticles.

We start the presentation by considering the enhancement of the electrical field of the electromagnetic radiation nearby a metallic spherical nanoparticle due to the LPR effect. The related key formulae were known in the literature [25, 26]. Then we shall establish the general theory of the enhancement of the electrical field in the electromagnetic radiation near some arbitrary network of identical metallic spherical nanoparticles due to the LPR effect in these nanoparticles. For illustration and also for future applications, the enhanced electrical field of the electromagnetic radiation due to the LPR effect on some particular systems of identical metallic spherical nanoparticles will be investigated.

For the description of the electromagnetic field in vacuum or in a homogeneous medium outside the sources, it is convenient to work in a special Lorentz gauge with the vanishing scalar potential of the electromagnetic field. Then the physical state of the electromagnetic field is completely determined by its vector potential

\[ \mathbf{H}(\mathbf{r}, t) = \nabla \times \mathbf{A}(\mathbf{r}, t), \]

and the electrical field \( \mathbf{E}(\mathbf{r}, t) \) is derived from the solution of the Maxwell equation

\[ \frac{\varepsilon_m}{c} \frac{\partial \mathbf{E}(\mathbf{r}, t)}{\partial t} = \nabla \times \mathbf{H}(\mathbf{r}, t), \]

where \( \varepsilon_m \) is the dielectric constant of the medium. In the case of a monochromatic electromagnetic field with the angular frequency \( \omega \), equation (2) becomes

\[ \mathbf{E}(\mathbf{r}, t) = i \frac{\omega}{k} \varepsilon_m \nabla \times \mathbf{H}(\mathbf{r}, t), \]

where \( k \) is the wavenumber of the electromagnetic wave.
where $k = \sqrt{\epsilon_m - \epsilon} \over \lambda$ [26]. Formulae (1) and (3) will be used in the sequel.

2. Single metallic spherical nanoparticle

Suppose that there exists a metallic spherical nanoparticle with radius $\rho$, and denote by $\varepsilon(\omega)$ the effective dielectric constant or electric permittivity of the metallic material with respect to the electrical field in the monochromatic electromagnetic radiation with the angular frequency $\omega$, by $\epsilon_m$ that of the dielectric medium surrounding the metallic nanoparticle. It was known that the electrical field

$$E^{(0)}(r, t) = e^{i(k\rho - \omega t)}E^{(0)},$$

$$k = {2\pi \over \lambda},$$

(4)

of the linearly polarized monochromatic incident light induces following electrical dipole moment $p(R, t)$ inside the metallic spherical nanoparticle with the center located at some point $R$ in the space [25]:

$$p(R, t) = 4\pi\rho^3L(\omega)E^{(0)}(R, t),$$

(5)

where

$$L(\omega) = {\varepsilon(\omega) - \epsilon_m \over \varepsilon(\omega) + 2\epsilon_m}.$$  

The induced electrical dipole moment located at some point $R$ emits into the surrounding space the electromagnetic radiation which will be called the induced electromagnetic field described by the vector potential $A_{ind}(r, t)$ or by a set of the induced electrical field $E_{ind}(r, t)$ and induced magnetic field $H_{ind}(r, t)$. It was shown (reference [26]) that near the location of the induced dipole moment (5) the vector potential $A(r, t)$ has the form

$$A_{ind}(r, t) = -{i \over 4\pi}\rho^3 e^{ikr}p(R, t).$$

(7)

It follows that the induced electrical field $E_{ind}(r, t)$ equals

$$E_{ind}(r, t) = {1 \over 4\pi}\rho^3 e^{ikr}e^{i\omega t}[\nabla \times (p(R, t) \times \nabla)]$$

$$\times \left\{ 1 + \left[ {3(np)n - p \over |r - R|} \right] \left[ {1 \over |r - R|} - {i \over |r - R'|} \right] \right\},$$

(8)

where

$$n = \frac{r - R}{|r - R|}.$$  

(9)

At a point $r$ very near to the metallic spherical nanoparticle, $k |r - R| \ll 1$, formula (7) has following approximate form

$$E_{ind}(r, t) = e^{-i\omega t}e^{ikr}{3(np)n - p \over 4\pi\rho^3} {1 \over |r - R|}.$$  

(10)

In terms of the components $E_{ind}(r, t)_x$ of $E_{ind}(r, t)$ and the components $p_x$ of the induced electrical dipole moment $p$, formula (8) can be rewritten in the form

$$E_{ind}(r, t)_x = {1 \over 4\pi\rho^3} e^{-i\omega t}e^{ikr} \sum_{\beta} C_{\beta \alpha}(r - R)p_{\beta},$$

(11)

where

$$C_{\beta \alpha}(r - R) = \delta_{\beta \alpha} \left\{ {k^2 \over |r - R'|} + {ik \over |r - R|} \right\} - n_{\beta} n_{\alpha} \left\{ {k^2 \over |r - R'|} - {3 \over |r - R|} \right\}.$$  

(12)

Formulae (5), (6) and (8) show that the enhancement effect due to the presence of a metallic spherical nanoparticle with the diameter $\rho$ depends on the value of the function $L(\omega)$ expressed in terms of the electric permittivity $\varepsilon(\omega)$ of the metal at the photon energy $\hbar\omega$. From the experimental data on $\varepsilon(\omega)$ of gold (see appendix) there follow the values of the real and imaginary parts of $L(\omega)$, the values of real and imaginary parts of $E^{(0)}(r, t)$ for the metallic spherical nanoparticle and the electric field $E^{(0)}(R, t)$ of the incident light at the point $R$ coinciding with the origin of the coordinate system ($R = 0$) and the vector $r$ to be parallel to $E^{(0)}$. Then from formulae (5), (6) and (8) we have

$$E_{ind}(r, t) = \chi(\omega, d)E^{(0)}(0, t),$$

(13)

where $d = r - \rho$. The values of real and imaginary parts of $\chi(\omega, d)$ versus $\omega$ at different distances $d$ for the metallic spherical
nanoparticle are presented in figures 2(a)–(d), the observation point \( r \) and the direction of the electrical field \( E(0) \) are shown in the inset of figure 2(a).

3. Network of identical metallic spherical nanoparticles

The main part of the present work is the establishment of the system of equations determining the enhanced electrical field in the spatial region surrounding a network of identical metallic spherical nanoparticles when this network is illuminated by a linearly polarized monochromatic light beam. Being induced by the electrical field of the incident light, each metallic nanoparticle as a dipole moment itself emits the electromagnetic radiation into the surrounding space. Therefore, the total electrical field at any point \( r \) nearby but outside the metallic nanoparticles must be the superposition of the electrical fields \( E^{(0)}(r, t) \) of the electromagnetic radiations emitted by the induced electrical dipole moments \( p(R_i, t) \) and that of the incident light beam:

\[
E^{(tot)}(r, t) = E^{(0)}(r, t) + \sum \limits_{i} E^{(i)}(r, t). \tag{14}
\]

However, the total electrical field \( E^{(tot)}(R_i, t) \) acting on the induced electrical dipole moment \( p(R_i, t) \) located at the point \( R_i \) is the superposition of the electrical field \( E^{(0)}(R_i, t) \) of the incident light and the electrical fields \( E^{(i)}(R_i, t) \) in the electromagnetic radiations emitted by other induced electrical dipole moments \( p(R_i, t), j \neq i \):

\[
E^{(tot)}(R_i, t) = E^{(0)}(R_i, t) + \sum \limits_{j \neq i} E^{(j)}(R_i, t). \tag{15}
\]

Because this total electrical field induces the electrical dipole moment \( p(R_i, t) \), according to formula (5) we have

\[
p(R_i, t) = 4\pi\varepsilon_0\rho^3 L(\omega) E^{(tot)}(R_i, t). \tag{16}
\]

Let us write the induced dipole moment (16) in the form

\[
p(R_i, t) = e^{i(kR_i - \omega t)} p^{(i)}. \tag{17}
\]

From the expression (8) it follows that

\[
E^{(i)}(R_i, t) = \frac{1}{4\pi\varepsilon_0} e^{i(kR_i - \omega t)} e^{i|R_i - R_n|} \times \left\{ \left[ p^{(i)} - (n_i p^{(j)} n_j) \right] \frac{k^2}{|R_i - R_j|} + \left[ p^{(j)} - 3(n_i p^{(i)} n_j) \right] \frac{k^2}{|R_i - R_j|^3} \right\}. \tag{18}
\]
where
\[ n_\beta = \frac{R_j - R_i}{|R_j - R_i|}. \] (19)

In terms of the components \( E^{(i)}_{ind}(R_i, t) \) of the electrical field \( E^{(i)}_{ind}(R_i, t) \) and the components \( p^{(i)}_\alpha \) of the induced electrical dipole moment \( p^{(i)} \), formula (18) can be rewritten as follows:
\[
E^{(i)}_{ind}(R_i, t) = \frac{1}{4\pi\varepsilon_0} e^{i(k|R_i-R|)} e^{i\beta|R_i-R|} \times \sum_\beta C_{\alpha\beta}(R_i - R_j)p^{(i)}_\beta, \] (20)
\[
\text{where}
\]
\[
C_{\alpha\beta}(R_i - R_j) = \delta_{\alpha\beta} \left[ \frac{k^2}{|R_i - R_j|^2} + \frac{ik}{|R_i - R_j|} - \frac{1}{|R_i - R_j|^3} \right]
- (n_i)_{\alpha}(n_j)_{\beta} \left[ \frac{k^2}{|R_i - R_j|^2} \right]
- \frac{3ik}{|R_i - R_j|^2} - \frac{3}{|R_i - R_j|^3} \right].
\] (21)

(\( n_i \))_{\alpha} being components of the vector \( n_i \).

By using equations (15), (16) and (18) as well as expressions (4) and (17), it is straightforward to derive the system of algebraic equations for determining the induced electrical dipole moments \( p^{(i)} \) of the metallic spherical nanoparticles in the network:
\[
p^{(i)} = 4\pi\varepsilon_0\rho^3L(\omega)E^{(0)} + \rho^3L(\omega) \sum_{j=1}^N e^{i(k|R_i-R_j|)} e^{i\beta|R_i-R_j|}
\times \left\{ p^{(i)} - (n_i p^{(i)})n_j \right\} \left[ \frac{k^2}{|R_i - R_j|^2} \right]
+ \left\{ p^{(i)} - 3(n_i p^{(i)})n_j \right\} \left[ \frac{3ik}{|R_i - R_j|^2} - \frac{3}{|R_i - R_j|^3} \right].
\] (22)

In terms of the components \( p^{(i)}_\alpha \) of the induced electrical dipole moments \( p^{(i)} \) and the components \( E^{(i)}_{0}(R_i, t) \) of the electric field \( E^{(i)}(R_i, t) \) in the incident radiation, system of equation (22) becomes
\[
p^{(i)} = 4\pi\varepsilon_0\rho^3L(\omega)E^{(0)} + \rho^3L(\omega) \sum_{j=1}^N e^{i(k|R_i-R_j|)} e^{i\beta|R_i-R_j|}
\times \left\{ p^{(i)} - (n_i p^{(i)})n_j \right\} \left[ \frac{k^2}{|R_i - R_j|^2} + \frac{3ik}{|R_i - R_j|^2} - \frac{3}{|R_i - R_j|^3} \right].
\] (23)

By solving the system of equations (22) or (23), we find the functions \( p^{(i)}_\alpha(t) \) determining the components of the induced electrical dipole moments of all metallic spherical nanoparticles in the network.

Formula (8) or (11) determines the electrical field of the electromagnetic radiation emitted by the electrical dipole moment
\[
p(R_i, t) = e^{i(k|R_i-R|)} p.
\]

From these formulae it is easy to derive the expression of the total electrical field (14)
\[
E^{(tot)}(R_i, t) = E^{(0)}(R_i, t) + \frac{1}{4\pi\varepsilon_0} e^{-i\omega t} \sum_\beta e^{i(k|R_i-R_j|)} e^{i\beta|R_i-R_j|}
\times \left\{ p^{(i)} - (n_i p^{(i)})n_j \right\} \left[ \frac{k^2}{|R_i - R_j|^2} + \frac{3ik}{|R_i - R_j|^2} - \frac{3}{|R_i - R_j|^3} \right],
\] (24)
\[
\text{where}
\]
\[
n^{(i)} = \frac{R_i - R_j}{|R_i - R_j|}.
\] (25)

In terms of the components \( E^{(tot)}(R_i, t) \) and \( E^{(0)}(R_i, t) \), the electrical fields \( E^{(tot)}(R_i, t) \) and \( E^{(0)}(R_i, t) \) as well as the components \( p^{(i)}_\alpha \) of the induced electrical dipole moments \( p^{(i)} \), formula (24) becomes
\[
E^{(tot)}(R_i, t) = E^{(0)}(R_i, t) + \frac{1}{4\pi\varepsilon_0} e^{-i\omega t}
\times \sum_\beta e^{i(k|R_i-R_j|)} e^{i\beta|R_i-R_j|}
\times \sum_\beta C_{\alpha\beta}(R_i - R_j)p^{(i)}_\beta,
\] (26)
\[
\text{where}
\]
\[
C_{\alpha\beta}(R_i - R_j) = \delta_{\alpha\beta} \left[ \frac{k^2}{|R_i - R_j|^2} + \frac{3ik}{|R_i - R_j|^2} - \frac{3}{|R_i - R_j|^3} \right].
\] (27)

(\( n_i \))_{\alpha} being components of the vector \( n_i \).

Finally we remark that the Hamiltonian of the interaction between the total electromagnetic field induced by all metallic nanoparticles in the network with the individual electrons and holes in the whole system explicitly contains the vector potential
\[ A_{\text{ind}}(r, t) = -\frac{ik}{4\pi\sqrt{\epsilon_m}} \sum_i e^{i\omega t - \gamma} \mathbf{p}(R_i, t) \]  

(28)

**4. Simple examples**

Consider first the simplest case of a system of two identical metallic spherical nanoparticles with the radius \( \rho \) located at the distance \( l \) (\( l \geq 2\rho \)). This system is called a dimer. We choose to work in such a Cartesian coordinate system that the centers \( R_1 \) and \( R_2 \) of two metallic spherical nanoparticles are located at two points with the coordinates \(-l/2, l/2\) respectively, in the axis \( Oy \) (figure 3), and consider the behavior of the dimer in the presence of a monochromatic incident electromagnetic field with the wave vector \( \mathbf{k} \) parallel to the axis \( OZ \).

It is straightforward to derive the system of equation (22) for two induced electrical dipole moments \( \mathbf{p}^{(1)} \) and \( \mathbf{p}^{(2)} \) of two metallic spherical nanoparticles. If the incident electromagnetic wave is linearly polarized along the axis \( Oy \), then we have following system of equations

\[ p^{(1)} = 4\pi\varepsilon_0 \rho^3 L(\omega) E^{(0)} + \xi p^{(2)}, \]
\[ p^{(2)} = 4\pi\varepsilon_0 \rho^3 L(\omega) E^{(0)} + \xi p^{(1)}, \]  

(29)

where

\[ \xi = \frac{2\rho^3}{\pi^2} L(\omega) e^{i\omega t - \gamma} (1 - ikl). \]  

(30)

Its solution is

\[ p^{(1)} = p^{(2)} = \frac{1}{1 - \xi} 4\pi\varepsilon_0 \rho^3 L(\omega) E^{(0)}. \]  

(31)

In comparison with formula (5) now there arises the factor \( 1/(1 - \xi) \).

The enhancement of the electrical dipole moment of each spherical nanoparticle due to the mutual influence of the other is characterized by the so-called enhancement factor \( F \) which is equal to \( 1/(1 - \xi) \) in the case when their polarization direction (that of the electrical field \( E^{(0)} \)) is parallel to the \( Oy \) axis and is equal to \( 1/(1 + \eta) \) in the case of polarization perpendicular to the \( Oy \) axis. The values of the complex values of the enhancement factor \( F \) for a dimer consisting of two identical metallic nanospheres with the radius \( \rho = 10 \text{ nm} \) and placed at the distance \( l = 25 \text{ nm} \) of their centers have been calculated on the basis of formulae (30) and (33). They depend on the photon energy \( h\omega \) and are plotted in figure 4(a) for both configurations of the arrangement of the polarization of the electrical field and the \( Oy \) axis. The picture of the dimer is presented in the inset of this figure. The dependence of the maximum values of the real and imaginary parts of the enhancement factor \( F \) for both configurations on the distance between two centers of two metallic spherical nanoparticles is presented in figure 4(b).

The second simple example of a network of identical metallic sphere nanoparticles is a linear chain of equidistant ones with the centers located at the points \( R_i = il, \) \( i \) being integers and \( l \) being some vector (figure 5). The center \( R_0 \) of one spherical nanoparticle is the origin of the coordinate system. Suppose that the wave vector \( \mathbf{k} \) is perpendicular to the direction of the chain: \( k_0 = 0. \) In the case of the linearly polarized incident electromagnetic wave with the electrical field \( E^{(0)}(r, t) \) parallel to the direction of the chain, \( E^{(0)}/\mathbf{A} \), the values \( p^{(i)} \) of the induced electrical dipole moments are determined by following system of equations

\[ p^{(1)} = 4\pi\varepsilon_0 \rho^3 L(\omega) E^{(0)} + 2\rho^3 L(\omega) \sum_{j\neq i} e^{i\omega t - \gamma} \]
\[ \times \left( \frac{1}{|j - i|^3} \right) \mathbf{p}^{(j)}. \]  

(35)
For the infinite linear chain, due to the translational invariance of this chain, the solution of equation (35) is

\[ p^{(i)} = p = \frac{1}{1 - \alpha} 4\pi\varepsilon_0 \rho^3 L(\omega) E^{(0)} \]  
(36)

with

\[ \alpha = 2\rho^3 L(\omega) \sum_{j \neq 0} \frac{e^{i\omega |l|}}{|l|} (1 - ikl |l|). \]  
(37)

Similarly, in the case of the linearly polarized incident electromagnetic wave with the electrical field \( \mathbf{E}^{(0)}(\mathbf{r}, t) \) perpendicular to the direction of the chain, \( \mathbf{E}^{(0)} \perp \mathbf{L} \), we have the following system of equations

\[ p^{(i)} = 4\pi\varepsilon_0 \rho^3 L(\omega) E^{(0)} - \rho^3 L(\omega) \sum_{j \neq 0} e^{i|l|} - \frac{1}{|l|} \frac{ik}{|j - i|} \frac{k^2}{|l|} p^{(i)}. \]  
(38)

For the infinite linear chain its solution is

\[ p^{(i)} = p = \frac{1}{1 + \beta} 4\pi\varepsilon_0 \rho^3 L(\omega) E^{(0)} \]  
(39)

with

\[ \beta = \rho^3 L(\omega) \sum_{j \neq 0} e^{i|l|} \left( \frac{1}{|l|} - \frac{ikl}{|j - i|} \frac{k^2}{|l|} \right). \]  
(40)

According to formulae (36) and (39) the enhancement factor \( F \) is equal to \( 1/(1 - \alpha) \) in the case of the electrical field \( \mathbf{E}^{(0)}(\mathbf{r}, t) \) parallel to the direction of the chain and it is equal to \( 1/(1 + \beta) \) in the case of the electrical field perpendicular to the direction of the chain. The numerical calculations have been done for the chain consisting of 3, 7, 11 and 15 identical metallic spherical nanoparticles with the radius \( \rho = 10 \text{ nm} \) and with the distance of two nearest ones \( l = 25 \text{ nm} \). The photon energy \( \hbar \omega \) dependent real (black) and imaginary (red) parts of the enhancement factor \( F \) for both polarization configurations are plotted in figure 6.

The third network, which would be more often used, is that of a two-dimensional square lattice of identical metallic spherical nanoparticles with their centers located at the points \( \mathbf{R}_{(i,j)} = (ie_x + je_y)l, i \) and \( j \) being integers, \( e_x \) and \( e_y \) being the unit vectors along the coordinate axes \( O_x \) and \( O_y \), respectively, \( l \) being the nearest distance between two spherical nanoparticles (figure 7). We write the dipole moment induced on the spherical metallic nanoparticle with the center located at the point \( \mathbf{R}_{(i,j)} \) in the form similarly to expression (17):

\[ \mathbf{p}(\mathbf{R}_{(i,j)}, t) = e^{i(\mathbf{kR}_{(i,j)} - \omega t)} \mathbf{p}^{(i,j)}. \]  
(41)

For definiteness we choose the center \( \mathbf{R}_{(0,0)} \) of one spherical nanoparticle to be the origin of the coordinate system. Suppose that the wave vector \( \mathbf{k} \) of the incident light is perpendicular to the plane of the network: \( \mathbf{kR}_{(i,j)} = 0 \).
and consider the case when the incident electromagnetic wave is linearly polarized and has the electrical field $E_r(0, t)$ parallel to the direction of the axis Ox. It is straightforward to derive following system of algebraic equations determining the induced electrical dipole moments $p_{ij}^{(ij)}$:

$$p_{ij}^{(ij)} = 4\pi e_0 L(\omega)E_{0}^{(i)} + \rho^3 L(\omega) \sum_{(i', j')} e_{ij}^{(i', j')} \left[ R_{ij} - R_{ij'} ight]$$

$$\times \left\{ \left[ p_{i'}^{(i')} - \left( n_{i(i,i')j'} p_{j'}^{(i')} n_{i(i,j')j'} \right) \right] \right\}$$

$$\times \frac{k^2}{\left[ R_{ij} - R_{ij'} \right]} + \left[ p_{i'}^{(i')} = 3 \right]$$

$$\times \left( n_{i(i,j')j'} p_{j'}^{(i')} n_{i(i,j')j'} \right)$$

$$\times \left( \frac{ik}{\left| R_{ij} - R_{ij'} \right|^3} \right) \left[ R_{ij} - R_{ij'} \right],$$  \hspace{1cm} (42)$$

where

$$n_{i(i,j')j'} = \frac{R_{ij} - R_{ij'}}{\left[ R_{ij} - R_{ij'} \right]^3}. \hspace{1cm} (43)$$

Due to the translational invariance of the infinite square lattice, the solution of the system of equation (42) for the network of infinite square lattice of identical metallic
spherical nanoparticles becomes

$$p^{(i)} = p = \frac{1}{1 - \zeta} \frac{4\pi\varepsilon_0}{\mu_0} L(\omega) E^{(0)}$$

with

$$\zeta = 2\frac{\rho^3}{l^3} L(\omega) \sum_{j \neq 0} \frac{e^{i\theta j}}{|j|} \left(1 - i k l |j|\right)$$

$$+ 2\frac{\rho^3}{l^3} L(\omega) \sum_{j > 0} \sum_{j > 0} \frac{e^{i\theta j^2 + j^2}}{j^2}$$

$$\times \left\{\frac{2j^2 - j^2}{j^2 + j^2} \left(1 - ik\sqrt{j^2 + j^2} + k^2 j^2\right) + k^2 j^2 \right\}$$

The first term in the rhs of equation (45) is expression (37) of the constant $\alpha$ in formula (36) for the induced electrical dipole moment in the infinite linear chain of identical metallic spherical equidistant nanoparticles located in the real axis Ox, while remaining terms are the contributions of all other linear chains different from that in the real axis Ox.

The photon energy $\hbar\omega$ dependent values of the real (black) and imaginary (red) parts of the enhancement factor $F$ (equal to $1/(1 - \zeta)$) of the square networks of $n \times n$ metallic spherical nanoparticles with $n = 3, 7, 11$ and $15$ are presented in figure 8.

Other more complicated networks of identical metallic spherical nanoparticles can also be considered in a similar manner. From the expressions of the induced electrical dipole moments $p^{(i)}$ of the metallic spherical nanoparticles it is now straightforward to calculate the total electrical field $E^{(tot)}(r, t)$ of the resulting electromagnetic radiation in the space by using formulae (24)–(27).

5. Conclusion and discussion

In this work, on the basis of formula (5) for the electrical dipole moment $p(R, t)$ induced on a metallic spherical nanoparticle with the radius $\rho$ and the center located at the point $R$ by the interaction of the electrical field $E^{(0)}(r, t)$ of the form (4) with the conduction electrons inside this nanoparticle as well as of formula (8) for the electrical field $E_{\text{mol}}(r, t)$ in the electromagnetic radiation emitted by the electrical dipole moment $p(R, t)$, we have investigated any network of nearby located identical metallic spherical nanoparticles and derived the systems of equations (22) and (23) determining their induced electrical dipole moments, taking into account the mutual electromagnetic interaction between these metallic nanoparticles. From this result there follow expressions (24)–(27) of the total electrical field

Figure 8. Photon energy dependence of the complex enhancement factor $F$ of the square networks of (a) $3 \times 3$, (b) $7 \times 7$, (c) $11 \times 11$ and (d) $15 \times 15$ metallic spherical nanoparticles with $\rho = 10$ nm and distance of two nearest ones $l = 25$ nm.
which was enhanced in comparison with the electrical field $E^0(r, t)$ in the incident electromagnetic radiation due to the presence of the network of metallic spherical nanoparticles. The magnitude of the enhancement significantly depends on two quantities: the ratio $\rho/l$ of the radius $\rho$ of each nanoparticle to the distance $l$ between two nearest nanoparticles in the network, and the parameter $L(\omega)$ defined by formula (6).

Denote by $\omega_p$ the plasma frequency of the free electron gas in the metallic material of the nanoparticles and by $\gamma$ the characteristic collision frequency in this electron gas. At the frequency angular $\omega$ near the plasmon resonance, the electric permittivity $\varepsilon(\omega)$ of the metallic material has the approximate form [25]

$$
\varepsilon(\omega) = \varepsilon_{\infty} - \frac{\omega_p^2}{\omega^2 + i\gamma\omega},
$$

(usually $1 \leq \varepsilon_{\infty} \leq 10$). From definition (6) it follows that

$$
\text{Re } L(\omega) = 1 - 3\varepsilon_{\infty}
\times \frac{\omega^2 \left( \varepsilon_{\infty} + 2\varepsilon_{\infty} \right) \left( \omega^2 + \gamma^2 \right) - \omega_p^2}{\left( \varepsilon_{\infty} + 2\varepsilon_{\infty} \right) \omega^2 - \omega_p^2},
$$

(47)

\[ \text{Im } L(\omega) = \frac{3\varepsilon_{\infty} \omega_0^2 \gamma}{\left( \varepsilon_{\infty} + 2\varepsilon_{\infty} \right) \omega^2 + \left( \varepsilon_{\infty} + 2\varepsilon_{\infty} \right) \gamma^2 \omega^2} \]  

(48)

At the localized plasma resonance of a metallic spherical nanoparticle $\omega = \omega_p$ with

$$
\varepsilon_{\infty} + 2\varepsilon_{\infty} \omega_p^2 = \omega_p^2,
$$

(49)

we have

$$
\text{Re } L(\omega_p) = \frac{\varepsilon_{\infty} - \varepsilon_{\infty}}{\varepsilon_{\infty} + 2\varepsilon_{\infty}},
$$

(50)

$$
\text{Im } L(\omega_p) = \frac{3\varepsilon_{\infty} \omega_p}{\varepsilon_{\infty} + 2\varepsilon_{\infty} \gamma}.
$$

(51)

Since $\gamma \ll \omega_p$, $\text{Im } L(\omega_p) \gg 1$, the enhancement effect is significant at the localized plasmon resonance frequency $\omega_p$.

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### Table 1. Photon energy dependent values of the permittivity of gold and of $L(\omega)$.

| Energy (eV) | Wavelength (nm) | $\varepsilon_1$ | $\varepsilon_2$ | $L_1$ | $L_2$ |
|------------|-----------------|-----------------|----------------|------|------|
| 0.64       | 1937.50         | -189.042        | 25.355         | 1.108| 0.015|
| 0.77       | 1610.39         | -125.351        | 12.555         | 1.170| 0.019|
| 0.89       | 1393.26         | -90.426         | 8.186          | 1.247| 0.026|
| 1.02       | 1215.69         | -66.129         | 5.702          | 1.359| 0.038|
| 1.14       | 1087.72         | -51.050         | 3.861          | 1.502| 0.051|
| 1.26       | 984.13          | -40.274         | 2.794          | 1.700| 0.071|
| 1.39       | 892.09          | -32.041         | 1.925          | 2.001| 0.101|
| 1.51       | 821.19          | -25.811         | 1.627          | 2.476| 0.186|
| 1.64       | 756.10          | -20.610         | 1.272          | 3.445| 0.403|
| 1.76       | 704.55          | -16.818         | 1.067          | 5.603| 1.254|
| 1.88       | 659.57          | -13.648         | 1.035          | 9.865| 12.317|
| 2.01       | 616.92          | -10.662         | 1.374          | -5.276| 3.848|
| 2.13       | 582.16          | -8.113          | 1.661          | -2.607| 1.250|
| 2.26       | 548.67          | -5.842          | 2.111          | -1.526| 0.752|
| 2.38       | 521.01          | -3.946          | 2.580          | -0.995| 0.575|
| 2.50       | 496.00          | -2.278          | 3.813          | -0.614| 0.579|
| 2.63       | 471.48          | -1.703          | 4.844          | -0.456| 0.630|
| 2.75       | 450.91          | -1.759          | 5.283          | -0.418| 0.672|
| 2.88       | 430.56          | -1.692          | 5.649          | -0.377| 0.694|
| 3.00       | 413.33          | -1.702          | 5.717          | -0.371| 0.700|
| 3.12       | 397.44          | -1.649          | 5.739          | -0.365| 0.696|
| 3.25       | 381.54          | -1.605          | 5.644          | -0.371| 0.685|
| 3.37       | 367.95          | -1.401          | 5.609          | -0.359| 0.663|
| 3.50       | 354.29          | -1.232          | 5.598          | -0.348| 0.647|
| 3.62       | 342.54          | -1.310          | 5.538          | -0.359| 0.649|
| 3.74       | 331.55          | -1.355          | 5.574          | -0.359| 0.656|
| 3.87       | 320.41          | -1.231          | 5.846          | -0.326| 0.664|
| 3.99       | 310.78          | -1.243          | 5.793          | -0.331| 0.661|
Appendix

The optical constants $n$ (index of refraction) and $k$ (the absorption coefficient) of gold were experimentally measured by Johnson and Christy [27]. From the values of the photon energy dependent physical parameters $n(\omega)$ and $k(\omega)$ we can obtain immediately the real and imaginary parts $\varepsilon_1(\omega) = n(\omega)^2 - k(\omega)^2$ and $\varepsilon_2(\omega) = 2n(\omega)k(\omega)$ of the electric permittivity of gold and subsequently to calculate the real and imaginary parts $L_1(\omega)$ and $L_2(\omega)$ of the function $L(\omega)$ defined by formula (6) with the value $\varepsilon_m = 6.45$ of the dielectric constant of titania. The results are presented in table 1.

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