

## Self-Similar Chain of Metal Nanospheres as an Efficient Nanolens

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As an efficient nanolens, we propose a self-similar linear chain of several metal nanospheres with progressively decreasing sizes and separations. To describe such systems, we develop the multipole spectral expansion method. Optically excited, such a nanolens develops the nanofocus (“hottest spot”) in the gap between the smallest nanospheres, where the local fields are enhanced by orders of magnitude due to the multiplicative, cascade effect of its geometry and high  $Q$  factor of the surface plasmon resonance. The spectral maximum of the enhancement is in the near-ultraviolet region, shifting toward the red region as the separation between the spheres decreases. The proposed system can be used for nano-optical detection, Raman characterization, nonlinear spectroscopy, nanomanipulation of single molecules or nanoparticles, and other applications.

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There has recently been great interest in the optical properties of metallic nanoparticles and their aggregates. Such nanoparticles induce giant local optical fields that greatly exceed the exciting fields. Among the most remarkable effects associated with such local fields is giant Raman scattering that allowed for the detection and spectroscopy of single molecules on colloidal metal fractal clusters [1,2]. The observed enhancement of Raman scattering with respect to an isolated molecule was  $\geq 10^{12}$ , while the average enhancement for silver fractal clusters was predicted and observed to be  $\leq 10^6$  [3,4]. That means that there are especially effective Raman sites that produce such colossal enhancements. Because the Raman enhancement is proportional to the fourth power of the local field, the latter should exceed the excitation field by a factor of  $g \geq 10^3$  in the Raman active centers of Refs. [1,2]. A single silver nanosphere provides much smaller field enhancement,  $g \leq 30$ . Hence, the active site of the giant Raman scattering must be a collective of many, or at least several, nanoparticles. It was shown that the enhanced Raman scattering originates from the gaps between metal nanocrystals [5], similar to what we find below for nanolenses.

The present Letter theoretically introduces self-similar systems built of a few silver nanospheres as nanolenses that, in a controllable way, create the “hottest spots” of local fields with  $g \geq 10^3$ , which are promising, in particular, as the giant Raman scattering active sites. The spectral maximum of the enhancement can be tuned; for the systems considered in this Letter it is in the near ultraviolet (uv) region in contrast to the conventional surface enhanced Raman scattering (SERS) where it is in the red region [3]. The maximum enhancement of the local fields originates at the minimum scale and is very sensitive to the structure of the system at this scale. Hence, no universal theory based on the description of the system on the intermediate scale, in particular, fractal

or percolation models, can possibly describe the colossal enhancement of Raman scattering.

To introduce our idea, consider a finite chain of metal nanospheres where for an  $i$ th nanosphere the radius is  $R_i$  and its surface-to-surface separation from the  $(i+1)$ th nanosphere is  $d_{i,i+1}$ . We assume self-similarity, i.e.,  $R_{i+1} = \kappa R_i$  and  $d_{i+1,i+2} = \kappa d_{i,i+1}$ , where  $\kappa = \text{const}$ ; see a schematic in the inset of Fig. 1(a). Consider  $\kappa \ll 1$ , so the local field of a given nanoparticle is only weakly perturbed by the next one. The local field in the proximity of the biggest nanosphere is enhanced with respect to exciting field  $E_0$  by the resonance quality factor,  $Q \sim \text{Re}\varepsilon(\omega)/\text{Im}\varepsilon(\omega)$ , where  $\varepsilon(\omega)$  is the relative dielectric function of the spheres’ metal, and  $\omega$  is the light frequency. Note that  $Q \gg 1$  for a good metal, which is assumed. This local field is uniform on the scale of that next smaller nanosphere and plays the role of the exciting field for it. Thus, in the proximity of the second nanosphere, the local field is enhanced by the factor of  $Q^2$ . Continuing this chain, at the  $n$ th nanosphere, the local field is estimated as  $Q^n E_0 \gg E_0$ . For example, for a realistic value of  $Q = 10$  and  $n = 3$  nanospheres, we obtain a very large local field at the smallest nanosphere  $\sim 10^3$ , corresponding to Raman scattering enhancement by a factor of  $10^{12}$ . Note that the enhancement of such an  $n$ -nanosphere cascade nanolens,  $g_n = E_n/E_0$ , can easily be expressed as  $g_n \sim Q(R_n/R_1)^{\ln Q/\ln \kappa}$ .

The reality is more complex than this estimate in two respects. First, the high enhancements are obtained for  $\kappa$  not very small, when the smaller nanospheres may considerably perturb the local fields of the bigger ones. Second, the smallest nanosphere, where one expects the highest local fields, is not in the self-similar intermediate part of the system, which requires special consideration.

For analytical theory and numerical computations to describe realistic systems, we develop a multipole spectral expansion (MSE) method that is based on the spectral

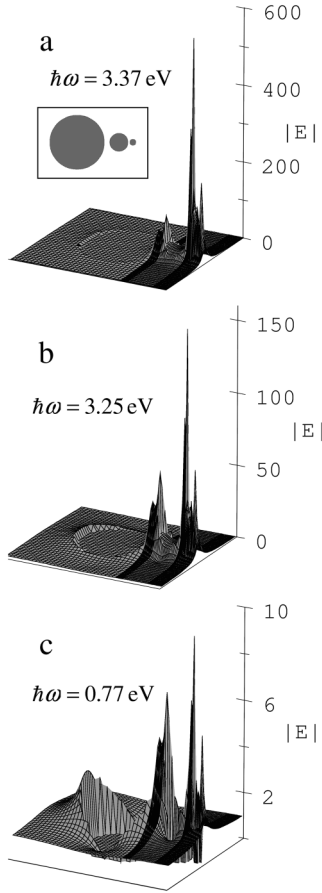


FIG. 1. Local fields (absolute value relative to that of the excitation field) in the equatorial plane of symmetry for the linear self-similar chain of three silver nanospheres. The ratio of the consecutive radii is  $\kappa = R_{i+1}/R_i = 1/3$ ; the distance between the surfaces of the consecutive nanospheres  $d_{i,i+1} = 0.6R_{i+1}$ . Inset: the geometry of the system in the cross section through the equatorial plane of symmetry.

method [6] in the differential form [7]. We assume that the total size of the system is much less than light wavelength  $\lambda$  and employ the quasistatic approximation.

The eigenmodes (surface plasmons) satisfy the generalized differential equation eigenproblem [7]:

$$\nabla \cdot [\Theta(\mathbf{r})\nabla\phi_\alpha(\mathbf{r})] = s_\alpha\nabla^2\phi_\alpha(\mathbf{r}), \quad (1)$$

with zero-field boundary conditions at infinity, where  $\phi_\alpha(\mathbf{r})$  and  $s_\alpha$  are the eigenfunctions and eigenvalues, and  $\Theta(\mathbf{r})$  is the characteristic function that is equal to 1 inside the metal particles and 0 elsewhere. The eigenmodes are orthogonal and are assumed to be normalized as  $-\int\phi_\alpha^*(\mathbf{r})\nabla^2\phi_{\alpha'}(\mathbf{r})d^3r = \delta_{\alpha,\alpha'}$ .

We seek the eigenmodes as an expansion over spherical harmonics, where inside a  $j$ th nanosphere

$$\phi_\alpha(\mathbf{r}) = \sum_{l,m} a_{lm}^j[\alpha] r_j^l Y_{lm}(\theta_j, \varphi_j), \quad (2)$$

and in the host (outside of the metal nanospheres)

$$\phi_\alpha(\mathbf{r}) = \sum_{j,l,m} b_{lm}^j[\alpha] \frac{1}{r_j^{l+1}} Y_{lm}(\theta_j, \varphi_j). \quad (3)$$

Here,  $r_j$ ,  $\theta_j$ , and  $\varphi_j$  are the spherical coordinates relative to the center of the  $j$ th nanosphere. To determine the coefficients  $a_{lm}^j[\alpha]$ ,  $b_{lm}^j[\alpha]$ , we use the boundary condition at the surface of each sphere and the well-known coefficients  $O_{lm,l'm'}(jk)$  that describe the reexpansion of the  $lm$ -multipole fields of a  $j$ th nanosphere over  $l'm'$  multipoles about the center of a  $k$ th nanosphere [8].

Using Eqs. (2) and (3), we find that Eq. (1) is equivalent to the generalized matrix eigenproblem,

$$(A - s_\alpha B)|\Phi_\alpha\rangle = 0, \quad (4)$$

where the eigenvectors  $|\Phi_\alpha\rangle$  are related to the surface plasmons through the coefficients of Eqs. (2) and (3) as

$$\langle j, l, m | \Phi_\alpha \rangle = \frac{2l+1}{R_j^l} b_{lm}^j[\alpha] = \frac{lR_j^{l+1}}{s_\alpha} a_{lm}^j[\alpha], \quad (5)$$

and matrices  $A$  and  $B$  are defined by their elements

$$\begin{aligned} \langle j, l, m | A | k, l', m' \rangle &= \frac{\delta_{l,l'} \delta_{m,m'} \delta_{j,k}}{(2l+1)R_j} \\ &+ \frac{(1 - \delta_{j,k})R_j^l R_k^{l'}}{R_{jk}^{l+l'+1}} O_{lm,l'm'}(jk), \end{aligned} \quad (6)$$

$$\langle j, l, m | B | k, l', m' \rangle = \frac{\delta_{l,l'} \delta_{m,m'} \delta_{j,k}}{R_j^l}. \quad (7)$$

We have numerically solved the generalized algebraic eigenproblem of Eq. (4) to find the retarded Green's function as a spectral expansion in the coordinate-frequency domain [9]:

$$G^r(\mathbf{r}, \mathbf{r}'; \omega) = \sum_{\alpha} \phi_\alpha(\mathbf{r}) \phi_\alpha^*(\mathbf{r}') s_\alpha / [s(\omega) - s_\alpha], \quad (8)$$

where  $s(\omega) = 1/[1 - \varepsilon(\omega)]$  is the spectral parameter [6]. The optical electric potential amplitude,  $\varphi(\mathbf{r})$ , is expressed in terms of this Green function and the external (excitation) potential,  $\varphi_0(\mathbf{r})$ , as

$$\varphi(\mathbf{r}) = \varphi_0(\mathbf{r}) - \int \varphi_0(\mathbf{r}') \frac{\partial^2}{\partial \mathbf{r}'^2} G^r(\mathbf{r}, \mathbf{r}'; \omega) d^3 r'. \quad (9)$$

Based on Eq. (9), we have carried out numerical computations for silver nanosphere chains with  $\varphi_0(\mathbf{r}) = -zE_0$ , where  $E_0 = 1$ , and the  $z$  axis is along the chain axis, for  $\omega$  from near infrared (ir) to near uv using the original interpolated optical data for silver of Ref. [10]. We truncate  $l \leq l_{\max} = 4R_j/d_{j,j+1}$ . Increasing  $l_{\max}$ , we have checked that the numerical error associated with such a truncation is negligible.

The local electric fields,  $\mathbf{E} = -\nabla\varphi$ , in the equatorial plane of the nanosphere chain for three particles are shown in Fig. 1, where  $R_{i+1} = \frac{1}{3}R_i$  and  $d_{i,i+1} = 0.6R_{i+1}$ . Though the theory depends only on the ratio of radii and

distances but not on their absolute scale, the sphere radii are limited by the applicability of the quasistatic dielectric susceptibility approximation,  $\lambda \gg R \gtrsim l \sim 5$  nm, where  $l$  is the electron mean free path estimated for light frequencies  $\hbar\omega$  under consideration. For instance, possible values of radii are  $R_1 = 45$  nm,  $R_2 = 15$  nm, and  $R_3 = 5$  nm. In Fig. 1, there is the cascade, multiplicative enhancement of the local fields from larger to smaller nanospheres. The hottest spot (nanofocus), where the local field is enhanced by a factor  $g = 580$ , is at  $\hbar\omega = 3.37$  eV ( $\lambda = 369$  nm in vacuum) [Fig. 1(a)] (cf. the surface plasmon frequency of an isolated nanosphere is at  $\hbar\omega_0 \approx 3.5$  eV). It is located *between* the smallest nanospheres and not at the geometric apex of the system (outside the chain at the smallest nanosphere) as one might expect intuitively. The maximum of fields between identical nanospheres (field “squeezing”) was found earlier [11]. The dependence on  $\omega$  is very sharp [cf. 1(b)], though some enhancement persists in the near ir region [1(c)]. The estimate  $g_n \sim Q(R_n/R_1)^{\ln Q/\ln \kappa}$  gives  $g_n \sim 300 - 10^3$  for  $\hbar\omega = 3.5 - 3.4$  eV, in a qualitative agreement with  $g$  calculated above.

The effect of decreased spacing between particles is illustrated in Fig. 2 for distance  $d_{i,i+1} = 0.3R_{i+1}$ . In the

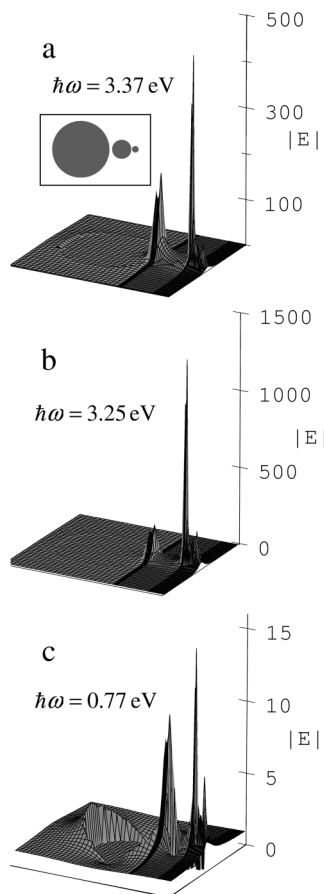


FIG. 2. Same as in Fig. 1, but for the distance between the sphere surfaces  $d_{i,i+1} = 0.3R_{i+1}$ .

hottest spot, the maximum enhancement  $g = 1300$  is twice larger and is redshifted in frequency to  $\hbar\omega = 3.25$  eV ( $\lambda = 382$  nm).

We have also studied centrally symmetric chains, one of them of five nanospheres is illustrated in Fig. 3 for  $d_{i,i+1} = 0.6R_{i+1}$ . In this case, the nanofocus (hottest spot) stays in the spaces between the smallest and the next nanospheres, and the maximum field is enhanced by a factor of  $g = 1023$ , i.e., about twice stronger with respect to the corresponding asymmetric system (Fig. 1).

The local fields for the symmetric nanolens of six particles are displayed in Fig. 4 for  $d_{i,i+1} = 0.6R_{i+1}$ . The nanofocus (the hottest spot) of the local field occurs at the center of symmetry, for  $\hbar\omega = 3.25$ , where the field enhancement  $g = 2500$ . At this site, the expected Raman enhancement is extremely high  $\sim g_n^4 = 4 \times 10^{13}$ .

Let us briefly discuss the results obtained. We have shown that a self-similar chain of a few nanospheres functions as a nanolens concentrating optical energy in

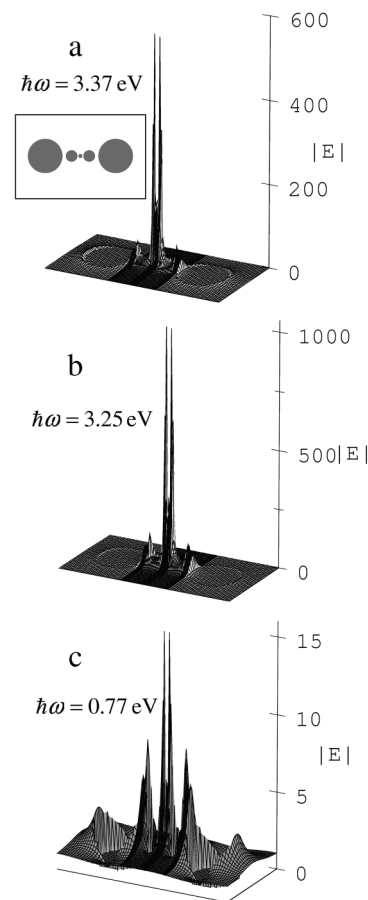


FIG. 3. Local fields (absolute value relative to that of the excitation field) in the cross section through the equatorial plane of symmetry for the linear center-symmetric self-similar chain of five silver nanospheres. The ratio of the consecutive radii is  $\kappa = R_{i+1}/R_i = 1/3$ ; the distance between the surfaces of the consecutive nanospheres  $d_{i,i+1} = 0.6R_{i+1}$ . Inset: the geometry of the system in the cross section through the equatorial plane of symmetry.

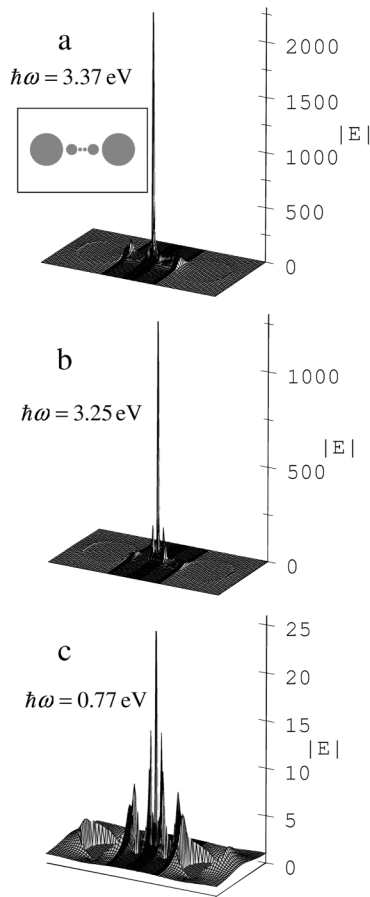


FIG. 4. Same as in Fig. 3, but for the symmetric chain of six nanospheres.

the hottest spot (nanofocus) in the gap between the smallest nanospheres, where the local fields are greatly, by a factor  $g \geq 10^3$ , enhanced. The giant magnitude of this enhancement is due to both the high quality factor of the surface plasmon resonance and to multiplicative, multi-stage enhancement in these nanolenses. The corresponding enhancement of Raman scattering for a molecule located at the nanofocus is  $\sim g^4 \sim 10^{12} - 10^{13}$ , i.e., is on the order of the record enhancements observed for fractal metal clusters [1,2]. The spectral maximum of enhancement is in the near uv region, shifting toward the red region as the distance between nanosphere surfaces decreases. The cascade structure of a nanolens consisting of separate nanospheres is important since if the spheres were in contact, the potential difference between them would decrease, causing the corresponding reduction of local fields. The *maximum* local field depends on the specific structure on the *minimum* scale that cannot be described in any generic model such as fractal or percolation. At the same time, the properties of the system do not depend on the absolute size scale of the nanostructures, as long as we are in the quasistatic regime. Note that analogous nanolenses can also be built of nanoparticles other than nanospheres. The exact self-similarity is not critical for obtaining the large enhancements; e.g.,

keeping  $d_{i,i+1} = 0.6R_{i+1}$  and  $\hbar\omega = 3.37$  eV, a three-nanosphere system with  $R_1:R_2:R_3 = 45:22:5$  yields approximately the same maximum field as in Fig. 1(a), while another such system with  $R_1:R_2:R_3 = 45:10:5$  yields the peak field approximately 2 times smaller.

The proposed nanolenses can be used for a wide range of applications, in particular, for detection and Raman spectroscopy of single molecules or nanoparticles. Similar to single-molecule SERS [1,2], the “hottest” active site is between the nanospheres where the molecules can bind spontaneously, be delivered by nanofluidic nanotubes, or be bound by strong optical fields (“optical nanotweezers” effect). There is also a smaller but still significant local field enhancement at the apex of the nanolens [cf. Fig. 1(a)], which can be used for local nano-optical scanning. These nanolenses can be used as terminators for a variety of nanophotonic devices, such as photonic-crystal waveguides to produce extremely high local fields. They can also be used for nanomanipulation and nanomodification of molecules and nanoparticles.

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