Superenhanced backscattering of light by nanoparticles

Zhigang Chen and Allen Taflove

Department of Electrical and Computer Engineering, Northwestern University, Evanston, Illinois 60208

Xu Li and Vadim Backman

Department of Biomedical Engineering, Northwestern University, Evanston, Illinois 60208

Received August 9, 2005; revised September 7, 2005; accepted September 18, 2005

We report a physical explanation for the phenomenon wherein the backscattering of light by dielectric particles of sizes between 100 and 1 nm is enhanced by 7–11 orders of magnitude. The phenomenon involves complex composite interactions between a dielectric microsphere and a nanoparticle positioned in close proximity to the microsphere. We provide both analytical and perturbation analyses that show that the enhanced backscattering intensity of a nanoparticle is proportional to the third power of its size parameter. Potential applications of this phenomenon include visible-light detection, characterization, and manipulation of particles as small as a few nanometers. © 2006 Optical Society of America

OCIS codes: 290.1350, 290.5850, 290.5870, 170.0170.

During the past decade there has been considerable interest in developing optical biosensing systems that have the capability to detect single molecules and single nanoparticles.[1–3] This interest has arisen from applications in various disciplines such as biotechnology, molecular biology, analytical chemistry, and nanostructured materials. Before a technique based on surface-enhanced Raman scattering was reported by Nie and Emory,[1] methods for probing single molecules included laser-induced fluorescence with near-field, far-field, and evanescent-wave excitation, frequency-modulated optical absorption,[4] and electrochemical detection of redox-active species.[5]

In this Letter we report a physical explanation of the phenomenon wherein backscattering of light by dielectric particles of sizes between 100 and 1 nm is enhanced by 7–11 orders of magnitude. The phenomenon involves complex mutual interactions of a dielectric microsphere and a nanoparticle positioned in close proximity to the microsphere. We provide both analytical and perturbation analyses that show that the enhanced backscattering intensity of the nanoparticle is proportional to the third power of its size parameter $x=\pi d/\lambda$, where d is a characteristic dimension of the particle and λ is the illuminating wavelength. This is a fundamental dimensional increase relative to the Rayleigh backscattering intensity, which is proportional to the sixth power of the size parameter of the nanoparticle. The giant scattering enhancement reported in this Letter stems from a photonic nanojet of strong localized optical fields induced by a properly chosen dielectric microcylinder or microsphere.[6,7] To a certain degree, an analogy could be drawn between the phenomenon of nanojet-enhanced elastic light scattering discussed in this Letter and surface-enhanced Raman scattering.[8] Both phenomena involve a giant scattering enhancement due to large local fields and complex composite interactions between two closely spaced structures.

A typical nanojet is shown in Fig. 1, which shows the electric field intensity distribution of a plane-wave-illuminated ($\lambda=300$ nm) microsphere of radius $r=3$ μm and refractive index $m=1.73$ located in free space. Here the calculation of the nanojet is conducted by using the Mie theory. We observe how the backscattering intensity of the microsphere is perturbed if a nanosphere is introduced into the nanojet.

To develop quantitative data, we apply the generalized multiparticle Mie (GMM) theory.[9] In the GMM theory, the interactive scattering coefficients for a microsphere coupled with a nanosphere are given by[9]

$$a_{mn}^{M}=a_{n}^{M}\left[p_{mn}^{M}-\sum_{\nu=1}^{\infty}\sum_{\mu=-\nu}^{\nu}(a_{\mu\nu}^{N}A_{mn}^{\mu\nu}+b_{\mu\nu}^{N}B_{mn}^{\mu\nu})\right], \qquad (1a)$$

$$b_{mn}^{M}=b_{n}^{M}\left[q_{mn}^{M}-\sum_{\nu=1}^{\infty}\sum_{\mu=-\nu}^{\nu}(a_{\mu\nu}^{N}B_{mn}^{\mu\nu}+b_{\mu\nu}^{N}A_{mn}^{\mu\nu})\right], \qquad (1b)$$

where the superscripts M and N denote the microsphere and nanosphere, respectively, a_{n}^{M} and b_{n}^{M} are the Mie scattering coefficients, p_{mn}^{M} and q_{mn}^{M} are the expansion coefficients of the incident wave, $a_{\mu\nu}^{N}$ and $b_{\mu\nu}^{N}$ are the interactive scattering coefficients for the nanosphere, and $A_{mn}^{\mu\nu}$ and $B_{mn}^{\mu\nu}$ are the vector transla-

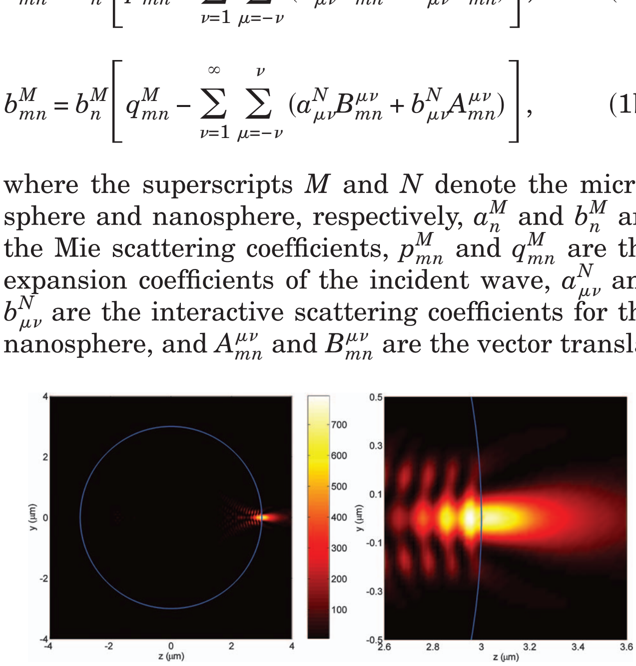

Fig. 1. Photonic nanojet emerging at the shadow-side surface (blue circle) of a dielectric microsphere. The electric field intensity (normalized to the incident intensity) is visualized on the meridian plane.

0146-9592/06/020196-3/$15.00

tion coefficients characterizing the transformation of the scattered waves from the nanosphere into the incident waves of the microsphere. The interactive scattering coefficients a_{mn}^N and b_{mn}^N for a nanosphere coupled with a microsphere have a form similar to a_{mn}^M and b_{mn}^M. The total scattering coefficients for the bisphere system are given by $a_{mn}=a_{mn}^M+a_{mn}^N\exp(-ikd\cos\theta)$ and $b_{mn}=b_{mn}^M+b_{mn}^N\exp(-ikd\times\cos\theta)$, where k is the wavenumber, d is the center-to-center distance between the two spheres, and θ is the scattering angle. Once the total scattering coefficients are known, the scattering amplitudes $S_1(\theta)$ and $S_2(\theta)$ can be calculated. In the backward direction, the dimensionless backscattering intensity of the bisphere system is given by $|S(180°)|^2=|S_1(180°)|^2=|-S_2(180°)|^2$.

Using the GMM theory, we first calculate the backscattering intensity $|S|^2$ of the bisphere system, where a nanosphere of $m=1.1$ is located in the nanojet of Fig. 1. The surface-to-surface distance between the two spheres is 25 nm. We also calculate the backscattering intensity for the isolated microsphere, denoted $|S^M|^2$. The perturbation in the backscattering intensity of the microsphere introduced by the nanosphere is given by $\delta|S^M|^2=||S|^2-|S^M|^2|$, which represents the enhanced backscattering intensity of the nanosphere due to its interaction with the microsphere. Figure 2(a) compares the enhanced backscattering intensity $\delta|S^M|^2$ (solid line) with the Rayleigh backscattering intensity of the isolated nanosphere, $|S^N|^2$ (dashed line), as a function of the size parameter of the nanosphere. Figure 2(a) also shows the lens focusing effect of the microsphere (dashed–dotted line), i.e., due to the illumination of the nanosphere by the high-intensity nanojet. Figure 2(b) graphs the ratio $\delta|S^M|^2/|S^N|^2$, i.e., the backscattering enhancement factor (solid line). Note that log–log scales are used.

Three striking features are observed in Fig. 2. First, the enhanced backscattering intensity of the nanosphere is 7–11 orders of magnitude higher than its Rayleigh scattering intensity. Second, the lens focusing effect of the microsphere can account for at most 3 orders of magnitude of this enhancement. Third, the superenhanced backscattering intensity is proportional to a lower power of the size parameter of the nanosphere compared with the Rayleigh scattering intensity.

Since the lens focusing effect of the microsphere by itself cannot account for the superenhanced backscattering, additional physical mechanisms are necessary to completely explain the phenomenon. To identify these mechanisms, we conduct a perturbation analysis based on the GMM theory. The perturbations δa_{mn}^M and δb_{mn}^M in the scattering coefficients of the microsphere that are due to the presence of the nanosphere are given by the second terms in Eq. (1). In the expressions of δa_{mn}^M and δb_{mn}^M, $a_{\mu\nu}^N$ and $b_{\mu\nu}^N$ are the interactive scattering coefficients for the nanosphere characterizing the scattering of both the original incident waves and the secondary waves scattered by the microsphere. Our calculations show that the internal intensity distribution of the nanojet-illuminated nanosphere is elevated by a factor of about 800 relative to that resulting from plane-wave illumination. Based on its internal electric field distribution, the far-field scattering intensity of the nanojet-illuminated nanosphere can be calculated, and it represents the lens focusing effect of the microsphere, as previously seen in Fig. 2 (dashed–dotted line). Therefore the interactive scattering coefficients of the nanosphere coupled with the microsphere can be written as

$$a_{mn}^N \approx (\tilde{I}_{\mathrm{jet}}/I_0)^{1/2} a_n^N p_{mn}^N, \qquad b_{mn}^N \approx (\tilde{I}_{\mathrm{jet}}/I_0)^{1/2} b_n^M q_{mn}^M, \tag{2}$$

where $\tilde{I}_{\mathrm{jet}}$ is the intensity of the nanojet averaged over the transverse cross section of the nanosphere, I_0 is the intensity of the original incident wave, and a_n^N and b_n^N are the Mie scattering coefficients. In the Rayleigh scattering limit of $|m|x \ll 1$, the higher-order Mie scattering coefficients in Eq. (2) involving terms of order x^5 and higher are negligible. As a result, δa_{mn}^M and δb_{mn}^M can be simplified considerably:

$$\delta a_{mn}^M = -a_n^M (\tilde{I}_{\mathrm{jet}}/I_0)^{1/2} a_1^N \sum_{\mu=-1}^{1} p_{\mu 1}^N A_{mn}^{\mu 1}, \tag{3a}$$

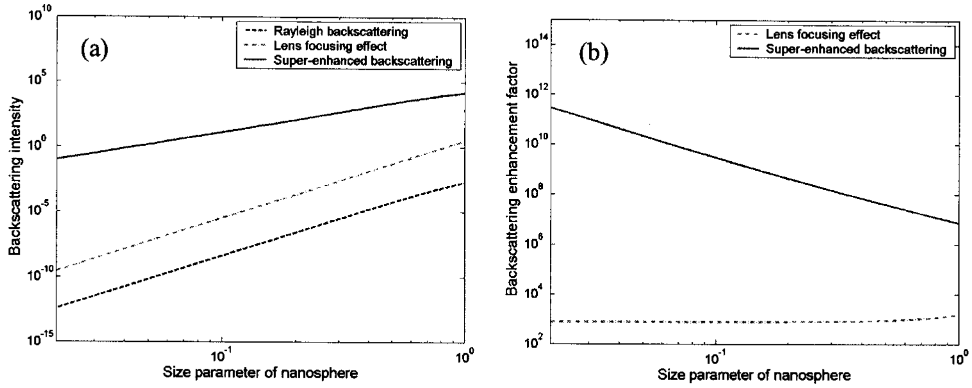

Fig. 2. (a) Comparison of the superenhanced backscattering intensity of a nanosphere (solid line) with the lens focusing effect of the microsphere (dashed–dotted line) and the Rayleigh scattering intensity (dashed line) as a function of the size parameter. (b) The backscattering enhancement factor. Logarithmic scales are used in both (a) and (b).

$$\delta b_{mn}^{M} = -b_{n}^{M}(\tilde{I}_{\text{jet}}/I_0)^{1/2} a_1^{N} \sum_{\mu=-1}^{1} p_{\mu 1}^{N} B_{mn}^{\mu 1}, \tag{3b}$$

where a_1^N is the Rayleigh scattering coefficient of an isolated nanosphere. The physical meaning of Eqs. (3) is as follows: 1, a_1^N represents the Rayleigh scattering; 2, $(\tilde{I}_{\text{jet}}/I_0)^{1/2}\, a_1^N$ embodies enhanced scattering from the nanosphere that is due to the lens focusing effect of the microsphere; 3, the enhanced scattered fields from the nanosphere that are due to the lens focusing effect are transformed into the incident fields of the microsphere, and this transformation is accounted for by $A_{mn}^{\mu 1}$ and $B_{mn}^{\mu 1}$; and, 4, the transformed scattered fields from the nanosphere are scattered again and collected by the microsphere in the backward direction, which is described by a_n^M and b_n^M.

On the basis of Eqs. (3), we now analyze the perturbation in the backscattering intensity of the microsphere introduced by a nanosphere located in the nanojet. The backscattering intensity of the bisphere system can be written as

$$|S(180\,°)|^2 = |S^M|^2 + \delta|S^M|^2. \tag{4}$$

Substituting Eq. (3) into $\delta|S^M|^2$ in Eq. (4) and neglecting higher-order terms involving products of δa_{mn}^M and δb_{mn}^M yield

$$\delta|S^M|^2 \approx (2/3)[(m^2-1)/(m^2+2)](\tilde{I}_{\text{jet}}/I_0)^{1/2} F^M(kd)x^3, \tag{5}$$

where x is the size parameter of a nanosphere and F^M is a function of kd for a given microsphere. For a nanosphere in the Rayleigh limit, F^M is approximately a constant for fixed wavelength and surface-to-surface distance between the two spheres. As a result, $\delta|S^M|^2$ is approximately proportional to the third power of the size parameter of the nanosphere. For the microsphere we consider in this Letter, F^M has an order of magnitude 10^4.

Figure 3 compares $\delta|S^M|^2$ calculated by using relation (5) with that calculated by using the GMM theory. We see very good agreement of the exact analytical results and the perturbation analysis for nanospheres having a size parameter less than 0.8. In this range, this agreement confirms that the superenhanced backscattering intensity is proportional to the third power of the size parameter of the nanosphere. For nanospheres having a size parameter greater than 0.8, the exact results and the perturbation analysis deviate. This is expected, since the derivation of relation (5) is based on the Rayleigh scattering coefficient.

In conclusion, we have provided a theoretical basis for the phenomenon of superenhanced backscattering of light by nanoparticles. We show that the enhanced backscattering intensity of the nanoparticle is proportional to the third power of its size parameter. The effective backscattering of the nearby nanosphere is superenhanced by the complex mutual interactions between the nanosphere and the microsphere. The nanosphere is first excited by the nanojet emerging from the microsphere, and its scattering intensity is elevated by 2 orders of magnitude, as determined by the intensity of the nanojet. The fields reradiated by the nanojet-excited nanoparticle interact with the normal electromagnetic modes of the microsphere. This interaction acts to modify the scattering properties of the nanoparticle in such a way as to elevate its backscattered intensity by 4–9 additional orders of magnitude. Using quantum electrodynamic terms to describe nanojet-enhanced backscattering, the microsphere acts to modify the density of radiation states of the adjacent nanoparticle in such a way as to enhance its backscattering. We believe that the nanojet enhancement phenomenon provides potential applications in visible-light ultramicroscopy, wherein nanoparticles consisting of as few as several hundred atoms could be detected and characterized.

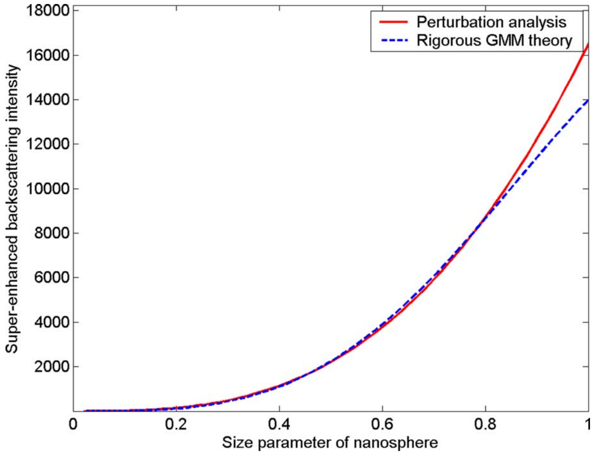

Fig. 3. (Color online) Comparison of the superenhanced backscattering intensity of a nanosphere calculated by using a perturbation analysis with that calculated by using the GMM theory, as a function of the size parameter.

This work was supported by National Science Foundation grant BES-0238903 and National Institutes of Health grant R01 EB003682. We thank Y.-L. Xu for making publicly available his FORTRAN codes for multiparticle light-scattering calculations. Z. Chen's e-mail address is z-chen@northwestern.edu.

References

1. S. Nie and S. R. Emory, Science **275**, 1102 (1997).
2. G. Wu, R. H. Datar, K. M. Hansen, T. Thundat, R. J. Cote, and A. Majumdar, Nat. Biotechnol. **19**, 856 (2001).
3. B. Schmidt, V. Almeida, C. Manolatou, S. Preble, and M. Lipson, Appl. Phys. Lett. **85**, 4854 (2004).
4. W. E. Moerner, Science **265**, 46 (1994).
5. F.-R. F. Fan and A. J. Bard, Science **267**, 871 (1995).
6. Z. Chen, A. Taflove, and V. Backman, Opt. Express **12**, 1214 (2004).
7. X. Li, Z. Chen, A. Taflove, and V. Backman, Opt. Express **13**, 526 (2005).
8. R. K. Chang and T. E. Furtak, *Surface Enhanced Raman Scattering* (Plenum, 1982).
9. Y.-L. Xu, Appl. Opt. **34**, 4573 (1995).