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Multilayered Nanoparticles for Maximized Forward Light Scattering

Rongheng Li, Ben Q. Li and W. Shi
Department of Mechanical Engineering, University of Michigan, Dearborn, MI 48128, United States
E-mail: benqli@umich.edu

***Abstract*-Computational electromagnetics modeling is presented for the design of multilayered nanoparticles for maximized forward light scattering. The design computation makes use of a recursive solution algorithm for multiscattering of light waves by multilayered core-shell nanoparticle aggregates. The algorithm is based on the analytical solution of Maxwell equations using the multipole-expansion method coupled with the translational addition and the Wigner-Eckart quantum projection theorems. Calculations are carried out to design the core-shell structured nanoparticles for maximized forward scattering. The nanostructured particles so designed are further tested by FDTD simulations for light scattering into a flat Si substrate. Computed data show that the designed multilayered particles with maximized forward scattering allows more incident light to be absorbed in the substrate than other good light scatters.**

I. Introduction

The nanoparticles, such as Ag spheres, SiO_2 spheres and Si nanoshells, possess large scattering cross sections, which lead to their applications in solar cells [1], light-emitting diodes [2] and biomedical sensing [3]. Other nanostructures, such as month-eye [4], nanopillars [5] and nanocone [6], have also been exploited for the enhancement of light absorption in substrates. Considerable literature, both theoretical and experimental, has been devoted to the study of these nanostructures in order to gain a better understanding of light-particle interaction and to develop devices with better photoelectric efficiencies. Kumar *et al.* [7] placed Au nanoparticles onto organic photovoltaic, and significant enhancement of light absorption was observed. Qu *et al.* [8] presented metal-dielectric core-shell nanoparticles in the active layer of thin film organic solar cells, leading to the light absorption improvement of up to 110%, which is superior to the bare metal particle. The separation of the metal core and the active layer by the dielectric shell restraints the metal to be the recombination center. Grandidier *et al.* [9] presented a periodic silica nanosphere array on the top of a thin-film amorphous silicon solar cell, which couples the light into whisper-gallery modes, and resulted in a significant increase of the photoelectric conversion efficiency. It is noteworthy that absorption loss can be avoided in these lossless dielectric structures. Yao *et al.* [10] reported a solar cell consisting of a thin Si spherical nanoshells layer, which also generates whisper-gallery modes, and produces a light absorption efficiency equivalent to that of thick monocrystalline silicon film. In addition, the absorption wavelength band is broadened in the structures.

The electromagnetic mechanism for these applications can be explained by the Mie solution of the Maxwell equations [11]. Detailed analysis of the Mie solution suggests that the radiation from these nanospheres comes mainly from the electric dipole and/or the magnetic dipole. The scattering pattern of the electric or magnetic dipole is symmetric about the sphere, which means the energy is equally scattered in the forward direction and the backward direction. By introducing the multilayered structure with a different material in each layer, a nanoparticle may be tuned such that electric and magnetic dipoles emit an equal amount of radiation, a condition known as the first Kerker's condition [12]. The condition may be satisfied by tuning the structural parameters of a composite nanoparticle such that electromagnetic waves produced by the electric and magnetic dipoles interfere constructively in the forward direction and destructively in the backward direction, thereby resulting in forward scattering being maximized while backward scattering being minimized. Moreover, it is known that nanoshell structures are in general frequency–tunable. Thus, the structure of multilayered particles may be tuned to deliver the light energy mainly in the forward direction within a certain wavelength range of interest, a useful feature of both theoretical and practical significance. Indeed, Liu *et al.* [13] showed that a spherical composite particle, which consists of silver core and dielectric shell, with tuned radii, scatters the light mostly in the forward direction in a certain wavelength range.

In this work, a general computational electromagnetics methodology is presented for design of nanostructured particles. Extensive design computations were carried to search for nanostructured multilayered composite particles that meet the first Kerker's condition. Computed results show that a Ag-air-Si three layered rattling structure maximizes the forward scattering at the peak wavelength of the scattering efficiency (around 420nm). To test the viability of these nanostructured particles for light absorption applications, FDTD simulations are conducted for a configuration where a periodic array of these nanostructured particles are placed on the top of a silicon substrate. Calculated results illustrate that light trapping in the substrate is enhanced by mainly-forward scattering three-layered structures better than by the other types. In addition, the resonance peak of forward scattering can be tuned to other wavelengths, for example 550nm, by keeping the same outmost radius while varying the core radius.

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II. THEORY

The physical behavior of the light scattering by multilayered multiparticle system, as illustrated in Fig.1 where the income light travels in the k direction, is described by the Maxwell equations. For a source-free medium, the Maxwell equations can be simplified to the electromagnetic wave equations,

$$\nabla^2\mathbf{E} + k^2\mathbf{E} = \mathbf{0}, \nabla\cdot\mathbf{E} = 0, \mathbf{B} = -(i/\omega)\nabla\times\mathbf{E}$$
$$\nabla^2\mathbf{B} + k^2\mathbf{B} = \mathbf{0}, \nabla\cdot\mathbf{B} = 0, \mathbf{E} = -(i/\omega)\nabla\times\mathbf{E} \quad (1)$$

where **E** and **H** are the electric and magnetic fields, ω the applied frequency and k the wave number.

The analytical solution of the electromagnetic waves scattered by a sphere is given by the Mie theory. The theory entails the expansion of a plane wave in spherical coordinates, followed by applying the boundary conditions between the sphere and the surrounding medium,

$$(\mathbf{E}_s + \mathbf{E}_i)\times\mathbf{n} = \mathbf{E}_c\times\mathbf{n},\ \ (\mathbf{H}_s + \mathbf{H}_i)\times\mathbf{n} = \mathbf{H}_c\times\mathbf{n} \quad (2)$$

By integrating the Poyting vector around the particle, the scattering efficiency is obtained,

$$Q_{sca} = \frac{C_{sca}}{\pi a^2 k^2 E_0^2}\sum_{l=1}^{\infty}\sum_{m=-1}^{1}(c_{lm}^{*s}c_{lm}^{s} + d_{lm}^{*s}d_{lm}^{s}) \quad (3)$$

where Csca is the scattering cross section, a the radius of the sphere, E0 the electric field strength of the incident field and c_{lm}^{s} and d_{lm}^{s} are the scattering coefficients. The solution can be extended to a multilayered spherical structure, with the interfacial boundary conditions applied between two adjacent layers. To reduce the intensity of the calculations, a recursive algorithm for multilayered sphere is introduced, by which the coefficients c and d are calculated from the innermost layer outward to the outmost layer. For a multiparticle system, the income electromagnetic field for an individual particle is the summation of the income field and the scattered field from other particles, which requires the transformation of the coordinates from one particle to another one. This, combined with the Wigner-Eckart quantum projection theorem, allows to be calculated the scattering efficiency of the whole aggregate of the multiple multilayered particles [14].

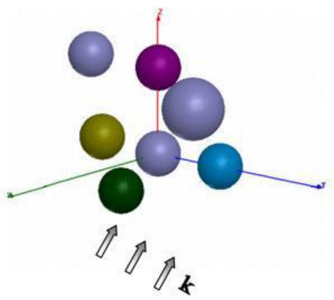

Fig.1. Electromagnetic multiscattering by multilayered multiparticles

Based on the analytical solutions for the scattering and consider the dipole effect only, the normalized intensity of the scattered radiation in the far-field is expressed as

$$\mathrm{NSI}(\theta,\varphi) = \frac{9}{4k^2}[\sin^2\varphi(a_1 + b_1\cos\theta)^2 + \cos^2\varphi(a_1\cos\theta + b_1)^2] \quad (4)$$

where θ is the zenith direction and φ the azimuthal direction of the spherical coordinates and a_1 and b_1 represent the effect of the electric and magnetic dipoles, respectively. It can be shown that the forward ($\theta = 0$) to backward ($\theta = \pi$) scattering ratio is maximized when a_1 is equal to b_1, which is the first Kerker's condition.

To investigate the feasibility of these particles for light absorption applications, the Finite-Difference Time-Domain (FDTD) simulations are conducted for a configuration where the nanostructured particles with maximized forward scattering are arranged on the top of a silicon substrate. The FDTD computations are carried out using general purpose FDTD software, Lumerical, which makes use of the Yee algorithm for the numerical solution of Maxwell's curl equations [15],

$$\frac{\partial\mathbf{D}}{\partial t} = \nabla\times\mathbf{H}\,,\quad \frac{\partial\mathbf{H}}{\partial t} = -\frac{1}{\mu_0}\nabla\times\mathbf{E}$$
$$\mathbf{D}(\omega) = -\,\varepsilon_0\varepsilon_r(\omega)\,\mathbf{E}(\omega) \quad (5)$$

where $\varepsilon_r(\omega)$ is the complex relative dielectric constant and ε_0 the dielectric constant of vacuum. To ensure the accuracy of results from FDTD calculations, an appropriate mesh size is required. This is done by comparing the FDTD calculations with the analytical solution for light scattering by a single sphere, of which the refractive index and the radius of the sphere are set to 5+0.4i and 50nm, respectively. Total-field scattered-field source is used in the FDTD numerical simulation in order to separate the scattered field from the incident field. A box monitor is applied to measure the power flowing out of the sphere. The light transmission is given by

$$\mathrm{T}(\lambda) = \frac{1}{2}\frac{\int real(\mathbf{P}(\lambda)^{Monitor})\cdot d\mathbf{S}}{Source\ Power} \quad (6)$$

where $T(\lambda)$ is the normalized transmission, **S** the surface of the box monitor and $\mathbf{P}(\lambda)$ the Poynting vector. Then, the absorption and scattering efficiency can be obtained through dividing the power by the source intensity and the particle area. The maximum difference between the numerical and analytical results of the scattering efficiency for different mesh sizes is shown in Fig. 2. Examination of the results shows that a mesh size of 0.75nm, which is used in the computations below, gives the maximum difference of 3.4% between numerical and analytical solutions.

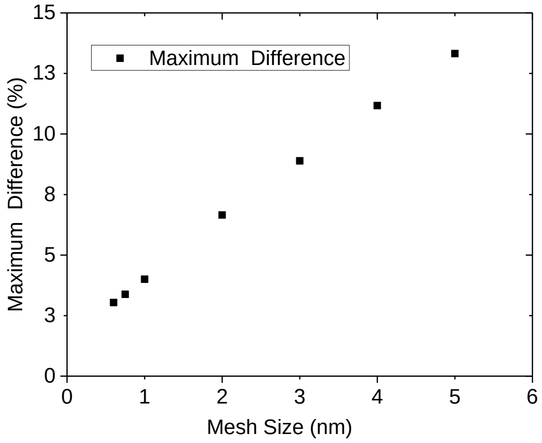

Fig.2: Maximum difference between analytical and Lumerical FDTD results.

III. CURRENT RESULTS

Multilayered spherical particles with different radius and material for each layer are studied by design computations in order to obtain the nanoparticle with maximized forward scattering. From analysis of extensive computed data, one such nanostructure is identified, which is the Ag-air-Si three layered rattling structure with the radii of 45nm, 75nm and 80nm, as shown in Fig.3. The total scattering efficiency of the Ag-air-Si structure is plotted in Fig. 4, where the results for a solid Ag sphere, and a Si nanoshell (core is vacuum) are also given for comparison. Inspection of the results indicates that the light scattered by the Ag sphere is mainly by the electric dipole and that by the Si nano-shell is mainly by the magnetic dipole. These dipoles are induced by the incident light, oscillating with the applied frequency to radiate light (that is, the light is scattered). Clearly, for the single layered nanoparticles, the light is scattered in both the forward and backward directions, as evident in the scattering pattern shown in Figs. 5(a) and (b), respectively. For the Ag-air-Si nanostructure, on the other hand, the radiation by the electric dipole equals to that by the magnetic counterpart at the wavelength of around 420nm, where the scattering efficiency reaches the resonance peak. This is consistent with the first Kerker's condition. Examination of the scattering spectrum in Fig. 4(c), and of the scattering pattern plotted in Fig. 5(c) indicates that the light is scattered mainly in the forward direction at 420nm.

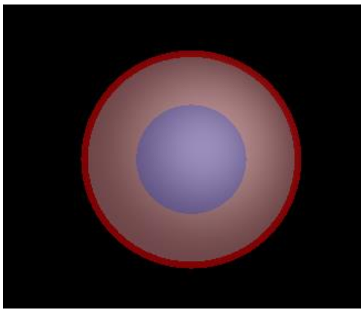

Fig.3. The Ag-air-Sithree layered rattling structure selected from design computations for maximized forward scattering.

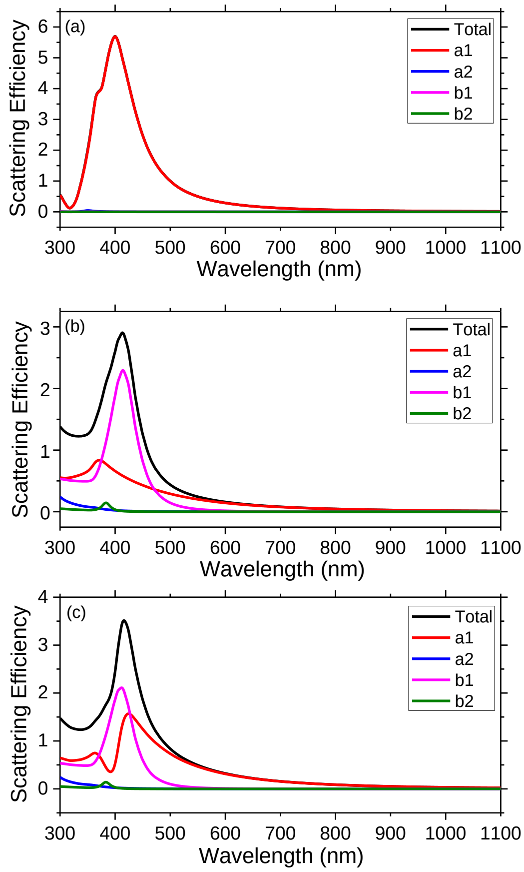

Fig.4. Total scattering efficiency with multipole contributions of (a) Ag sphere (b) Si nano-shell and (c) Ag-air-Sithree layered rattling structure. Here a_1 denotes the contribution from the electric dipole, b_1 the magnetic, a_2 the electric quadruple and b_2 the magnetic quadruple

Turning to their relative importance in scattering process, the forward and backward scattering efficiencies of the Ag sphere, Si nano-shell and Ag-air-Si nanostructured particle are shown in Fig. 6. Clearly, the Ag-air-Si composite particle gives a higher forward scattering efficiency at resonance than either of the other two structures; but only the backward scattering efficiency of the Ag-air-Si structure is minimized. This is reasonable in that the most energy is delivered in the forward direction by the Ag-air-Si nanoparticle. One of the useful applications of these light scatters is in the enhancement of light trapping in optoelectronic devices. A typical and somewhat idealized configuration is a particle on a flat substrate, as in Fig.7, which also shows the domain for FDTD simulations. Three types of nanoparticles, that is, Ag sphere, Si nano-shell and Ag-air-Si rattling structure, are considered. The light is incident upon the structure from the above. Two monitor surfaces are positioned at the top surface of and 500nm below the substrate. The light absorption in the substrate is then calculated by taking the difference of the transmission between the top and bottom monitors.

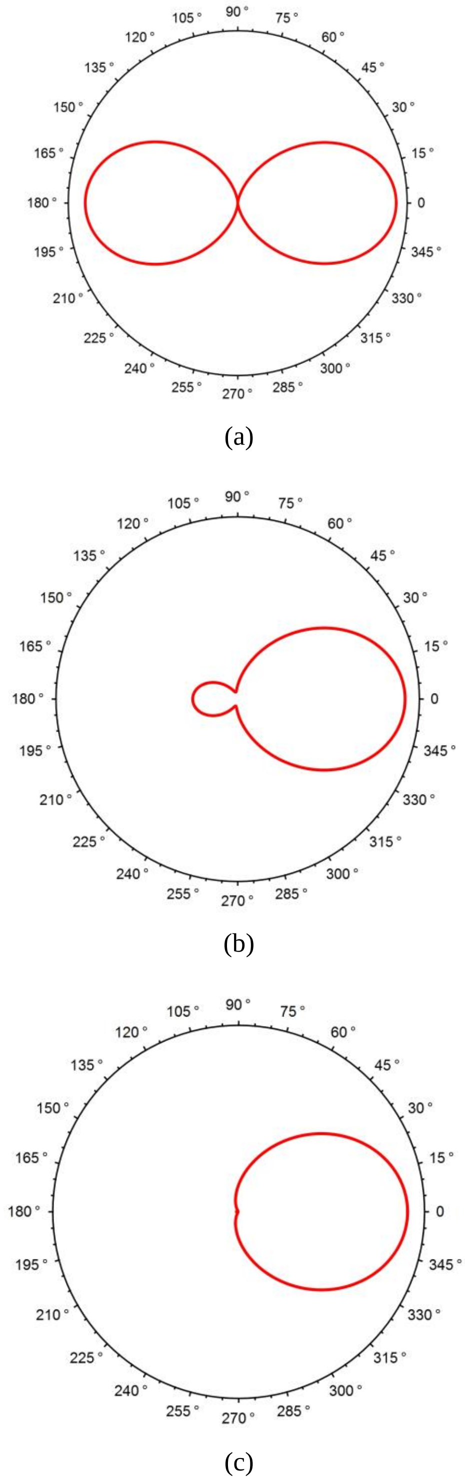

Fig.5. The scattering pattern of (a) a Ag sphere, (b) a Si nano-shell and (c) Ag-air-Sithree layered nanorattler.

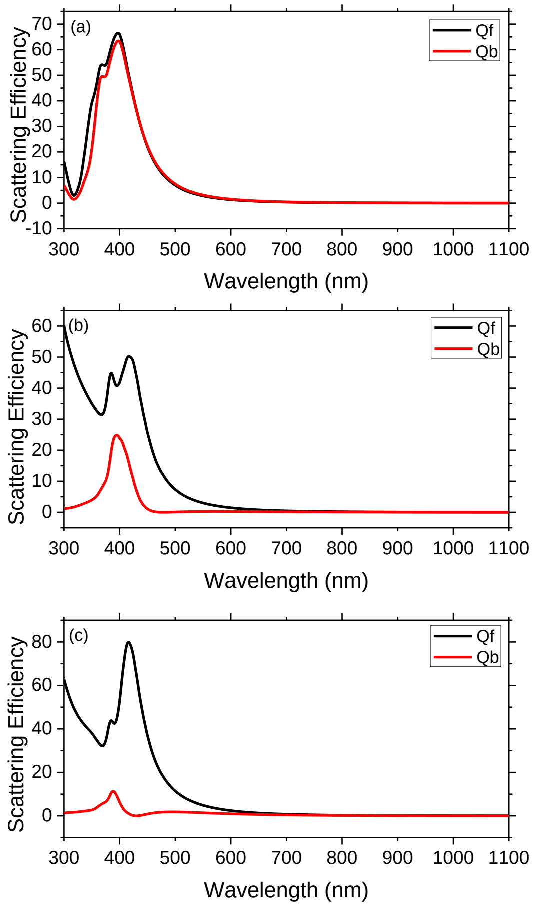

Fig.6. The forward and backward scattering efficiencies of (a) Ag sphere (b) Si nano-shell and (c) Ag-air-Sithree layered rattling nanoparticle.

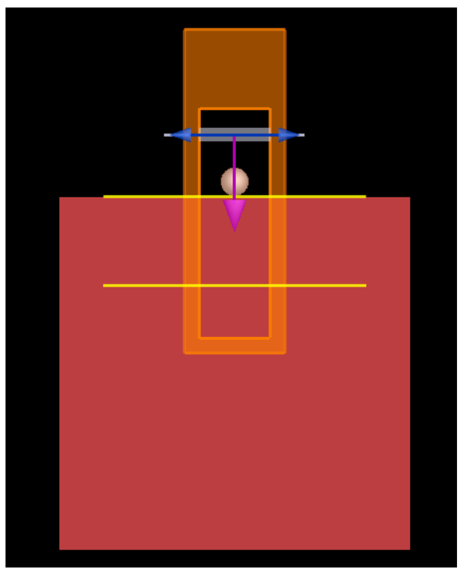

Fig.7. The FDTD model for light scattering by a particle, where the monitor planes are indicated by the two yellow lines.

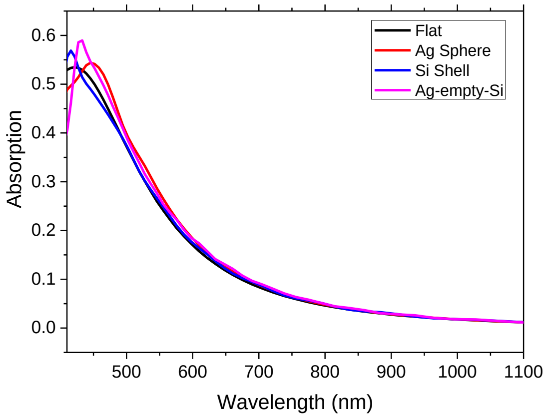

Fig.8. The absorption in the substrate for different types of particles on the substrate.

The calculated results for the three types of particles are plotted in Figs.8. Compared with the bare substrate, the absorption is enhanced for all these three types of particles at their own scattering peak wavelengths. The Ag-air-Si nanostructure enhances light absorption by about 10% near the 420nm wavelength, which is superior over the other two types of particles. This can be explained by the fact that the Ag-air-Si composite particle scatters more light in the forward direction. To investigate the sensitivity of the maximized forward scattering condition to the layer thickness, the efficiency ratio of the forward and the backward scattering is calculated for different Ag core thicknesses. The calculated results are given in Fig. 9, where the ratio of maximized forward to backward scattering is maintained in a vertical region, which means a certain deviation of the layer thickness during the fabrication is allowed.

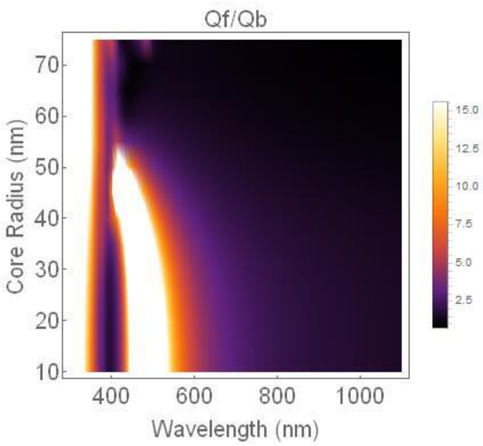

Fig.9. The forward to backward scattering ratio with different Ag core radius.

It is note that the Ag-air-Si rattling structure predicted by the model may not be fabricated as easily as solid particles. Nonetheless, they are possible with the current state of nanofabrication technology. Our laboratory experience with synthesis of nanostructures suggests that a viable process for the Ag-air-Si rattling structure may involve the preparation of the Ag core with $AgNO_3$ and Na_3Ct solution, the formulation of a SiO_2 layer on the surface of the Ag core by the Stober method, the growth of the Silicon shell by the plasma-enhanced chemical vapor deposition and the corrosion of the SiO_2 layer by using the hydrogen fluoride solution.

To further demonstrate the capability of the design computational methodology presented above, a Si-Ag-Si three layered nanostructure is identified though the design computations. The composite particle has a 50nm silicon core, coated with a 10nm thick Silver layer and followed by a 20nm thick Silicon layer. The total scattering efficiency, with the contributions by the electric and magnetic dipoles or multipoles, for the Si-Ag-Si nanoparticle is shown in Fig.10, and the efficiencies of forward and backward scattering in Fig.11. These results show that the electric dipole term equals to the magnetic counterpart at the wavelength of around 550nm, and the forward scattering efficiency is maximized at the same wavelength, while the backward scattering is minimized. The material and radius of each layer may be further tuned for different resonance scatterting.

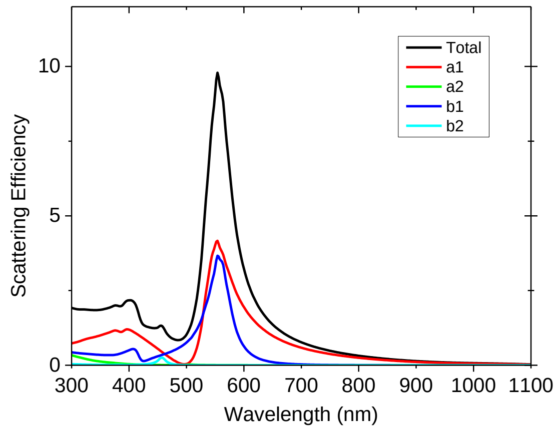

Fig.10. Total scattering efficiency with multiple contributions of Si-Ag-Si three layered rattling structure.

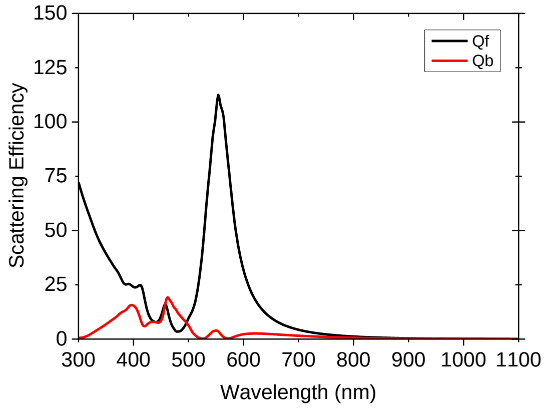

Fig.11. The forward and backward scattering efficiency of Si-Ag-Si three layered rattling structure.

IV. CONCLUSION

This paper has presented a computational electromagnetics model for the design of nanostructured particles for maximizing the forward scattering efficiency. The model is developed on the basis of the Mie solution of the Maxwell equations, enhanced by coupling with the translational addition and the Wigner-Eckart quantum projection theorems for multilayered particle aggregates. Model computations were carried out to design the core-shell structured nanoparticles for maximized forward scattering by fine tuning nanostructural parameters to meet the first Kerker's condition. FDTD simulations were performed for light scattering by these optimally-designed particles into a flat substrate. Computed results show that the designed multilayered particles with maximized forward scattering allows more incident light to be absorbed in the substrate than other reported good light scatters such as Ag nanosphere, SiO_2 nanosphere and Si nano-shell particles.

ACKNOWLEDGMENT

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REFERENCES

[1] L. Jang, H. Park, S. Lee, A. Y. Polyakov, R. Khan, J. Yang, and I. Lee, "Device performance of inverted polymer solar cells with AgSiO 2 nanoparticles in active layer," vol. 23, no. 7, pp. 211–218, 2015.

[2] S. Jiang, Z. Hu, Z. Chen, X. Fu, X. Jiang, and Q. Jiao, "Resonant absorption and scattering suppression of localized surface plasmons in Ag particles on green LED," vol. 21, no. 10, pp. 12100–12110, 2013.

[3] L. A. Austin, M. A. Mackey, E. C. Dreaden, and M. A. El, "The optical , photothermal , and facile surface chemical properties of gold and silver nanoparticles in biodiagnostics , therapy , and drug delivery," pp. 1391–1417, 2014.

[4] F. Jiao, Q. Huang, W. Ren, W. Zhou, F. Qi, Y. Zheng, and J. Xie, "Microelectronic Engineering Enhanced performance for solar cells with moth-eye structure fabricated by UV nanoimprint lithography," *Microelectron. Eng.*, vol. 103, pp. 126–130, 2013.

[5] R. Kapadia, Z. Fan, K. Takei, and A. Javey, "Nanopillar photovoltaics: Materials, processes, and devices," *Nano Energy*, vol. 1, no. 1, pp. 132–144, 2012.

[6] J. Zhu, Z. Yu, G. F. Burkhard, C.-M. Hsu, S. T. Connor, Y. Xu, Q. Wang, M. McGehee, S. Fan, and Y. Cui, "Optical absorption enhancement in amorphous silicon nanowire and nanocone arrays.," *Nano Lett.*, vol. 9, no. 1, pp. 279–282, 2009.

[7] V. Kumar and H. Wang, "Plasmonic Au nanoparticles for enhanced broadband light absorption in inverted organic photovoltaic devices by plasma assisted physical vapour deposition," *Org. Electron.*, vol. 14, no. 2, pp. 560–568, Feb. 2013.

[8] D. Qu, F. Liu, X. Pan, J. Yu, X. Li, W. Xie, Q. Xu, and Y. Huang, "Plasmonic core-shell nanoparticle enhanced optical absorption in thin film organic solar cells," *Conf. Rec. IEEE Photovolt. Spec. Conf.*, pp. 000924–000928, 2011.

[9] J. Grandidier, D. M. Callahan, J. N. Munday, and H. a Atwater, "Light absorption enhancement in thin-film solar cells using whispering gallery modes in dielectric nanospheres.," *Adv. Mater.*, vol. 23, no. 10, pp. 1272–6, Mar. 2011.

[10] Y. Yao, J. Yao, V. K. Narasimhan, Z. Ruan, C. Xie, S. Fan, and Y. Cui, "whispering gallery modes in spherical nanoshells," *Nat. Commun.*, vol. 2, pp. 664–667, 2012.

[11] C. F. Bohren and D. R. Huffman, "Absorption and scattering of light by small particles," *Research supported by the University of Arizona and Institute of Occupational and Environmental Health New York WileyInterscience 1983 541 p*, vol. 1, no. 1. p. xiv, 530 p., 1983.

[12] M. Kerker, D.-S. Wang, and C. L. Giles, "Electromagnetic scattering by magnetic spheres," *J. Opt. Soc. Am.*, vol. 73, no. 6, p. 765, 1983.

[13] W. Liu, J. Zhang, B. Lei, H. Ma, W. Xie, and H. Hu, "Ultra-directional forward scattering by individual core-shell nanoparticles," *Opt. Express*, vol. 22, no. 13, pp. 16178–16187, 2014.

[14] C. Liu and B. Q. Li, "Computational Multiscattering of Spherical Multilayered Gold Nanoshells," *J. Phys. Chem. C*, vol. 115, no. 13, pp. 5323–5333, Apr. 2011.

[15] A. Taflove and S. C. Hagness, "Computational Electrodynamics: The Finite-Difference Time-Domain Method, Third Edition," *Artech House*. p. 1038, 2005.