Coating of Au nanoparticle by Si shell for enhanced local heating

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Abstract. Gold nanoparticles are widely used as a nano-sources of heat, but their properties are governed by skin depth which is usually less than 10 nm. In this work, we propose a mechanism for increasing efficiency of gold nanoparticles heat absorption in optical range. By ‘wrapping’ Au sphere in Si spherical layer we achieved significantly increased heating the nanoparticle in comparison with the gold filled sphere of the same size. The strong heating is caused by radiative losses suppression and more effective electric field concentration around the gold nanoparticle owing to adding of the Si layer.

1. Introduction
Thermotherapy at nanoscale is an important area of medicine where cancer cells are treated by local hyperthermia [1–3]. Metallic nanoparticles are commonly used as a local source of heat [4]. Indeed, plasmonic nanoparticles are well known for their heat absorption properties and strong degree of electromagnetic field localization, which allow to apply them in wide range of areas, including optics and biomedicine [5]. However, small thickness of a skin depth limits efficiency of plasmonic nanoparticle heating owing to very small volume of effective heat source, i.e. mode volume.

On the other hand, dielectric nanoparticles of high refractive index and low extinction coefficient maintain strong electric and magnetic Mie-resonances [7] in the visible range [8]. In comparison with the plasmonic particles, dielectric ones have much greater filling factors for excited optical modes, being useful for a number of applications [9–11]. In this paper, we are taking advantages of both types of nanoparticles: plasmonic and dielectric ones, for effective localized heating. In particular, by covering gold nanoparticle with spherical layer of silicon we increase the heating temperature of a gold core and extend spectral range of effective heating from near-UV to near-IR region.

2. Model
Our theoretical approach is based on Mie-theory which describes the scattering of an electromagnetic plane wave by a homogeneous sphere. Absorbed power by spherical nanoparticle can be described through its’ absorption cross-section $C_{abs}$ and light source intensity $I$:

$$Q = C_{abs} I \quad (1)$$

Absorption $C_{abs}$ cross-section for spherical nanoparticles and core-shells(layered spheres) are linked with extinction and scattering cross-sections $C_{abs} = C_{ext} - C_{sca}$, whereas $C_{ext}$ and $C_{sca}$
are following:

\[
C_{sca} = \frac{W_{sca}}{I_i} = \frac{2\pi}{k^2} \sum_{n=1}^{\infty} (2n+1)(|a_n|^2 + |b_n|^2), \quad C_{ext} = \frac{W_{ext}}{I_i} = \frac{2\pi}{k^2} \sum_{n=1}^{\infty} (2n+1)Re(a_n + b_n) \tag{2}
\]

where \( W_{sca}, W_{ext} \) - scattered and extinct energy by core-shell, \( k = \frac{2\pi \chi}{\lambda} \), \( I_i \) - incident intensity, \( a_n \) and \( b_n \) are, so called, scattering coefficients, that describes interaction of nanoparticle with plane wave. For most cases, we can consider same magnetic permeabilities for surrounding medium and a core-shell. These assumptions lead to simplified form of scattering coefficients:

\[
a_n = \frac{\psi_n(y)|\psi_n'(m_2y) - A_n\kappa_n(m_2y)| - m_2\psi_n'(y)|\psi_n(m_2y) - A_n\kappa_n(m_2y)|}{\xi_n(y)|\psi_n'(m_2y) - A_n\kappa_n(m_2y)| - m_2\xi_n'(y)|\psi_n(m_2y) - A_n\kappa_n(m_2y)|} \tag{3}
\]

\[
b_n = \frac{m_2\psi_n(y)|\psi_n'(m_2y) - B_n\kappa_n(m_2y)| - \psi_n'(y)|\psi_n(m_2y) - B_n\kappa_n(m_2y)|}{m_2\xi_n(y)|\psi_n'(m_2y) - B_n\kappa_n(m_2y)| - \xi_n'(y)|\psi_n(m_2y) - B_n\kappa_n(m_2y)|} \tag{4}
\]

where:

\[
A_n = \frac{m_2\psi_n(m_2x)|\psi_n'(m_1x) - m_1\psi_n'(m_2x)|\psi_n(m_1x)}{m_2\kappa_n(m_2x)|\psi_n'(m_1x) - m_1\kappa_n(m_2x)|\psi_n(m_1x)} \tag{5}
\]

\[
B_n = \frac{m_2\psi_n(m_1x)|\psi_n'(m_2x) - m_1\psi_n'(m_2x)|\psi_n(m_1x)}{m_2\kappa_n(m_2x)|\psi_n'(m_1x) - m_1\kappa_n(m_2x)|\psi_n(m_1x)} \tag{6}
\]

\[\psi_n(\rho), \kappa_n(\rho), \xi_n(\rho)\] - Riccati - Bessel functions, \( a \) - core radius, \( b \) - shell radius, \( m_1 \) and \( m_2 \) - relative refractive indices of a sphere and a shell, \( x = ka, y = kb \). Thus, calculation of heat power \( Q \) delivered into core-shell turns out to be an optical problem with a known solution. Meanwhile, in order to define temperature distribution inside and outside a core-shell we need to solve a stationary heat transfer eq. 7 below:

\[
\nabla \cdot [\kappa_{in}(r)\nabla T_{in}(r)] = -q(r) \quad \text{inside,} \quad \nabla \cdot [\kappa_{out}(r)\nabla T_{out}(r)] = 0 \quad \text{outside} \tag{7}
\]

Where \( q \) power density (in our case is \( q = \frac{3Q}{\pi b^2} \)) and \( \kappa(r) \) - is thermal conductivity. This leads us to following temperature increment distribution inside and outside core-shell:

\[
\Delta T(r)_{in} \approx \Delta T_{CS} \quad r < b, \quad \Delta T(r)_{out} = \Delta T_{CS} - \frac{b}{r} \quad r > b \tag{8}
\]

\( \Delta T_{CS} = \frac{Q}{4\pi \kappa_{out} b} \) - temperature increment in core-shell. This solution is only valid for the case of poorly thermal conductive medium - \( \kappa_{in} \gg \kappa_{out} \).
3. Results and discussions
The above expressions allow us to study scattering and heating behaviour of the core-shell nanoparticles and track their modes evolution with different parameters (e.g. wavelengths, shell and core radii). We consider golden core of 15 nm radius as suitable for most common biomedical applications [baffou review]. Also, it is important to study heating properties of nanoparticles in, so called, transparency window of biological tissues (between 700 and 1300 nm). Working in this spectrum range allows to increase light propagation length into biological tissues minimizing absorption and thus heating of healthy cells. Although spherical gold nanoparticles show the best light absorption in visible range between 500 and 600 nm, its’ resonant can be shifted into near-IR region by placing golden sphere inside homogeneous spherical silicon layer - shell.

In Fig. 2(a) light scattering by silicon shell with a spherical hole in the centre with a 15 nm radius is presented. The modes evolutions give an insight into the contribution of shell into Au-Si core-shell nanoparticles properties. Particularly, in relatively small nanoparticles the strongest contribution to scattering is given by electric dipole (ED) mode, magnetic dipole (MD) and quadrupole (MQ) modes of the shell.

![Figure 2](image_url)

**Figure 2.** 2D maps for core-shells with fixed core radius of $a = 15$ nm; x-axis corresponds to incident wavelength, y-axis corresponds to shell radius $b$, i.e. $b = a = 15$ nm means appearance of only core. (a) Scattering cross-section of a core-shell with silicon shell and air ‘core’ in the units normalized by geometrical cross-section; (b) scattering cross-section of gold-silicon core-shell nanoparticle in arbitrary units (normalized by geometrical cross-section); (c) temperature increment of gold-silicon core-shell nanoparticle in degrees of Kelvin irradiated by plane wave with intensity $I_0 = 0.2mW/\mu m^2$

Putting gold inside the silicon shell, then appears scattering dropping around 900 nm (see Fig. 2(b), where ED of the shell is excited. On the other hand, temperature increase (see Fig. 2(c), which is related to absorption (eq. 1, 8) in the same region shows local peak of heating. This peak corresponds to the core-shell with $b = 150$ nm shell radius. Such configuration demonstrates heating in air up to 500 K (see Fig. 3(a)).

In comparison with spherical gold nanoparticle of the same size, core-shell demonstrates more efficient heating in the transparency region of spectrum up to 10 times (Fig. 3(a)). To evaluate gold core contribution, we have added heating of the silicon shell with excluded gold core. Such comparison of heating improvement possibilities shows the advantage of covering gold sphere by silicon, instead of increasing size of the sphere. Heating properties of gold are limited by skin depth and absorption peak positions, whereas by manipulating shell size we both can control peak position and localize electromagnetic field in the center of the shell, which can dramatically increase temperature. In Fig. 3(b) one can see electric field distribution in the vicinity of the core-shell with considered parameters. Propagation direction of the plane wave is normal to the figure plane and $E$-vector is set to be in x-direction. Typical behaviour of ED resonance both of a shell and a core is manifested in field enhancement on particle/medium boundary in initial electric field vector direction. It means that local dip of scattering noticed in Fig. 2(b)
can be explained via destructive interference of these two resonant ED modes, which almost completely cancels far-field scattering from the core-shell. Also, the temperature maximum in the same region (Fig. 2(c)) is partially described by the near-field localization and enhancement up to 20 times in the core centre owing to specific mode structure of the shell ED. Therefore, such electric fields overlapping of ED modes in core and shell provides necessary conditions for the most effective heating.

4. Conclusions
In this paper we have shown that optimized gold-silicon core-shell nanoparticle can serve as a effective as nanoscale heater for potential photothermal applications. The origin of the 10fold increased heating efficiency is the reducing of radiative losses and electric field localization around lossy plasmonic core.

5. Acknowledgements
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6. References
[1] Kennedy L C et al 2011 Small vol 7.2 pp 169–183.
[2] Huang X et al 2006 Journal of the American Chemical Society vol 128.6 pp 2115–2120.
[3] Atwater H A 2007 Scientific American vol 296.4 pp 56–62.
[4] Baffou G and Quidant R 2012 Laser & Photonics Reviews vol 7 pp 171–187
[5] Maier S A 2007 Plasmonics: fundamentals and applications (Springer Science & Business Media)
[6] Kuznetsov A I, Miroshnichenko A E, Fu Yu H, Zhang J, Luk’yanchuk B 2012 Scientific Reports vol 2 492
[7] Mie G 1908 Annalen der physik vol 330 pp 377–445
[8] Krasnok A, Makarov S, Petrov M, Savelev R, Belov P and Kivshar Y 2015 Proc. SPIE vol 9502 pp 950203
[9] Makarov S, Kudryashov S, Mukhin I, Mozharov A, Milichko V, Krasnok A et al 2015 Nano letters vol 15 (9) pp 6187–6192
[10] Dmitriev P A, Baranov D G, Milichko V A, Makarov S V, Mukhin I S et al Nanoscale vol 8 (18) pp 9721–9726
[11] Kuznetsov A I et al 2016 Science vol 354.6314 aag2472.
[12] Bohren C F and Huffman D R 1983 Absorption and scattering of light by small particles (Wiley interscience).