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Optical properties and photo-heating of aqueous suspensions of silicon-based nanocomposite particles with deposited gold

© A.V. Kornilova[1,2], S.B. Ikramova[3], D.U. Musayeva[4], A.V. Syuy[5], V.Yu. Timoshenko[1,2]

[1] Department of Physics, Lomonosov Moscow State University, Moscow, Russia
[2] Lebedev Physical Institute, Russian Academy of Sciences, Moscow, Russia
[3] Al Farabi Kazakh National University, Almaty, Kazakhstan
[4] National Research Nuclear University „MEPhI", Moscow, Russia
[5] Moscow Institute of Physics and Technology (State University), Dolgoprudnyi, Moscow region, Russia

e-mail: shargenga@mail.ru

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The optical properties of nanocomposite particles consisting of silicon cores about 100 nm in size with smaller gold nanoparticles deposited on their surface have been studied. An increase in the absorption of light in the near-infrared region of the spectrum for the obtained nanoparticles is observed in comparison with that for nanoparticles of pure silicon or gold. Experiments on measuring the temperature of aqueous suspensions showed significantly higher rates of photoheating of nanocomposite particles upon irradiation with laser radiation at a wavelength of 810 nm compared to the case of pure silicon nanoparticles. Calculations of the distribution of the electric field showed multiple increases in its strength near nanocomposite particles upon irradiation with light in the visible and near-infrared ranges and also made it possible to find the scattering and absorption contributions to the extinction spectra of nanoparticle suspensions. The observed enhanced photoheating of nanocomposite particles can be used for application in antibacterial treatment and cancer hyperthermia.

Keywords: nanophotonics, plasmonics, nanoparticles, photohyperthermia, silicon, gold.

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Introduction

At present, the optical properties of isolated semiconductor and metallic nanoparticles (NPs), which exhibit, respectively, the quantum size effect for charge carriers and localized plasmon resonance [1,2], are well studied. Thus, it is known that gold NPs have a localized plasmon resonance in the absorption and scattering spectra of light, the position and shape of which depend on the shape of NPs and the refractive index of their surrounding medium. At the same time, for widely used colloidal solutions of gold NPs, such a resonance usually corresponds to the green region of the spectrum, which is not always convenient for biophotonic applications due to the strong scattering and absorption of light in this range. To shift the plasmon resonance peak to the infrared (IR) region, one can use complex-shaped NPs or their aggregates, which, however, is technically difficult and is often accompanied by an increase in an undesirable load on the biosystem. Another method of resonance shifting is deposition of NPs on substrates or other NPs with high refractive index [3]. As the later silicon NPs can be used.

A possible biophotonic application of nanocomposite particles can be their using as effective absorbers of light energy in the biomedical method of photohyperthermia, which consists in increasing the temperature of a biological object above 41–42°C for a certain period of time [4]. Recently, we have found that with the help of gold NPs immobilized on the surface of halloysite nanotubes, local photoheating at the wavelength of localized plasmon resonance is possible, which makes it possible to achieve controlled destruction of unwanted cells [5].

It is of interest to study immobilized plasmonic NPs on the surface of a compact carrier, for example, a semiconductor silicon NP, and also to study the possibility of additional enhancement of local electric fields and the efficiency of light absorption in the region of coupled plasmon and dielectric resonances in silicon/gold nanocomposite particles. To solve this problem, gold NPs were deposited onto the surface of spherical silicon NPs and the optical and photothermal properties of an aqueous solution of the resulting nanocomposite were studied.

Experimental procedure

Silicon (Si) NPs obtained by radiofrequency decomposition of silane (ACS Materials, USA) with an average diameter of about 100 nm, were used. The deposition of gold (Au) NPs was carried out according to the methodology from the work [6] by holding silicon NPs in an aqueous solution of $HAuCl_4$ (0.4 mM)/HF (5 M) within 10 s, which gave an average Au NP size of about 20 nm The obtained nanocomposite was washed several times with deionized water and sonicated for 5 min, then centrifuged for 10 min at a centrifugal acceleration of 10^4 g.

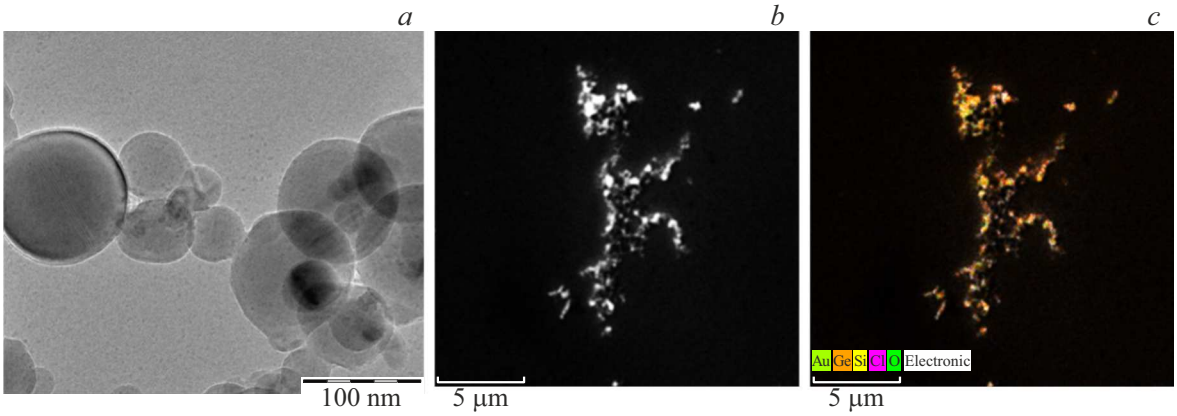

Figure 1. (*a*) TEM-image of initial Si NPs; (*b*) SEM image of composite Si/Au NPs and (*c*) corresponding element distribution map obtained by the EDA method.

The concentrations of elements (Si and Au) in the obtained samples of nanocomposite particles based on silicon with deposited gold NPs (hereinafter Si/Au NPs) were determined by X-ray fluorescence analysis (XRF) on x-ray diffractometer DR-02 "Radian" for air-dried suspensions of Si/Au NPs. The sizes of initial Si NPs were measured using a JEOL JEM-2100 transmission electron microscope (TEM). The morphology and chemical composition of the obtained nanocomposite particles deposited from solution on optically polished germanium plates were studied on a Tescan Vega scanning electron microscope (SEM) with an energy dispersive analysis (EDA) auxiliary device by Oxford Instruments. For comparison, colloidal solutions of Au NPs obtained by laser ablation of solid targets made of gold with a purity of 99.9% [7] were also studied. The extinction spectra of aqueous suspensions of Si/Au NPs and pure Si and Au were measured on a UV-Vis 752P spectrophotometer in the range 300−1000 nm with spectral resolution of 0.5 nm.

The heating of aqueous suspensions of the studied NPs under the action of laser radiation was studied using Flir C3 thermal imaging camera with accuracy of 0.01°C and measurement frequency of 15 Hz in the temperature range from +5 to +50°C. Aqueous solutions of silicon NPs and nanocomposite particles based on silicon with gold were placed in plastic cuvettes with a volume of 0.3 ml. Solution concentrations were 1.8 g/l, initial temperature was 20°C. During irradiation, continuous wave semiconductor lasers with wavelengths of 532, 667, and 800 nm and a power of the order of 200 mW at beam diameters of 2 mm were used.

Simulation of optical properties

Calculations of optical properties and spatial distribution of local electric fields were carried out for an NP consisting of a silicon core with a diameter of 100−150 nm with gold NPs with diameters of 10−20 nm deposited on its surface, using the Lumerical Finite Difference IDE software (by ANSYS, Inc.). The dispersion dependences for the refractive indices of water and silicon were taken from the Palik database, the gold indices were taken from the CRC database for the wavelength range from 300 to 1000 nm. It was assumed that the gold NPs were randomly distributed over the outer surface of the silicon NP. Scattered light source with an amplitude of 1 V/m and a pulse duration of 10 fs was prescribed. The scattering and absorption cross-sections were calculated using numerical solutions of the Maxwell equation for given boundary conditions, by adding the averaged Poynting vectors and normalizing to the source intensity. The spatial distribution of the electric field intensity modulus normalized on the source field when irradiated with light with wavelengths corresponding to the wavelengths of the lasers used in the experiment, was also calculated.

Results and discussions

Fig. 1, *a* shows a TEM-image of the original Si NPs. From the analysis of TEM-images, the average NP diameter was determined to be 125 ± 25 nm. Fig. 1, *b* shows the SEM-images of the obtained nanocomposite particles, which are seen as separate NPs with sizes of about 100 nm, as well as their aggregates of large sizes. Investigation of the elemental composition of NPs by the EDA method (Fig. 1, *c*) made it possible to estimate their chemical composition, which included 50.2 at.% silicon, 49.4 at.% oxygen, and 0.4 ,at.% gold. The percentages of silicon and gold close to the indicated values were also determined by XRF for air-dried macroscopic amounts of NP suspensions.

Based on the TEM and SEM data, a model of the studied composite NP was constructed, which represents a spherical core with diameter of 125 nm from crystalline Si and an array of randomly distributed over its surface Au NPs with diameter of 20 nm and a surface density of about $200\,\mu m^{-2}$ (Fig. 2, *a*). Fig. 2, *b*−*d* shows the calculated

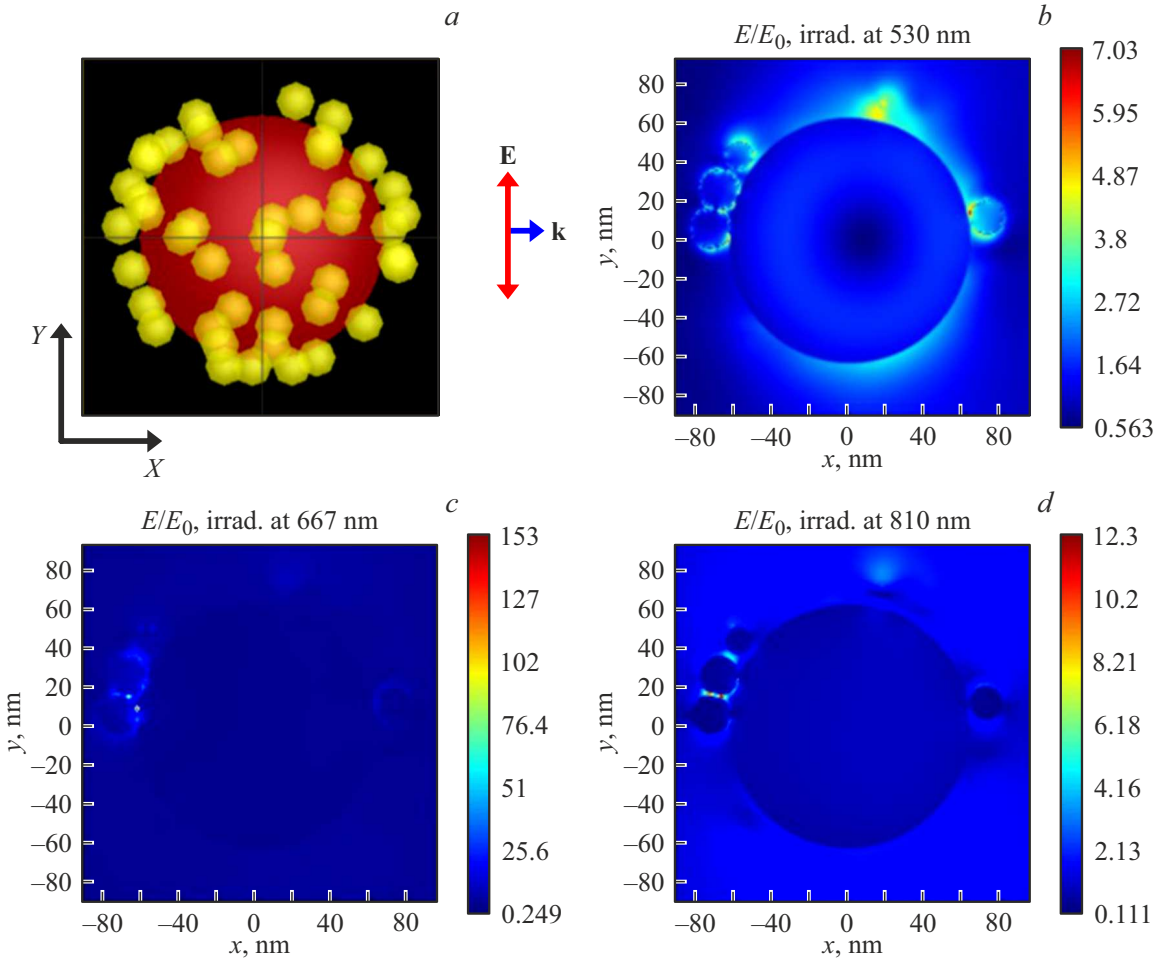

Figure 2. (*a*) Model of a silicon NP with diameter of 125 nm with randomly deposited gold NPs 20 nm and (*b, c, d*) cross-sections of the distributions of the electric field strength, normalized to the initial value, under illumination light with wavelengths 530 (*b*), 667 (*c*) and 810 nm (*d*). The directions of the electric field and wave vector are shown by blue and red arrows.

distributions of the modulus of electric field strength in cross-section of a nanocomposite particle. The values of field strength were normalized to the magnitude of the source field. The patterns of the electric field that form when NPs are exposed to light with wavelengths equal to those used in the experiment are considered. When Si/Au NPs were irradiated with light with a wavelength of 532 nm, the electric field strength between gold NPs increased by 7 times compared with the initial one (Fig. 2, *b*), at 667 nm by 153 times (Fig. 2, *c*), at 810 nm by 12 times (Fig. 2, *d*). The results obtained can be explained by the fact that the wavelength 667 nm is in the region of enhanced light absorption associated with a combination of the effects of localized plasmon resonance in Au NPs and Mie resonance in NP Si [1].

Figure 3 shows the results of calculations of the absorption (Fig. 3, *a*) and scattering (Fig. 3, *b*) cross-sections of a Si/Au nanocomposite particle in water, as well as Si NPs and ensemble of Au NPs with the same parameters and spatial arrangement. The complex structure of resonances in the spectrum of the latter is associated with the mutual superposition of scattered fields of Au NPs from due to their close location to each other. For the Si/Au nanocomposite particle, there is also an additional enhancement of the absorption and scattering cross-sections in the spectral region of superimposition of the plasmon resonance of gold and the Mie resonance of silicon NPs. In this case, for Si/Au NPs, both the absorption cross-section and the scattering cross-section in the near-IR region increased by more than an order of magnitude compared with the values for pure Si NPs and the NP Au ensemble.

Fig. 4 shows the experimentally measured extinction spectra of aqueous solutions of Si/Au NPs and suspensions of pure Si and Au NPs. The spectra of the latter clearly show the peak at wavelength of 520 nm, which corresponds to localized plasmon in gold NPs [2]. For the solution of silicon NPs, a usual decrease in the degree of absorption in the long-wavelength part of the spectrum is observed, while for the sample with Si/Au NPs, the increase in the

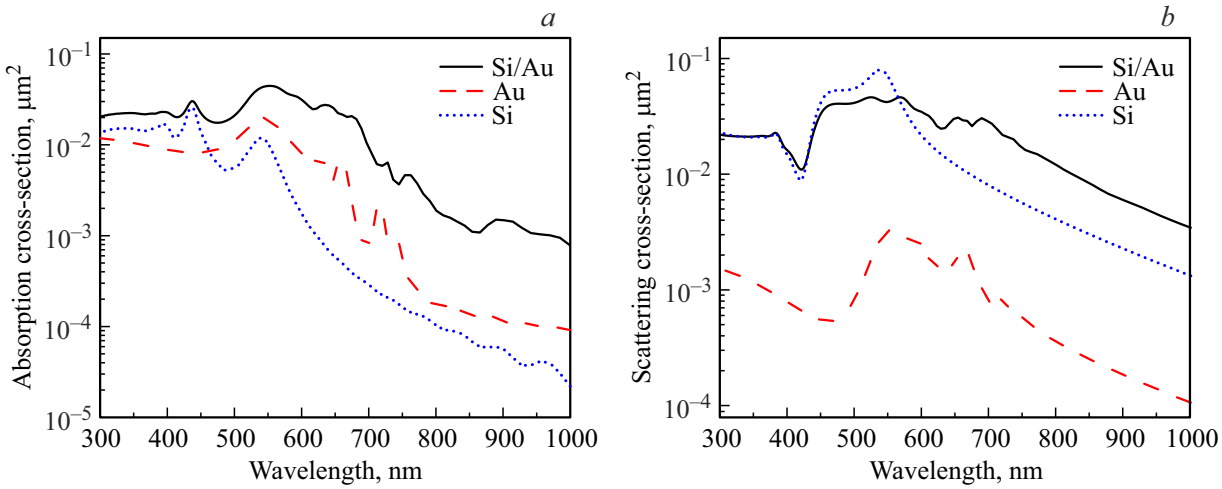

Figure 3. The calculated spectra of (*a*) absorption and (*b*) scattering cross-sections for a nanocomposite particle consisting of a 125 nm silicon core with 20 nm gold NPs deposited on its surface (solid line is Si/Au) and spectra of the same amount of gold NPs (dashed line is Au) and individual silicon NPs (dashed line is Si) in water.

extinction coefficient in the near-IR region by more than 2 times is seen.

Fig. 5 shows the measured dependences of the temperature rise for aqueous suspensions of initial Si NPs (Fig. 5, *a*) and composite Si/Au NPs (Fig. 5, *b*) on the time of laser irradiation. The heating rate of aqueous suspensions of Si NPs under illumination by green (532 nm) and red (667 nm) lasers was 8 K/min at the initial stage, while when irradiated by laser with a wavelength of 810 nm, the rate heating was no more than 1 K/min. or Si NPs with gold NPs, the amount of suspension heating increased in accordance with an increase in the particle absorption cross-section (Fig. 3, *a*). The heating rate of the Si/Au sample under the action of lasers with wavelengths of 532 and 667 nm at the initial moment was 12 K/min, when irradiated with light with a wavelength of 810 nm is 7 K/min. The data obtained confirm that aqueous suspensions of Si/Au NPs have a significantly higher efficiency of light absorption, especially in the near-IR region of the spectrum, which is in good agreement with both the calculation results (Fig. 3) and experimental results (Fig. 4).

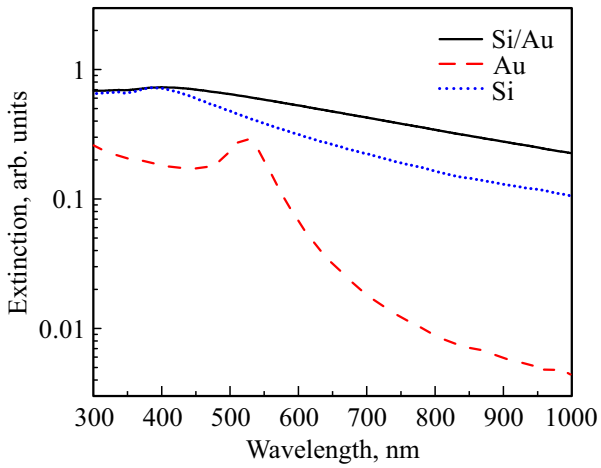

Figure 4. Extinction spectra of aqueous solutions of silicon NPs with gold (solid line is Si/Au), gold (dashed line is Au), and silicon (dotted line is Si).

Conclusion

Thus, composite NPs, which are silicon NPs with sizes on the order of 100 nm, with smaller gold NPs deposited on their surface, were obtained and studied in this work. Significant increase in absorption and scattering in aqueous suspensions of Si/Au composite NPs compared to the same amount of pure silicon or gold NPs has been experimentally and theoretically found. The dependences obtained are explained by the simultaneous interaction of the light wave both with Si NPs near the Mie scattering resonance and with Au NPs in the region of localized plasmon resonance, which leads to the appearance of combined resonances observed in the extinction spectra of aqueous suspensions of Si/Au NPs. In this case, according to the performed calculations, the sharp increase in the electric field strength occurs near Au NPs upon irradiation with light with a resonant wavelength. Increase in the light absorption cross-section also manifests itself in more efficient heating of the suspension of nanocomposite NPs, especially upon laser irradiation in the near-IR region of the spectrum. The results obtained are promising for further use in cancer photohyperthermia with irradiation in the transparency window of biological tissues.

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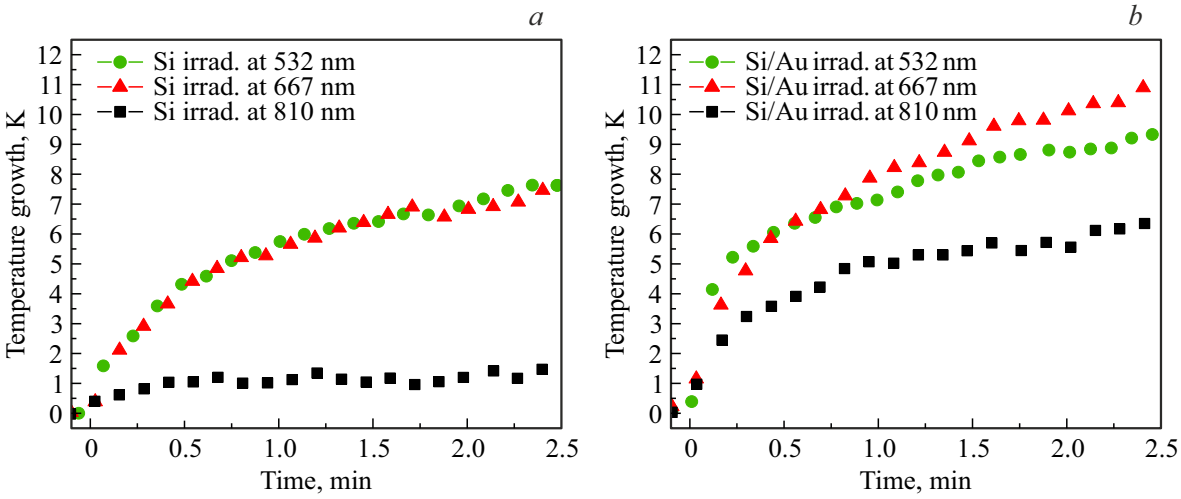

Figure 5. (*a*) Time dependences of temperature changes in aqueous suspensions of silicon NPs and (*b*) nanocomposite Si/Au NPs under laser irradiation with a wavelength of 532 nm (green circles), 667 nm (red triangles), and 810 nm (black squares). Initial temperature 20°C, concentration LF 1.8 g/l.

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Conflict of interest

The authors declare that they have no conflict of interest.

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