Laser printing of Au/Si core-shell nanoparticles

G P Zograf\textsuperscript{1,}\textsuperscript{*}, D A Zuev\textsuperscript{1}, V A Milichko\textsuperscript{1}, I S Mukhin\textsuperscript{1,2}, M A Baranov\textsuperscript{1}, E V Ubyivovk\textsuperscript{1,3}, S V Makarov\textsuperscript{1,}\textsuperscript{*} and P A Belov\textsuperscript{1}

\textsuperscript{1}ITMO University, St. Petersburg 197101, Russia
\textsuperscript{2}St. Petersburg Academic University, St. Petersburg 194021, Russia
\textsuperscript{3}St. Petersburg State University, St. Petersburg, 199034 Russia

*g.zograf@metalab.ifmo.ru
*s.makarov@metalab.ifmo.ru

Abstract. We develop a novel method of core-shell nanoparticles fabrication based on laser ablation of multilayer thin films using femtosecond laser pulses. Transmission electron microscopy proves that the obtained structures have Si and Au separated parts. We theoretically show that the combination of high refractive index dielectric and plasmonic nanoparticles shows possibility of interplay between magnetic optical responses and plasmon resonances. This opens a possibility to manipulate by both scattering power pattern and local optical field enhancement via precise engineering of the core/shell nanoparticles.

1. Introduction

Plasmonic nanoparticles actively studied in the last two decades because of their ability to localize and amplify light at the nanoscale [1]. However, metal nanoparticles of simple shapes (nanospheres, nanocubes, nanorods, etc.) have only resonances of electrical nature [2]. For magnetic response in the optical range it is necessary to create nanoparticles of more complex shapes applying lithographic techniques [3-5]. More recently, magnetic optical response has been observed experimentally in dielectric nanoparticles with a high refractive index (for example, silicon spheres) [6]. Indeed, according to the classical Mie theory, dielectric nanostructure can exhibit optically induced resonant magnetic response in the optical range. This opens up opportunities for controlling radiation pattern of such nanoparticles due to the interference of electric and magnetic resonances [7]. The combination of dielectric and plasmonic nanoparticles shows magnetic optical response due to dielectric part together with a high degree of localization by metal one.

There are fundamentally different configurations of metal-dielectric (hybrid) nanoparticles. The first type corresponds to a case where metal and dielectric parts are separate closely spaced particles. Such particles can be created using nanolithography techniques, laser ablation or colloidal chemistry [8-10]. Completely different type of a structure such as "core-shell", where one component is integrated into another one. Such structure is mechanically much more stable and compact. However, until now state-of-the-art technologies allows to create only core-shell particles of low-index dielectrics (oxides of metals and semiconductors), which hinders the induction of magnetic resonances in the visible range [11]. Indeed, covering a semiconductor nanoparticle by a thin metal layer faces the
problem of shell dewetting [12], whereas fabrication of a crystalline semiconductor shell on a metallic core is still challenge for chemical and lithographical approaches.

2. Results and discussion

2.1 Fabrication

In our work, we developed, for the first time, a method to create core-shell nanoparticles made of gold and silicon. Our novel method based on laser ablation of multilayer thin films using femtosecond laser pulses (figure 1).

Figure 1. Femtosecond laser ablation method scheme.

Ablation is a method of removing material from the surface by a laser pulse. At low laser powers vaporizes or sublimes the substance in the form of free atoms and clusters. When the intensity of the laser pulse exceeds the ablation threshold, there is a micro-explosion with the formation of a hole in a thin film together with liquid particles erupting off the surface. In our case, we place a receiving substrate to catch the ablated particles above the films. Gold and amorphous silicon thin films (different thickness) were deposited on a glass substrate. Firstly, a gold layer was deposited by thermal deposition. Then, a-Si:H films with thicknesses in the range of 15-100 nm were deposited on a substrate of fused silica with the 15-nm gold layer by plasma enhanced chemical vapor deposition from SiH$_3$ precursor gas (initial hydrogen concentration 10%), were used. Energy regime was chosen to ablate both films but to keep glass substrate unaffected. As simulations and Raman scattering demonstrated that in the process of ablation amorphous silicon is restructuring into crystalline silicone [13]. The crystalline silicon is known to be better material for nanoptical applications as compared with amorphous one.

Our ablation setup (figure 2) consisted of commercial femtosecond laser system (TeMa, Avesta Project), which has central wavelength of $\lambda \approx 1050$ nm (monitored by a spectrometer) and a pulse duration of 150 fs (monitored by an autocorrelator) with 80 MHz repetition rate. Laser pulses energy is varied by two attenuators and selected by a Pockels cell-based pulse picker (Avesta Project). Pulses were tightly focused on films with microscope objective (Olympus 40x) with numerical aperture of 0.75.

The resulting nanoparticles fabricated from 15/15 nm Au/Si films were studied experimentally by transmission electron microscopy. The electron microscopy shows that the fabricated nanoparticles have Au-core and Si-shell structure with an average size of less than 200 nm (figure 4-a).
2.2 Optical properties

Despite we obtained experimentally only Si-core/Au-shell nanoparticles, the two main scenario are possible. In our case, Si part is crystallized much earlier than Au one, yielding a solid Si core covered by a thin Au layer, which is dewetted at large sizes of the Si core. However, in the case of formation of core-shell nanoparticle by liquid Au and Si parts, the Si is covered by Au with much higher surface energy. These two possible regimes are governed by kinetics of cooling and solidification, which depends on laser intensity (i.e. on initial temperature) and time of flight before deposition on a substrate with relatively high thermal conductivity (i.e. on time of slow cooling rate). Therefore, we consider two possible cases in our theoretical analysis of optical properties of Au/Si core-shell nanoparticles.

The numerical analysis in commercial software CST Microwave Studio of electromagnetic field distribution around a Si-core/Au-shell nanoparticle reveals three peaks corresponding to three resonances when the inner and outer diameters are 80 nm and 140 nm, respectively (figure 3a). The numerical simulations of near fields at these resonances are shown in figure 3, confirming their origin. As shown in figure 3b the high-frequency resonance at \( \lambda = 410 \) nm corresponds to magnetic dipolar response of Si core, whereas the other two resonances at \( \lambda = 550 \) nm and \( \lambda = 760 \) nm are hybridized plasmon resonances of the Au shell. According to previous studies [14], the low-frequency plasmon resonance is symmetric mode, whereas high-frequency plasmon resonance is asymmetric mode of the shell. The low-frequency plasmon (symmetric coupling of the cavity and sphere plasmon), couples to light much more strongly than the high-frequency plasmon. The near-field enhancement is up to 3 times. This is because the dipole moment of the symmetric plasmon is much larger than the antisymmetric plasmon, where the dipole moment of the bare cavity and sphere plasmons oppose each other. Therefore, the resulting electric field inside the Si-core Au-shell is much stronger for the low-frequency plasmon (figures 3b,c). We also studied numerically power patterns at the resonances, which show the possibility of manipulation by scattering properties only around magnetic dipolar resonance owing to its interference with high-frequency plasmon in shell.

![Image of optical setup](image-url)
In turn, calculated Au-core/Si-shell nanoparticle scattering spectrum (figure 4-a) indicates the presence of three types of resonances - the electric dipole (ED), magnetic dipole (MD) and magnetic quadrupole (MQ) - in the visible range. These results were confirmed by the numerical calculations of the total scattering cross section and vector maps of electric field of hybrid core-shell nanoparticles with a geometry corresponding to the dimensions defined by the electron microscopy. Moreover, numerical calculations show the ability to effectively control the radiation pattern of the scattered light by nanoparticles. In figures 4-d,e we show power patterns of electric and magnetic dipole resonances, respectively. It is inherent for these types of resonances the absence of radiation in the far field along the E-vector direction for electric and along H-vector for MD resonance, as well as equal scattering to front and back directions. The power-pattern at MQ resonance is given in figure 4-f. In comparison with MD, the side radiation is decreased. In case of overlapping MD and ED resonances, there is, so-called, Huygens-source with almost complete scattering in forward direction (figure 4-g). In addition, core-shell nanoparticles allow for strong field localization and enhancement up to 5 times at ED as well as high Purcell factor in the dielectric shell due to the presence of the resonance of the gold core.

**Figure 3.** a) Theoretical scattering cross-sections for Si-core/Au-shell with diameters of 80/140 nm. Electric near-fields at ED, MD, MQ resonances b) cross-section is normal to E-vector direction. c) cross-section is normal to Z-axis through the core-shell center. Power patterns for d) MD, e) antisymmetric ED, and f) symmetric ED.

**Figure 4.** a) Theoretical scattering cross-sections for Au-core/Si-shell with diameters of 126/174 nm. Electric near-fields at ED, MD, MQ resonances b) cross-section is normal to E-vector direction. c) cross-section is normal to Z-axis through the core-shell center. Power patterns for d) ED, e) MD, f) MQ and g) Huygens source at 750 nm.
3. Conclusions
In conclusion, we have shown for the first time that the laser printing allows to achieve fabrication of nanoparticles made of noble metal shell and high-refractive index dielectric core. Our numerical simulations provided insight into mode structure of the obtained core-shell nanoparticles, revealing plasmons excitation and magnetic optical response in the visible range. Such type of nanoparticles is a promising platform for creation of directional nanolasers, all-optical switches and biosensors.

Acknowledgements
This work was supported by the Ministry of Education and Science of the Russian Federation (project №14.584.21.0009 with unique identificator RFMEFI58414X0009).

References
[1] S.A.Maier, 2007 Plasmonics: Fundamentals and Applications.
[2] V.V.Klimov 2010 Nanoplasmonics.
[3] A.E.Krasnok 2015 Proc. SPIE 950203.
[4] J.Zhou et al. 2005 Phys. Rev. Lett. 95 22390
[5] S.V.Makarov et al. 2015 Nano Lett. 15(9) 6187
[6] A.I.Kuznetsov et al. 2012 Sci. Rep 2 492
[7] A.E.Krasnok et al. 2014 Nanoscale 6 7354
[8] L.Shi et al. 2012 Adv. Mater. 24 5934
[9] U.Zywietz et al. 2014 Nature Comm. 5 3402
[10] D.A. Zuev et al. 2016 Advanced Materials 28 3087
[11] G.Chen et al. 2012 ACS Nano 6(9) 8280
[12] Liu P et al. 2015 J. Phys. Chem. C 119(2) 1234
[13] P.A.Dmitriev et al. 2015 Nanoscale 8 5043
[14] E. Prodan and P. Nordlander 2004 J. Chem. Phys. 120(11) 5448