Tunable Optical Antennas Based on Metallic Nanoshells with Nanoknobs

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We investigate optical properties of a new complex plasmonic nanostructure, which consists of a spherical metallic nanoshell and a small metallic nanoparticle (“nanoknob”) situated on its surface. The plasmon resonance wavelength of the entire structure is guided by the geometrical and material properties of the nanoshell whereas the electromagnetic field of the incident light is localized and enhanced near the “nanoknob.” The idea is supported with electromagnetic modeling and near-field optical microscopy imaging. In addition, we proposed and demonstrated a new method of nanoparticle precise manipulation under electron beam, which could be used in fabrication of such plasmonic structures and other nanosized elements.

Keywords: Optical Antenna, Plasmonic Nanostructure, Surface Plasmon Resonance, Plasmon Hybridization, Nanoparticle Manipulation.

1. INTRODUCTION

Optical antennas based on metallic nanostructures attract lots of attention nowadays due to their unique optical properties.1 These elements are able to effectively couple the energy of incident light to a confined region of subwavelength size. The effect is underpinned by surface plasmon resonance, which guides optical properties of metallic nanostructures. Optical antennas can find potential application in tip-enhanced spectroscopy of biological structures and as future connector elements between photonic and plasmonic waveguides.

Optical antennas can be created on the basis of single spherical metallic nanoparticles.2 Some theoretical works suggest creating optical antennas from a chain of metallic spheres of decreasing size3,4 or metallic nanostars (a sphere with a number of caps).5 These structures provide large field enhancement near the smallest element. However, the plasmon resonance frequency of metallic spheres has just faint dependence on the particle diameter so it is hardly possible to tune the resonance to the desired part of the spectrum. Plasmon resonance tuning is possible using such particles as spherical metallic nanoshells (a dielectric sphere covered with a metallic layer), whose resonance frequency has a strong dependence on dielectric sphere diameter and metallic shell thickness.6

Here we investigate a new complex plasmonic nanostructure, which consists of a spherical metallic nanoshell and a small spherical metallic nanoparticle (“nanoknob”) on its surface. The plasmon resonance frequency of this structure is guided by the parameters of the metallic nanoshell, however the local field enhancement is observed near the metallic “nanoknob.” The idea is supported with electromagnetic modeling near-field microscopy imaging. The designed structures were created by means of a novel method based on precise manipulation under electron beam.

2. ELECTROMAGNETIC MODELING

Electromagnetic modeling of investigated structures was performed by means of the finite element method in Comsol Multiphysics software. We investigated nanoshells made of 40 nm diameter spherical dielectric core with gold coating of various thicknesses so that the entire diameter of the nanoshell varied from 48 to 84 nm. The gold “nanoknob” had a diameter of 8 nm and the overlapping with the nanoshell varied as well. If the “nanoknob” was deepened inside the nanoshell, the dielectric core always
consumed the material of the “nanoknob.” The refractive index of the core material in the nanoshell was taken as 1.46 at all wavelengths, which is typical for silica, and some polymers. The optical constants for gold were taken from Ref. [7]. We investigated the case of illumination of this structure with a linearly polarized plane electromagnetic wave (polarization direction is parallel to the axis of rotational symmetry of the structure) and monitored the extinction spectra and near-field spectra and maps.

3. EXPERIMENTAL DETAILS

3.1. Optical Properties Single Gold Nanoshells

Nanoshells were based on polystyrene spherical particles of 120 nm diameter were dispersed on a glass substrate. In order to create metallic nanoshells the substrate together with nanoparticles was coated with 20 nm thick gold layer by means of magnetron sputtering. Optical properties of metallic nanoshells were investigated by means of scanning near-field optical microscopy (SNOM). The experimental setup was NT-MDT Ntegra Spectra scanning probe microscope, which combines a classical atomic force microscope (AFM) with a SNOM unit and spectroscopic system. We used inverted configuration of SNOM. The sample was locally illuminated at the laser wavelength of 633 nm with a SNOM probe (an apertured cantilever) while scattered light at the same wavelength was collected with an objective lens (NA = 0.4) situated underneath the sample (Fig. 3(a)). Atomic force microscope was used to find individual nanoshells on the substrate whereas their plasmon modes were investigated by means of the SNOM unit.

3.2. Fabrication of Optical Antenna Probes

Finally, we investigated a route of fabrication structures designed in electromagnetic modeling. The structures were created in a Carl Zeiss Neon 40 EsB scanning electron microscope which was additionally equipped with a micromanipulator Kleindiek MM3A-EM for mechanical positioning nanoobjects under electron beam and a gas injection system for electron beam induced deposition.8

In the fabrication process, we used a novel method of precise manipulation under electron beam, which was based on electrostatic interaction between objects charged by passing electrons. In this method, a tungsten needle sharpened to the tip curvature radius of less than 50 nm by means of electrochemical etching was attached without grounding to micromanipulator. Polystyrene spherical particles of 120 nm diameter were dispersed on a silicon substrate. A sample area of 5.5 × 4 μm² was raster scanned with an electron beam (5 keV electrons, 60 pA beam current, 0.6 sec frame time). While approaching the tip of the tungsten needle to one of particles visible in the electron image frame we found that this particle jumped to the tip of the needle. Then the tungsten needle with a particle on its tip was coated with a 20 nm gold layer by means of magnetron sputtering (to create a metallic shell). Finally a platinum “nanoknob” was grown on the nanoshell surface by means of electron beam induced deposition of platinum from the C₃H₄CH₃Pt(CH₃)₃ gas.

4. RESULTS AND DISCUSSION

4.1. Electromagnetic Modeling

The results of electromagnetic modeling are presented in the Figures 1 and 2. The extinction spectra of the investigated structures are shown in the Figure 1(a). The maximum of each curve determines the position of plasmon resonance wavelength. It changes from 530 nm to 630 nm upon the decreasing of outer shell diameter from 84 nm to 48 nm (solid curves in Fig. 1(a)). We deliberately chose such geometrical parameters of the nanoshells so that their resonance wavelengths matches frequently used laser wavelengths of 532 and 633 nm. When small gold nanoparticle (“nanoknob”) is added to the nanoshell (the center of the “nanoknob” is situated on the outer nanoshell surface) we can see that the surface plasmon resonance
of the entire structure nearly does not change in compare to the case of a single nanoshell. This suggest that the plasmon resonance of the entire structure is guided by the nanoshell parameters. However if we look at near-field maps we can see that in the case of nanoshell with “nanoknob” the field of the incident light is localised and enhanced near the “nanoknob.” Thus, the structure consisting of a metallic nanoshell with “nanoknob” behaves like an optical antenna; it can effectively concentrate the energy of incident light into an area of subwavelength size. Moreover, one can tune the resonance frequency of the antenna to the desired part of spectrum via changing the shell thickness.

In addition to the results presented in the Figure 1 we decided to investigate the influence of overlapping rate between the particles on the plasmon modes of the entire structure. The results presented in the Figure 2 demonstrate electric field spectra at the surface of the “nanoknob” at different overlapping rate. The Figures 2(a) and (b) corresponds to the cases of the nanoshell inner/outer diameter of 40/84 and 40/48 nm respectively. For the both structures one can see that upon decreasing of the overlapping rate the peak on the spectrum redshifts.

The plasmon resonance modes of a single nanoshell is dictated by hybridization of the surface plasmons on its inner and outer surfaces which causes strong bonding and weak anti-bonding modes to appear. Upon decreasing of the shell thickness, the dominant bonding mode redshifts. This effect is quite well known for metallic nanoshells nowadays.6 The situation of surface plasmon interaction in overlapping metallic nanoshell and small metallic nanoparticle is more complicated. We suppose that upon decreasing the overlapping rate the “nanoknob” behaves more like a separated particle with its individual plasmon mode. Interaction between the modes of the “nanoknob” and the nanoshell causes mode hybridization and resonance redshift. Moreover when the resonance wavelengths of the nanoshell and the “nanoknob” are close to each other (as it happens in the case of 40/84 nm diameter nanoshell and an 8 nm diameter “nanoknob”) the hybridization effect becomes stronger which results in more significant redshift of the bonding resonance and weak antibonding mode appearance (Fig. 2(a), the case \(x = 3\)). To the best of our knowledge the case of overlapping metallic nanoshell and small metallic particle has not been studied. So far just the cases of overlapping spheres9 and non-touching spheres and nanoshells10 were investigated.

While nowadays researches investigated various designs of optical antennas (single rods,11 Uda-Yagi antennas,12 bow-tie structures13) the major challenge is fabrication of such elements with reproducible geometrical characteristics because this is crucial for optical antenna functionality. Here optical antennas that are based on spherical nanoparticles may have an advantage since modern methods of synthesis allows producing small spheres with very narrow size distribution. Thus, one need to find an effective way of assembling these spheres together.

### 4.2. Optical Properties of Single Gold Nanoshells

An AFM image of a group of four separated nanoshells is shown in the Figure 3(b). A SNOM image of the same is presented in the Figure 3(c). One can clearly see that in the SNOM image each nanoshell has two bright regions across it, which is in line with the polarization plane of the illumination laser (indicated with an arrow in Fig. 3(c)). We suppose that we observe with a dipolar surface plasmon mode of nanoshells. It is exited by means local illumination with a SNOM probe and caused enhanced light scattering in the far-field. When the local illumination source is situated so that polarized electric field of the source penetrates a nanoshell across, the dipolar plasmon mode is exited the most effectively. This explains the appearance of the two...
bright regions across each nanoshell. Our modeling confirmed that such nanoshells should have a plasmon resonance at the wavelength of 630 nm.

4.3. Fabrication of Optical Antenna Probes

The fabrication process of an optical antenna based on a metallic nanoshell with a “nanoknob” is shown in the Figure 3. The manipulation with polystyrene spheres under electron beam, which results in obtaining a single particle at the tip of the tungsten needle, is shown in the Figure 3(a). Further process of optical antenna fabrication in presented in the Figure 3(b): a single 120 nm diameter polystyrene sphere obtained at the tip of tungsten needle; the same structure after coating with 20 nm thick gold layer to form a nanoshell with core/shell diameter of 120/160 nm; the final view of the antenna with platinum “nanoknob” grown on the nanoshell surface.

While the techniques of magnetron sputtering and electron beam induced deposition are very well known the method of manipulation under electron beam requires discussion. The technique is apparently based on electrostatic interaction between objects charged by passing electrons (since we did not observe the effect of nanoparticle attraction when the tungsten needle was grounded). We suggest the following explanation of the effect: the non-grounded tungsten needle charges under the electron beam and create electrostatic field gradient, which should have maximum at the tip of the needle. Polystyrene nanoparticles are attracted to silicon substrate by means of Van-der-Waals force. However, the field of the charged tungsten needle polarizes the particle, which causes it to move along field gradient to the tip of the needle. The phenomenon of dielectric nanoparticle motion in non-uniform electric field is known as dielectrophoresis. Although we suppose that dielectrophoresis plays the major role in nanoparticle manipulation we should also take into account the other effects related to polystyrene nanoparticle charging. The later could cause repulsion between negatively charged needle and particle or attraction of negatively charged nanoparticle to its positive image in the tungsten needle. However the observed effect of nanoparticle attraction requires further experimental and theoretical investigation.

A literature search performed in this field of nanoparticle manipulation showed that quite similar effect can be observed in a scanning probe microscope when voltage is applied to the probe. However to the best of our knowledge nanoparticle manipulation based on charging effects and electrostatic forces was performed in an electron microscope for the first time. The advantage of nanoparticle manipulation in electron microscope is that the process and the result are observed on electron images in real time. Moreover, the electron beam provides the possibility of local charging a desired nanoobject. These peculiarities potentially allow to create complex structures based on nanoparticle assembly (such as optical antennas made of self-similar nanoparticle chain which was theoretically studied in Ref. [4]).

5. CONCLUSIONS

We investigated optical properties of new plasmonic structure, which consists of partially overlapping spherical metallic nanoshell and small metallic nanosphere (“nanoknob”). The electromagnetic modeling showed that the plasmon resonance wavelength of the entire structure is determined by the geometrical and material properties of the nanoshell whereas the electromagnetic field of the incident light is localized and enhanced near the “nanoknob.”
The effect is also influenced by the hybridization of the nanoshell and the “nanoknob” plasmon modes, which becomes stronger as overlapping between the particles decreases. Optical properties of single gold nanoshell were investigated by means of scanning near-field optical microscopy that revealed dipolar surface plasmon mode in these particles. Finally, we proposed and experimentally demonstrated a route of fabrication of optical antenna probes based on metallic nanoshells with “nanoknobs.” The fabrication process mainly involved a new method of precise manipulation under electron beam, which is based on electrostatic interaction between objects charged by passing electrons.

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References and Notes


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