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САМООРГАНИЗУЮЩАЯСЯ НАНОПЛАЗМОНИКА

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SELF-ASSEMBLED NANOPLASMONICS

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Известные к настоящему времени плазмонные структуры можно разделить на два класса в зависимости от того, получены ли они с использованием традиционных микро-технологических методов, как например, электронной и фотолитографии (top-down), или в процессе химического синтеза (bottom-up). Первые интенсивно изучаются вплоть до настоящего времени, но остаются большими и простыми в смысле размеров и особенностей архитектуры соответственно. Плазмонные структуры, формирующиеся в результате bottom-up процессов, стали доступными для исследования только недавно, и необходимо исследовать их оптические свойства в ближней зоне. Bottom-up подход расширяет возможности объединения малых наноструктур в сложные по архитектуре системы. Самоорганизация наночастиц в сложные суперструктуры – один из предложенных процессов, связанных с усложнением структуры. В данной статье мы обсуждаем проблемы синтеза самоорганизующихся наноструктур, оптической адресации в таких структурах и вводим понятие многомерных плазмонных структур.

Ключевые слова: *субволновая оптика, нанофотоника, наноструктуры, коллоид металла, оптика ближнего поля, плазмоника, самоорганизующиеся наноструктуры.*

State-of-the-art plasmonic structures can be splitted into two classes depending on whether they were obtained by top-down or bottom-up processes. The former have been extensively studied but they remain to be large and simple in terms of feature size and architecture, respectively. The latter have only been made available recently and need much investigation of their near-field optical properties, yet they push the integration limit further and provide a new approach to complex architectures. Self-assembling of nanoparticles in complex superstructures is one of the suggested bottom-up approaches. We discuss the challenging problem of the light evanescent wave optical addressing in such structures and introduce a concept of multi-scale plasmonic architectures.

Keywords: *sub-wavelength optics, nanophotonics, nanostructures, metal colloid, near-field optics, plasmonics, self-assembled nanostructures.*

Introduction

The prospect of combining small dimensions of an electronic circuit with the large bandwidth of a photonic network has driven rapid expansion of research into the area of nanoplasmonics and light flow control particularly at the sub-wavelength scale. The metal nanoscale features that can carry both optical signals and electric currents are surface plasmons (SPs). SPs are collective oscillation of surface electrons that can interact strongly with light resulting in optical energy confinement and enhancement of the near metal-dielectric surface. SPs coupled with light can propagate along the metallic structure and transport optical energy below the photon diffraction limit. By tailoring optical properties of metallic nanostructures it is possible to guide propagating SPs and thereby optically address single nanoscale and molecular systems with an unprecedented degree of spatial resolution lacking in conventional photonic devices [1]. The advances in nanoplasmonics and nanofabrication will lead to further miniaturization of electro-optic photonic devices and their implementation in molecular electronics, nano-resolution optical imaging, ultra-sensitive sensors and information technology. The latter includes future all-optical integrated circuits, novel optical components for electro-optic devices, optical data transmission and communication.

1 State-of-the-art of the plasmonics nanostructures

1.1 Top-down and bottom-up approaches

The top-down approach to fabricate plasmonic structures is mainly based on electron beam lithography and has been ubiquitous for implementation of the plasmonics ideas. The approach allows producing structures of the desired but rather simple shape and geometry. Moreover it suffers from lack of spatial control (dimensions and definition of shapes and interstices) and energy dissipation due to poorly defined objects' structure. Chemically synthesized crystalline plasmonic nanostructures (so called bottom-up approach) have defined surfaces and morphology better than the top-down amorphous or polycrystalline nanostructures, exhibit lower losses and superior enhancement [2]. They also allow more accurate tuning of nanostructure's optical properties due to precisely known morphological features which also makes theoretical investigation be more straightforward. In spite of the superior optical properties of crystalline nanostructures their application has been limited by difficulties in assembling of colloidal nanoparticles (NPs) of arbitrary shapes and sizes and in transferring from colloid onto a solid substrate. Thus, another approach is being developed, such as growing the desired nanoscale plasmonic systems right on the substrate surface.

1.2 Self-assembly of NP architectures

Higher order architectures can be obtained by spontaneous self-assembly which yields, for example, metal NP short chains or extended networks (figure 1.1). We foresee that the diversity of colloidal chemistry principles that can be applied to such systems will not only allow the design and production of well-defined superstructures such as dimers, trimmers, short chains with controlled length and topology but also offer a versatile platform for post-assembly functionalization with active molecular moieties [3].

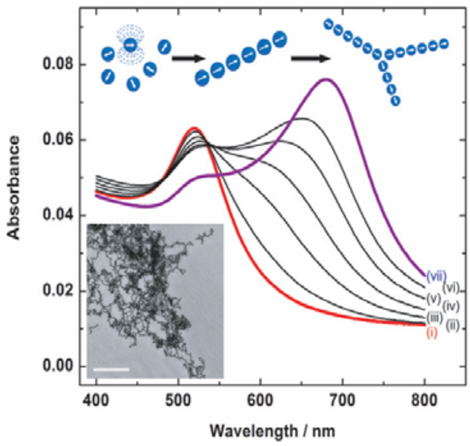

Figure 1.1 – Formation of plasmonic particle networks from colloidal gold. Isolated 13nm diameter gold nano-crystals are self-assembled by addition of mercaptoethanol (MEA). The self-assembly into chains and then branched networks by induced dipolar interactions (scheme in the upper insert) is followed in time by UV-VIS spectrophotometry, which shows the decrease of the 520 nm band as the 700 nm band emerges. After 24-48 hours, the networks are fully formed and can be observed in the transmission electron microcopy (image in the lower insert, bar 500nm). Spectra are taken at (i) 0 min, (ii) 30 min, (iii) 1 h, (iv) 1.5 h, (v) 2 h, (vi) 2.5 h and (vii) 24 h after addition of MEA [5]. Spectra reproduced from [5] with permission of John Wiley and Sons, Inc. All rights reserved.

Dipolar interactions are common for magnetic NPs, which bear an intrinsic dipole moment, leading, for example, to the alignment of iron oxide NPs inside magnetotactic bacteria [4]. In the case of spherical metallic NPs no intrinsic electric dipole should be expected. Nevertheless, citrate-capped NPs can be seen as highly negatively charged spheres. When a fraction of the citrates is replaced by another neutral capping group prone to forming a self-assembled monolayer on gold surfaces, one may expect the molecules to segregate into domains. Provided that the spatial distribution of the domains is slightly non-uniform, an induced electric dipole will be generated on the NP surface and linear self-assembly and branching will proceed as for the previous systems. This is precisely what we observed when we mixed enough 2-mercaptoethanol (MEA) with 13 nm citrate-capped gold NPs to cover 60% of the gold surface with a SAM as shown in figure 1.1 [5].

2 Multi-scale plasmonic architectures

By combining different bottom-up approaches such as self-assembling and self-organizing with lithography and other top-down methods, it becomes conceivable to produce integrated multi-scale plasmonic architectures able to channel light from a micron-sized laser beam to nanoscopic entities (figure 2.1) [3]. To date, several approaches to explore capabilities of multi-scale plasmonic structures to propagate and confine light at nanoscale have been tested. In the pioneering work of J.C. Weeber focused beam launched SP polaritons (electromagnetic surface waves resulting from the coupling of incident light and SPs) on a homogeneous wide metal film which further propagated on thin metal stripes [5]. Direct excitation of SPs in metallic nanowires by a tightly focus beam [6] and electromagnetic energy transfer in chains of weakly coupled metal NPs upon excitation by the tip of the near-field scanning optical microscope [7] have been studied. Hybrid approaches combining plasmonic and dielectric wave guiding have been demonstrated by coupling light propagating along the microscopic polymer waveguide into a nanoscopic plasmonic waveguide, when two waveguides are perpendicular to each other [8] and by hybrid compact near-field interaction between plasmonic and photonic waveguides [9]. However, in spite of the great effort applied by research groups worldwide in the area, the problems of high propagation losses and spatial control in plasmonic NP systems are still unsolved.

Optical energy propagation in plasmonic nano- and micro-structures is at the heart of the plasmonic based future electro-optic devices, which may offer new solutions for optical signal processing and data transmission. Therefore the capacities of plasmonic nanostructures to (i) confine (ii) propagation and funnel light and (iii) optically address nanoscale entities are being studied by research groups worldwide. In pursuing the goal of effective light flow control at nanoscale the major challenges have been formulated, such as: (i) synthesis, fabrication and manipulation of metal nanosystems with desired optical properties, (ii) fabrication and manipulation of complex multi-scale plasmonics based electro-optic devices, (iii) optical energy plasmonic nanosystems coupling and decoupling, (iv) optical addressing spatial resolution control, (v) propagating optical energy dissipation and losses decrease and compensation.

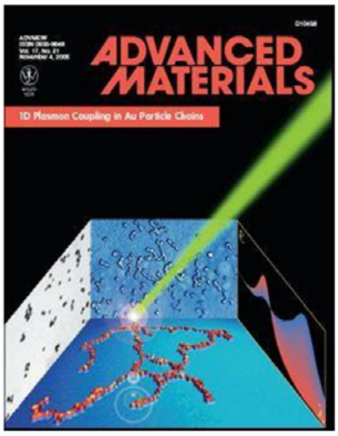

Figure 2.1 – Underlying principle and challenges of self-assembled nanoplasmonics. Laser beam is incident on one end of the complex metal NP network. Optical energy is transported to another end of the network via near-field coupling. Fluorescence of the coupled to metal fluorophore is due to interaction of the transported light with the fluorophore [5]. Inside front cover reproduced with permission of John Wiley and Sons, Inc. All rights reserved.

The investigation of fundamental aspects and optimization of functionalities of the bottom-up plasmonic nanostructures require intensive support of both theoretical modeling and numerical simulations. For example, understanding how plasmon couple with each other and with nearby molecules, accurate evaluation of dissipation in the developed multi-scale plasmonic structures, study of the disorder consequences on the efficiency of self-assembled plasmonic structures will be among the major questions associated with future bottom-up plasmonics. In order to realize these objectives numerical tools mainly based on the Green dyadic methods (GDM) will enable us to compute accurately the local electromagnetic properties of three-dimensional metal superstructures with complex geometries lying on the substrate [3].

Techniques for optical characterization of such multi-scale fabricated devices include near-field, far-field, single molecule and electron loss spectroscopy methods. To investigate near-field optical properties of nano-objects, near-field experimental methods such as photon scanning tunneling microscopy and scanning near-field optical microscopy were initially developed. They, however, need to accurately locate a near-field detector (tip) in the vicinity of the sample, making the system difficult to describe theoretically since the detector has the influence on the system itself. Recently, an alternative method based on two photon luminescence has been developed to give access to near field information through a far field measurement [10]. Together with GDM, TPL microscopy will be used to probe near and far field optical properties of the developed self-assembled metal superstructures.

Conclusion

We discussed the advantages and disadvantages of bottom-up and top-down approaches to synthesize and fabricate plasmonic nanostructures. Bottom-up structures possess superior optical, structural and morphological properties as compared with their top-down counterparts and present a promising solution for nanoplasmonics applications requiring optical addressing of nano and molecular systems with sub-wavelength spatial resolution, better control of optical energy propagation and reduced energy dissipation at nanoscale. Example of a bottom-up system of self-assembled gold nanoparticles was given. Finally, we presented a concept of multi-scale plasmonic architectures and outlined the associated scientific and technological challenges.

REFERENCES

1. *Girard, C.* Near-field optical properties of top-down and bottom-up nanostructures / C. Girard, E. Dujardin // Journal of Optics A : Pure and Applied Optics. – 2006. – Vol. 8. – P. 73 – 86.

2. *Silver nanowires as surface plasmon resonators* / H. Ditlbacher [et al.] // Physical review letters. – 2005. – Vol. 95. – P. 257403.

3. *Shaping and manipulation of light fields with bottom-up plasmonic structures* / C. Girard [et al.] // New Journal of Physics. – 2008. – Vol. 10. – P. 105016.

4. *Tlusty, T.* Entropic networks in colloidal self-assembly / T. Tlusty, S.A. Safran // Philosophical Transactions of the Royal Society A. – 2001. – Vol. 359. – P. 879–881.

5. *One-dimensional plasmon coupling by facile self-assembly of gold nanoparticles into branched chain network* / S. Lin [et al.] // Advanced Materials. – 2005. – Vol. 17. – P. 2553–2559.

6. *Plasmon polaritons of metallic nanowires for controlling submicron propagation of light* / J.-C. Weeber [et al.] // Physical Review B. – 1999. – Vol. 60. – P. 9061.

7. *Dickson, R.M.* Unidirectional plasmon propagation in metallic nanowires / R.M. Dickson, L.A. Lyon // Journal of Physical Chemistry B. – 2000. – Vol. 104. – P. 6095.

8. *Local detection of electromagnetic energy transport below the diffraction limit in metal nanoparticle plasmon waveguides* / S.A. Maier [et al.] // Nature Materials. – 2003. – Vol. 2. – P. 229–232.

9. *Integration of photonic and silver nanowire plasmonic waveguides* / A.L. Pyayt [et al.] // Nature Nanotechnology. – 2008. – Vol. 3. – P. 660–665.

10. *Spectroscopic mode mapping of resonant plasmon nanoantennas* / P. Ghenuche [et al.] // Physical Review Letters. – 2008. – Vol. 101. – P. 116805.

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