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Plasmonics in composite nanostructures

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Plasmonics is a rapidly developing research field with many potential applications in fields ranging from bioscience, information processing and communication to quantum optics. It is based on the generation, manipulation and transfer of surface plasmons (SPs) that have the ability to manipulate light at the nanoscale. Realizing plasmonic applications requires understanding how the SP-based properties depend on the nanostructures and how these properties can be controlled. For that purpose composite nanostructures are particularly interesting because many novel and extraordinary properties unattainable in single nanostructures can be obtained by designing composite nanostructures with various materials. Here, we review recent advances in the studies of three classes of composite nanostructure that are important for plasmonics: metal–metal, metal–dielectric, and metal–semiconductor composite nanostructures.

Introduction

With the development of nanoscience and nanotechnology, various nanostructures based on different materials can be fabricated in controllable ways. Among these, composite nanostructures have been intensively studied because many novel properties unattainable in single nanostructures can be obtained. Particularly, composite nanostructures are widely used in plasmonics, a booming research field aiming at the manipulation of light at the nanoscale. Plasmonics is based on the excitation of surface plasmons (SPs) – collective oscillations of free electrons at metal–dielectric interfaces, which can confine electromagnetic (EM) field at the metal's surface enabling light manipulation beyond the diffraction limit of light [1]. Most researches in plasmonics are within the visible and near infrared spectral regions, whereas some studies, noticeably those on plasmonic metamaterials, have extended plasmonics to the THz wave and microwave regions [2–6]. The plasmonic properties of metal nanostructures are strongly dependent on the geometrical parameters, the materials and the surrounding media of the nanostructures, which makes composite nanostructures extremely important in plasmonics to realize highly tunable and designable optical properties.

Based on the excitation of SPs, metal nanostructures show many prominent optical properties, for example, huge EM field enhancement, supersensitive plasmon resonance and propagation at the nanoscale. The huge EM field enhancement can be obtained in close-packed metal nanostructures, where the SP resonances can tightly confine EM field into tiny gaps due to the strong EM coupling of two metal surfaces, similar to the strong EM resonance in a cavity [7,8]. This effect enables the amplification of weak light–matter interactions, and is the basis for many very important research directions in plasmonics, including nanogap or ''hot spots'' for surface-enhanced Raman scattering (SERS) [7–10], optical antenna [11,12], plasmonic optical forces [13,14], plasmochemistry [15], quantum plasmonics [16,17] and nonlinear plasmonics [18,19]. For super sensitivity, the SP resonance frequencies are extremely sensitive to the change of the surrounding dielectric environment of the metal nanostructures, which has been used to develop ultrasensitive sensors [20]. For propagation at nanoscale, SPs can propagate in one-dimensional nanostructures with EM field tightly confined around the nanostructure, which can be used to realize light transmission beyond the diffraction limit and build nanophotonic circuits [21,22]. Because of these properties, plasmonics has shown potential applications in many fields, such as biological and chemical sensing [7,20], disease

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diagnosis and therapy [23–25], information processing and communication [21,22,26], quantum optics [27], photovoltaics [28], catalysis [15,29,30], lithography and imaging [31–33].

The tailoring of the plasmonic properties for implementation in these applications relies on the design and fabrication of composite nanostructures. It is therefore essential to investigate the properties of such composite plasmonic nanostructures to understand how the composite nanostructures determine their specific plasmon-related properties. Here we briefly review recent advances in studying three classes of composite plasmonic nanostructures: metal–metal, metal–dielectric, and metal–semiconductor composite nanostructures.

Metal–metal composite nanostructures

Here the metal–metal composite nanostructures mean the nanostructures composed of two or more metal nanostructure components, not the alloy nanostructures. As the SP resonance frequencies of gold and silver nanostructures are at visible and near infrared spectral range, gold and silver are the most popular metal materials used in plasmonics. Due to SP resonance, single metal nanoparticles (NP) are able to concentrate EM energy, leading to locally enhanced EM field near the NP [34]. This effect can be enhanced in systems where metal nanoparticles (NPs) are brought into close proximity to another metal structure. For a dimer consisting of two metal nanoparticles, the coupling between the localized SP modes will strengthen the EM field in the interparticle nanogap and red-shift the resonance frequency for incident polarization along the dimer axis [7,8], which can be theoretically described by the coupling of two dipoles. Although decreasing the separation between two coupled metal nanostructures can increase the electric field intensity and red-shift the resonance frequency, an extreme decrease in the separation to the dimension of angstrom scale can decrease the enhancement factor and blue-shift the SP resonance frequency due to quantum effects [16,17,35,36].

The large EM field enhancement in the nanogaps (also called the nanogap effect) is the most pronounced phenomenon in metal–metal composite nanostructures, which leads to many plasmon-enhanced phenomena. The nanogap with enhanced EM field becomes the ‘hot spot’ for SERS and surface-enhanced fluorescence [7,8,37–39]. The EM enhancement has been employed to enhance some nonlinear optical processes such as high-harmonic generation and four-wave mixing [19,40]. Lasing has been reported to occur around EM hot spots in Au bow-tie-shaped NPs supported by an organic gain material [41]. The hot spots can also enhance optical forces, which can be used for trapping NPs and molecules [13,14,42–44]. Composite metal nanostructures can function as antennas to modulate the polarization and direction of emitted light, which provides large flexibility for light manipulation at the nanoscale [11,12,45,46]. Recently, plasmon-enhanced chemical reactions have drawn much attention. The hot electrons generated by SP resonances assist the occurrence of some chemical reactions, for example dimerizing 4-nitrobenzenethiol to dimercaptoazobenzene [15,30].

As SPs are strongly dependent on the geometry of nanostructures, metal–metal composite nanostructures of various geometries have been investigated [47]. Besides Au–Au and Ag–Ag composite nanostructures, heterometal structures of Au–Ag have also been studied for tuning SP resonances and routing light of different colors [48,49]. The EM coupling in composite metal nanostructures is strongly dependent on the structure configuration, which offers a unique strategy to tune the optical properties [50,51]. For example, end-to-end aligned gold nanorods show red-shifted SP resonance compared to single nanorod, while side-by-side gold nanorods show blue-shifted SP resonance. In composite structures of specific configurations, the interference of different SP modes results in Fano resonances and electromagnetically induced transparency, which have sharp resonance features and may be used for ultrasensitive sensing [52–54].

Hot spots for surface-enhanced Raman scattering (SERS)

Raman spectroscopy is an important technique for detecting and analyzing molecules with the molecular ‘‘fingerprints’’ contained in the spectra. But the Raman signals of molecules are usually very weak due to the small scattering cross sections, which limits the sensitivity of the Raman spectroscopy for detecting analytes. SERS greatly improves the sensitivity of Raman by using the field enhancement effect of metal nanostructures. The huge EM field enhancement in the nanogaps, that is, hot spots, of metal composite nanostructures can enhance the Raman intensity by a few orders. Nanoparticle dimers are the simplest composite structures that contain such nanogaps. Actually, the large EM field enhancement in the nanogap was first revealed in the study of single-molecule SERS [7,8]. The scanning electron microscopy (SEM) image in Fig. 1a shows a dimer of Ag NPs, which was used to detect the SERS signal of single hemoglobin molecules. The EM coupling strength strongly depends on the separation of the two particles and the polarization of excitation light. From the calculated electric field distributions in Fig. 1a, it can be seen that the highest EM field is obtained with polarization parallel to the dimer axis due to the two induced dipoles in NPs strengthening each other. For perpendicular polarization, no enhancement is generated in the nanogap as the two dipoles cancel each other [55].

Apart from dimers of two nanospheres, dimers composed of nanospheres and other structures can also generate hot spots (Fig. 1b–d shows three types of asymmetrically coupled structures). For example, by placing an Au NP into a nanosized hole in an Au film, a hole–particle pair is formed (Fig. 1b). The hole–particle nanogap provides a large-volume hot spot that gives rise to a strongly enhanced Raman signal for molecules located in the nanogap [56]. A second example of a structure in which such a hot-spot is formed is the junction between a nanowire (NW) and an adjacent NP (Fig. 1c) [57]. Because the NW can function as a waveguide for SPs, the hot spot at the NW–NP junction can be remotely excited by focusing the excitation light at one end of the NW [58]. Finally, the EM coupling between a metal NP and a metal film can also generate a hot spot in the nanogap formed between them (Fig. 1d). The ease-of-fabrication of this type of structure makes it a good candidate for SERS substrate [59]. We note that the apex of a metal tip on scanning probe microscope can be regarded as a controllable nanoparticle. By coupling the tip with a metal film or a metal nanoparticle on the film, nanogap can be controllably created. Tip-enhanced Raman spectroscopy (TERS) has been developed based on the hot-spots in the tip-substrate coupled structures [15,60–63].