MATERIALS SCIENCE

Optical tuning by the self-assembly and disassembly of chain-like plasmonic superstructures

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Plasmonic nanostructures possess novel optical properties due to the collective oscillation of conduction electrons in the nanoparticles upon interaction with light, which is known widely as localized surface plasmon resonance (LSPR). This phenomenon has inspired a variety of applications, such as colorimetric sensors, optoelectronics and biomedical diagnosis etc. [1]. Since the optical properties of plasmonic nanostructures are determined by resonance modes and

frequencies, which are highly dependent on the size and shape of the plasmonic nanostructures as well as their spatial arrangement, consequently, synthesis and assembly of plasmonic nanostructures in predictable manners is the prerequisite for their effective performance in applications.

Compared to size- and shape-controlled synthesis, effective strategies towards controllable assembly of plasmonic nanostructures are less mature. Building superstructures by self-assembling gold nanoparticles (AuNPs) in solution represents an advanced topic on optical tuning. Strategies for solution-based self-assembly of AuNPs can generally be divided into two categories: template-assisted and template-free self-assembly. The former involves inorganic or polymeric templates to physically guide the arrangement of AuNPs into desired superstructures [2], while the latter strategy relies on delicate manipulation of the colloidal interactions among AuNPs. The capping ligands on AuNPs are generally recognized to be critical for controlling the colloidal interactions. In order to obtain anisotropic assembly of AuNPs, previous studies adopted thiol ligands to exchange citrate, which were the capping ligands of AuNPs prepared by the traditional Turkevich method, to initiate the assembly process. It was proposed that the partial ligand exchange process caused inhomogeneous ligand (charge) distribution on the AuNP surface and induced electric dipole–dipole interactions leading to anisotropic self-assembly of the NPs into 1D chains, which may further connect to produce chain networks [3,4]. However, in some other cases, anisotropic AuNP assembly can be formed but cannot be fully ascribed to the dipolar mechanism. For instance, AuNPs capped with citrate and a small amount of tannic acid can be dispersed in ethanol. Upon addition of salt, 1D chains of AuNPs can be formed [5]. In this case, the driving force for AuNP assembly is the weakening of electrostatic repulsion rather than the induced dipole interaction. In our opinion, the essential prerequisite in anisotropic self-assembly process is the reduction of electrostatic repulsion force.

When the electrostatic repulsion among the AuNPs is reduced to a certain extent, the particles start to form the primary aggregates—dimers. Other neighboring NPs can preferentially attach to the ends of dimers where the repulsion is weaker than that at the sides, and this process initiates the construction of chain structures, as schematically shown in Fig. 1.

Compared to the assembly process, the disassembly of plasmonic superstructures is also fundamentally important and technically useful. However, studies on effective disassembly are even fewer in number. Our previous work demonstrated that modification of negatively charged AuNPs with bis (*p*-sulfonatophenyl)–phenylphosphine (BSPP) ligands can offer strong short-range steric repulsion, which can counter the Van der Waals force at a short interparticle distance, prevent permanent aggregation of interacting AuNPs and therefore ensure reversibility of the assembly process [5,6]. In this case, the considerably large size of the ligands and their strong binding to Au surface are believed to contribute critically to the strong short-range steric repulsion, making effective disassembly possible. As a result, any stimuli that can cause increase in the electrostatic repulsion, e.g. reduced ionic strength by dilution or enhanced charge dissociation by heating, could effectively induce disassembly.

Assembly and disassembly of AuNPs enable reversible tuning of plasmon coupling, which causes spectral shift of the LSPR band and realizes optical tuning [7]. In colloidal systems, since the external stimuli including temperature, pH, specific molecules and ions etc. can drive the assembly process, in turn, these factors can be quantitatively detected by colorimetric sensing. It is also demonstrated that AuNP assemblies can be transferred to solid polymer films and be used for colorimetric sensing of pressure by taking advantage of nanoparticle disassembly associated with the polymer deformation in response to pressure (Fig. 2b) [8]. However, applications by the optical tuning of plasmonic nanostructures through assembly and disassembly are still at the infant stage. The major challenge that limits the applications is the lack of precise structural control of nanoparticle assembly, which impedes the accurate prediction of the optical properties of plasmonic nano-assemblies. Strategies for accurate control of colloidal interactions are therefore expected to be further explored to help in solving this challenge [9]. Extending plasmonic building blocks from AuNPs to nanostructures of other materials and morphologies for reversible assembly is another important topic to be studied for improving the performance of plasmonic nano-assemblies in applications. Silver (Ag) nanostructures are known to have higher LSPR intensity than their Au counterparts. Therefore, optical tuning with better sensitivity is expected if AgNPs can substitute AuNPs as building blocks for assembly. An increase in the diversity of plasmonic building blocks can also induce different assembly behaviors
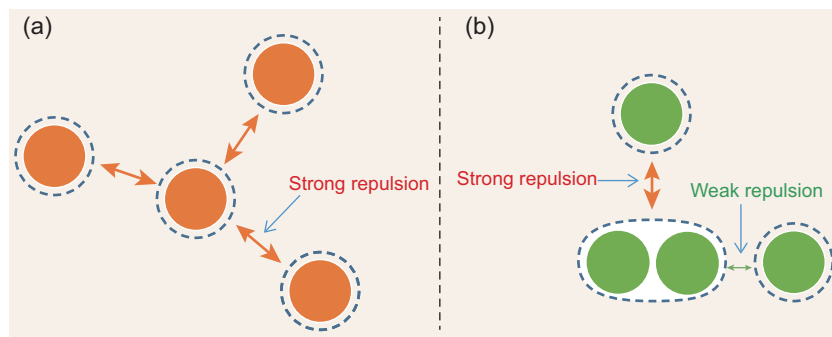

Figure 1. Schematic illustration of the proposed mechanism of the anisotropic assembly of AuNPs. (a) AuNPs are dispersed when the electrostatic repulsion is strong. (b) AuNPs form a 1D assembly when the electrostatic repulsion is weakened.
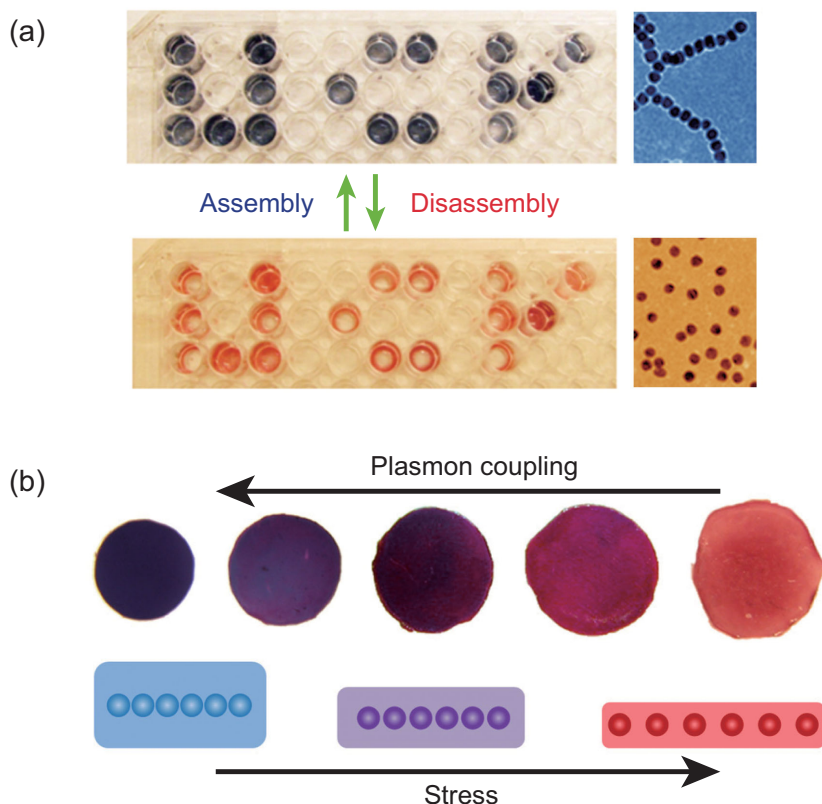
Figure 2. (a) Optical tuning through assembly and disassembly of AuNPs by controlling the ionic strength of the solution. (b) Colorimetric stress memory sensor based on the disassembly of AuNP chains embedded in a polymer film. Reproduced with permission from [5,8].

[10] or introduce different LSPR modes, which may extend the operational optical window from the visible range to UV and IR regimes. The lack of generalized techniques for transferring nanoparticle assemblies from colloidal suspension to solid substrate without destruction of the assembled structures is another challenge that limits the application of plasmonic nano-assemblies. Relevant novel strategies are highly demanded for plasmonic nano-assemblies to be applied in on-chip applications such as flexible optical devices. Since other noble metals with excellent catalytic activity could be incorporated into Au and Ag nanostructures, reversible assembly and disassembly of such superstructures are also expected to benefit the construction of novel switchable photocatalysis systems and 'smart' catalytic materials.

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