Plasmonic nanoparticle strings: threading nanoparticle chains with light

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Abstract

Light-matter interactions in the nanoscale can be efficiently controlled by novel plasmonic materials, opening the path for important techological applications in sensing, optical communications and electronics [1-3]. Several techniques, such as nanolithography and self-assembly, have been developed to fabricate and tailor the optical response of such nanomaterials. A particularly attractive approach for nanofabrication, which has not been much explored yet, consists of using light itself for laser-welding metallic nanoparticles (NPs). Here we demonstrate an efficient way to exploit light for threading gold (Au) NP strings, i.e., chains of Au nanospheres conductively connected via Au threads (cylindrical bridges between NPs) with well-controlled dimensions [4]. These strings can be exploited as the main building blocks in the design of more complex nanostructures, such as active and chiral photonic metamaterials.

The successive steps of fabrication of Au NP strings are shown schematically in Fig. 1a. Au NP clusters are first self-assembled in aqueous solutions using appropriate rigid organic molecular linkers, namely cucurbiturils (CBs), which fix the interparticle gaps with exquisite precision at 0.9 nm [5]. As the self-ssembly procedure evolves in time, disordered and linear NP chains are formed within the clusters. These chains are traced by the emergence of collective plasmonic modes that involve several NPs (Capacitive Chain Plasmons, CCP), strongly redshifted in the spectrum with respect to the individual Au NP plasmonic modes. As the particle chains are formed, the CCP modes eventually dominate the extinction spectra (Fig. 2a). These modes are accompanied by strong near-field enhancement at the interparticle gaps [6,7], as shown in Fig. 2b for a linear chain of six 50-nm Au spheres in water, illuminated by a plane wave with amplitude E_0 polarised along the chain axis (taken to be the z axis). The wavelength of these modes and the resulting near-field enhancement are very robust with respect to deviations from linearity of the chains [6,7], thus the presence of the CCP modes is maintained over kinks and turns, facilitating the use of such clusters in practical applications.

Once the CB-assisted self-assemblies have been prepared, the large intragap near-field enhancement can be exploited for threading. Illumination of the clusters with ultrafast lasers, whose wavelength coincides with that of the CCP mode, leads to non-thermal melting of Au at the gaps. In this way, Au threads connecting several particles are formed, to produce a Au NP string (Fig. 1b). The Au threads allow charge transfer within the entire NP strings, leading to the appearance of new modes at wavelengths even more to the infrared of the spectrum, that we name as Threaded Chain Plasmons (TCPs) (Figs. 1c and 2c). These modes are hybrid chain/rod modes, as can bee observed in Fig. 2d for the first two TCP modes. They exhibit a strong antenna-like character, with charge oscillations along the entire string, while large near-field enhancements at the gaps between individual NPs (around the formed Au threads) are maintained. The nature of these modes becomes even clearer by examining the phase of the z component of the electric field (Fig. 2d) for the first two TCP modes, which has the characteristics of the first and second-order antenna mode, respectively, while phase changes (which imply the presence of surface charges) can be seen at the gaps.

The evolution and the optical properties of the TCP modes depend strongly on the length of the strings and the width of the threads. The latter can be adjusted by controlling the initial nanoparticle size, the laser power and its wavelength, thus providing unique control of the threading procedure. On the other hand, while the threads are not easily accessible by electron microscopy, the excitation of TCP modes acts as proof that threading has indeed taken place. The exact thread widths can then be identified with great precision by comparing experimental and simulated extinction spectra.

In summary, we showed that ultrafast lasers can be used to fabricate Au threads, which connect the individual Au NPs in self-assembled clusters, leading to a new plasmonic unit, namely the Au NP string. Such strings, whose optical response is characterised by hybrid rod/chain plasmonic modes in the

infrared, can be controlled with great precision, and may be exploited as building blocks for novel plasmonic materials.

References

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Figures

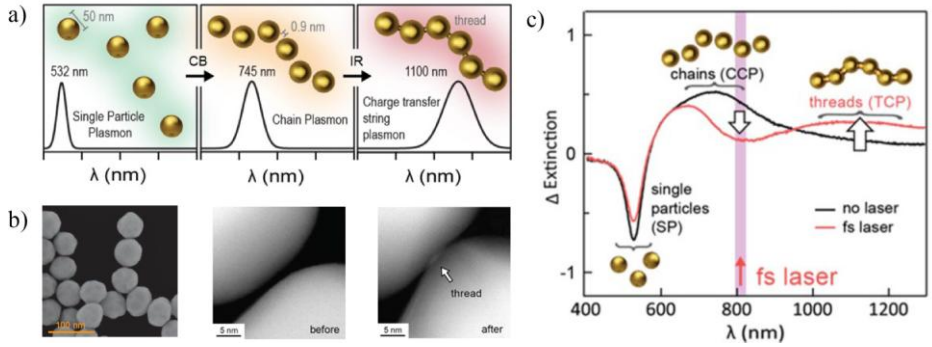

Figure 1. a) Schematic representation of the self-assembly and nano-threading procedures. At first, Au NPs are assembled into chains by appropriate molecular linkers (CBs), leading to a near-infrared capacitive chain plasmon (CCP) mode. The chains are then illuminated by ultrafast lasers, non-thermal melting of Au takes place at the gaps and Au threads connecting the NPs are formed, resulting in the excitation of threaded chain plasmon (TCP) modes in the infrared that allow charge transfer along the string of particles. b) SEM image of a Au NP string (left) and TEM images of the gap between two NPs before (middle) and after (right) threading. c) Experimental differential extinction spectra before (black curve) and after (red curve) laser illumination.

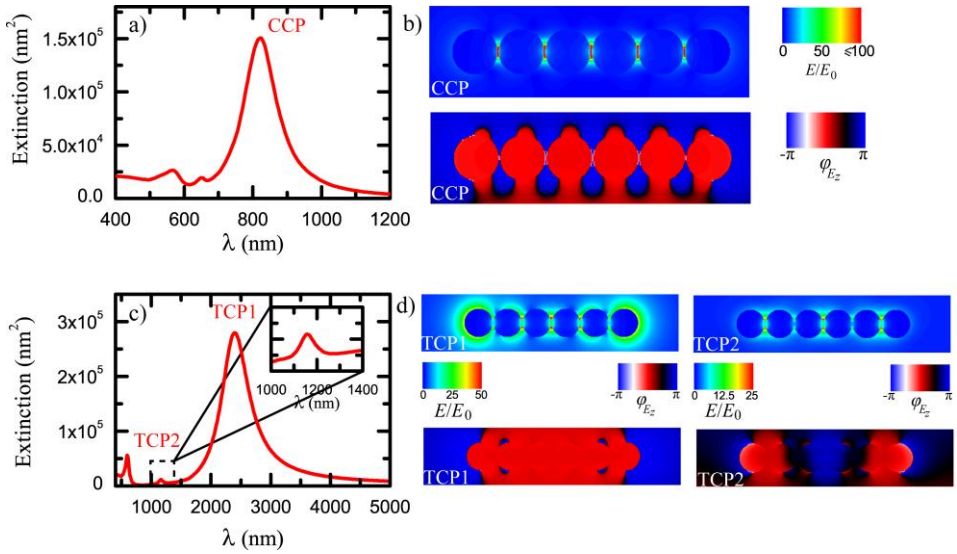

Figure 2. a) Simulated extinction spectrum of a linear chain of six CB-linked 50-nm Au NPs in water, illuminated by a plane wave polarised along the chain's axis (*z* axis). b) Contour plots of the amplitude of the electric field, *E*, normalised to the incident field, E_0, and the phase of the *z* component of the electric field (φ_{Ez}) at the wavelength of the CCP resonance (λ = 820 nm). c) Extinction spectrum of a threaded chain of six 50-nm Au NPs (thread width 12 nm). d) Contour plots of E/E_0 and φ_{Ez} at the wavelengths of the two first TCP modes (TCP1: λ = 2200 nm, left contours, and TCP2: λ = 1160 nm, right contours).