Organized Plasmonic Clusters with High Coordination Number and Extraordinary Enhancement in Surface-Enhanced Raman Scattering (SERS)**

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Noble metal nanoparticles exhibit optical excitations known as surface plasmons that produce large enhancement of the local light intensity under external illumination, particularly when the nanoparticles are arranged in closely spaced configurations.[1] The interparticle gap distance[2] plays a critical role in the generation of hotspots with high electromagnetic fields, and thus such assembled nanoparticles find application to ultrasensitive detection, for example through surface-enhanced Raman scattering[3] (SERS) and nonlinear optics, among other feats.[4] Controlled assembly using colloid chemistry is an emerging and promising field for high-yield production of metal nanoparticle clusters with small interparticle gaps.[5] However, most of the reported methods rely on the use of nucleic acids or other organic molecules as linking elements,[6] which yield long separation distances and thus weak plasmon coupling. Additionally, only simple clusters, such as dimers and trimers, have been efficiently synthesized. Herein, we report the controlled assembly of gold nanospheres into well-defined metal nanoparticle clusters with large coordination numbers (up to 7) and high symmetry. We further demonstrate ultrasensitive direct and indirect SERS sensing, thus corroborating the outstanding optical performance of these clusters with robust enhancement factors that are over three orders of magnitude higher than those of single particles.

The optical response of plasmonic particles upon light irradiation is mainly determined by particle size and shape, as well as the dielectric environment and geometrical arrangement.[6–8] Recent advances in wet-chemical synthesis enable the fabrication of nanostructures with engineered complex size, shape, and composition.[9] However, the colloidal synthesis of organized assemblies of these particles to fully exploit their plasmonic couplings remains a challenge, despite increasing efforts to produce monodisperse stable colloidal clusters. Pioneering work[6–10] demonstrated the possibility of obtaining nanoparticle dimers and trimers by using molecular linkers such as thiolated nucleic acids or other long organic molecules. This molecular linking approach is still frequently used, even though the final product is a mixture of clusters with different numbers of particles. Actually, numerous variations of this method exist for the production of homogeneous samples containing dimers and other geometries with low coordination numbers.[10b,11] With this approach a purification process is always required, typically including sedimentation,[12] electrophoresis,[13] and/or density gradient centrifugation.[14] However, the application of these clusters to plasmonics in general, and to SERS in particular, is still limited because of three severe constraints. First, the use of thiolated linkers chemically passivates the plasmonic surface, thereby inhibiting the adsorption of other target species; second, the linker itself produces a SERS signal. These issues are crucial, considering that the thiolated molecule is placed precisely at the hotspot. And finally, perhaps the most important limitation is the size of the molecule: linkers based on nucleic acids require a minimum size of approximately 10 nm, leading to interparticle distances that are too long to produce effective hotspots. To avoid this drawback, a novel approach based on the linkage and purification of dimers and subsequent in situ overgrowth was recently reported.[15] Despite the improvement, this method is still subject to vibrational contamination from the DNA linkers, and it has been only demonstrated for dimers.

Other approaches for the generation of dimers in colloidal solution include the use of asymmetric functionalization or polymer ligands. In the former, particles are functionalized with different capping agents, which can chemically bind to each other through simple reactions. The most popular choice is the functionalization of separate nanoparticle batches with amino and carboxylic groups. After mixing, carbodiimide chemistry serves to bind the two different fragments, thereby leading to formation of particle clusters.[10] This approach, however, is affected by the same problems as those observed when using DNA or organic linkers. In contrast, polymer ligands exploit electrostatic interactions between a polyelectrolyte and the particles. This method has proven effective to form nanoparticle dimers with poly(vinyl pyrrolidone),

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poly(ethylene glycol), and poly(methyl methacrylate).\[17\] The use of polymers instead of DNA or organic linkers not only allows efficiently gluing colloidal particles with smaller interparticle gaps,\[18\] but also concentrating the analytes\[19\] allowing the analyte to diffuse inside the cluster. With such considerations in mind, clusters with 2 nm gaps combine high optical coupling, generated by the strong electromagnetic fields from 50 nm particles,\[23\] and sufficient space for diffusion of small- and medium-size analytes within the gaps.

The size of the particles is also appropriate to carry out optical and SERS characterization at the single-cluster level. To this end, dilute solutions of each sample were spin-coated onto a marked glass window. The slide surfaces were imaged with SEM to localize isolated clusters with different coordination numbers. Then, the areas containing the clusters were studied by dark-field optical microspectroscopy\[24\] and SERS after retention of benzenethiol from the gas phase (Figure 2). This experiment allowed us to record the scattering spectrum and the optical enhancement from the same clusters.

Figure 3 shows measured and calculated\[25\] (gold spheres of 50 nm in diameter were considered, with the metal described through its measured dielectric function\[26\] and including a 0.6 nm coating of refractive index 1.3 to effectively represent the linking copolymer layer) Vis-NIR spectra of clusters with CNs ranging from 1 to 7. The agreement for low CNs is reasonably good, thus corroborating the optical behavior expected from plasmon hybridization and interaction between different gaps in the corresponding particle arrangements (see below). However, the comparison for CNs above 4 is less satisfactory, presumably owing to structural deformations of the clusters in the immersion oil (required to match the dielectric constants between the objective and the sample), thereby leading to more elongated arrangements that result in a strong redshift of the spectral weight. The
of additional spheres and the interaction among different gaps. While the dimer maintains a strong polarization dependence of its optical spectrum, a fully symmetrical trimer ($D_{3h}$) has, by symmetry, a polarization-isotropic extinction spectrum. This results in the two experimentally observed bands, with a resolvable distortion revealed by a shoulder in the experiment; we attribute this distortion to symmetry breaking from slight differences in the shape of the gold particles. Theoretical predictions for the tetrahedral clusters ($T_d$) show two main contributions, the electric-dipole resonance at 580 nm and the magnetic-dipole resonance around 800 nm.[27] Analogously to the trimer, both resonances are distorted by symmetry breaking in the experimental spectra. Higher coordination numbers (5 ($D_{3k}$ symmetry), 6 ($D_{4h}$), and 7 ($D_{5h}$)) present complex calculated spectra that reflect an intricate interplay between electric and magnetic multipoles in the different spherical particles, conforming by the symmetry of each cluster configuration, although the experimental spectra are strongly affected by the immersion oil, as noted above.

While much work has been invested into the optimization of dimer geometries to produce large electric field enhancements, as well as the resulting giant enhancement of SERS signals,[15,17c,28] more complex geometries have not been thoroughly analyzed. As we show below, our results demonstrate that such higher coordination clusters can be used as efficient SERS platforms. To that end, we allowed adsorption of benzenethiol, a well-known SERS probe, from the gas phase[15] onto the isolated clusters, previously localized on the marked slide. High-resolution confocal SERS was then used to study the clusters at the same positions where the dark-field microspectroscopy images had been acquired. Results for the measured optical enhancement of each structure are shown in Figure 4, normalized to the signal observed for a number of individual particles equal to the CN (enhancement = 1). All clusters exhibit the strong SERS signals characteristic of benzenethiol (C-H bending at 1022 cm$^{-1}$ and ring breathings at 1073 and 999 cm$^{-1}$). Notably, individual single particles yielded no signal, and therefore their SERS spectrum was obtained from samples containing 27 well-separated particles within the sampled area. As expected, the SERS signals of a dimer and a trimer show an intensity increase around 100- and 300-fold, respectively. These enhancement factors (EFs) with respect to non-interacting individual particles, are well-understood and ascribed to the generation of optical hotspots within the gaps formed between the particles.[15,28] For tetrahedral clusters, the SERS enhancement dramatically increases up to the level of three orders of magnitude. A similar abrupt step is observed for the trigonal bipyramid and the octahedra, while the pentagonal bipyramid reaches EFs close to 5000-fold. It should be stressed that the long-wavelength plasmon features observed in Figure 3 are displaced to the blue when the clusters are placed in air (see Figure S1 in the Supporting Information), so that the current illumination conditions (at 633 and 785 nm) are off-resonant. Furthermore, the near-field distributions show large field enhancement at the gaps between the particles (Figure 4b). This finding is consistent with a tight-binding description of the optical response of
the number of gaps results as receiving a contribution to the EF proportional to SERS. Therefore, as a first approximation, we interpret our and thus, other regions in the clusters are rather inactive for showing that the enhancement is associated with the gaps, these structures (see the Supporting Information), thus the latter is not always present at the gap center, where the field enhancement is maximum.

In summary, we have shown that by using PF68 coating and emulsion clustering it is possible to produce plasmonic nanoparticle molecules with high symmetry and coordination index, and that they can be separated by applying density gradient centrifugation. PF68 produces narrow interparticle gaps with subsequent strong optical interactions while allowing the analytes to diffuse inside the gaps, where gigantic electric fields are generated, as we have shown by directly measuring the SERS enhancement in the clusters. Our geometrical nanostructures not only open a new path for the investigation of optical interactions between nanoparticles, but they also have great potential for applications to sensing and nonlinear nanophotonics.

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Notice that $G$ increases strongly with the CN (e.g., $G = 1$, 3, 6, 9, 12, and 15 for CN = 2–7, respectively). The constant prefactor $A$ equals the EF of the dimer relative to the individual particle. We show in Figure 4c a fit of our data to this simple expression, which yields $A = 288.1 \pm 8.83$ under 633 nm excitation and $A = 98.6 \pm 9.46$ under 785 nm excitation. The smaller enhancement in the latter is expected, because the light wavelength is more displaced towards the red with respect to the airborne cluster plasmon bands (see the Supporting Information). Incidentally, the SERS EFs expected for these energies from the surface-integrated intensity enhancement calculated from MESME$^{[30]}$ at the excitation and emitted wavelengths are 2092 and 297, respectively. The smaller values observed in the experiment can be attributed to a combination of nonlocal effects$^{[31]}$ and nonuniform coverage of the gold surface by the analyte, so that the latter is not always present at the gap center, where the field enhancement is maximum.

Figure 4. Optical enhancement of nanoparticle clusters with coordination numbers from 1 to 7. a) Comparison between the enhancement factors obtained for each sample, normalized to the enhancement produced by a single particle excited with a 633 nm laser line. Inset: SERS spectra of benzenethiol on the pentagonal bipyramid (CN 7). b) Near-field intensity (log thermal scale) for low-CN clusters in air at 633 nm along planes passing by the centers of the lower spheres. The maximum intensity relative to the incident intensity $|E_{\text{inc}}|^{2}$ is 14, 10 100, 5400, and 4000 for CN = 1–4, respectively. c) Experimental data fitting with the following expression $\text{EF} = \text{CN} + AG$, where $G$ represents the number of gaps and $A$ is a constant factor reflecting the effective enhancement of the gap relative to the surface of an isolated sphere.

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