Porous plasmonic nanoparticles for surface-enhanced Raman scattering applications

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A novel strategy is used to synthesize porous gold-silver alloy nanospheres encased in ultrathin silica shells that can act as highly sensitive single-particle probes.

Gold (Au) and silver (Ag) nanoparticles are typical plasmonic nanoparticles that exhibit an intense electromagnetic field in their proximity when they are irradiated by incident light. Within these fields—known as ‘hotspots’—the Raman scattering of molecules can be magnified by many orders of magnitude (depending on the intensity of the local electric field). In this so-called surface-enhanced Raman scattering (SERS) phenomenon, the Raman scattering signals contain information relating to the bond vibrations and thus provide ‘fingerprints’ of the molecules (which enables their spectroscopic detection). In the pursuit of high-sensitivity SERS analyses, it is therefore highly desirable to specifically construct hotspots. In particular, it is thought that by integrating a high density of hotspots in a single nanoparticle, it may be possible to significantly broaden the use of the materials in many SERS analyses (especially for analytical and biomedical applications that are conducted in vitro or on live cells for on-site biosensing or imaging purposes).\textsuperscript{2} Conventional strategies for the construction of hotspots for SERS applications typically involve the synthesis of a rough surface, sharp tips, and ultrasmall nanogaps of Au and Ag nanoparticles.\textsuperscript{3–7} Great success has so far been achieved with these approaches, but there is still plenty of opportunity to further enhance the density of the hotspots within a single nanoparticle, and thus for even greater SERS sensitivity.

In the conventional hotspot construction methodologies, capping ligands (‘surfactants’) on the nanoparticles are often used to form a stable colloid (which is a prerequisite for many analytical and biomedical applications).\textsuperscript{8} Commonly, the capping ligands are organic molecules that attach onto the surface of the plasmonic Au and Ag nanoparticles. These capping ligands, however, are detrimental to the SERS performance. This is because the strongest electromagnetic field around the metal surface is located right in its proximity. This region, however, is unaccessible to other molecules of interest because it is occupied by the organic capping ligands.

To overcome this problem, we have proposed a new ‘smart’ strategy for the synthesis of colloidal, highly porous Au-Ag alloy nanospheres. In our technique, we circumvent the need for organic capping ligands by encasing the porous Au-Ag nanospheres within inorganic ultrathin silica shells, as shown in Figure 1(a). These ultrathin silica shells serve as pseudosurfactants and provide charges for the colloidal property. Moreover, the clean metal surface of the nanospheres is retained for convenient access to the hotspots by target molecules.

\textit{Figure 1.} (a) Transmission electron microscope image of porous gold-silver (Au-Ag) alloy nanospheres encased within ultrathin silica shells. Inset: Photograph of a colloidal solution of the nanospheres. (b) Numerical simulation of the electromagnetic field distribution within the porous Au-Ag alloy nanospheres. The irradiation wavelength for this simulation was 818nm. The color scale represents the electromagnetic field intensity, which is expressed in terms of the amplitude of the local and incident electromagnetic fields ($E$ and $E_0$, respectively).

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In our route for the synthesis of colloidal, highly porous Au-Ag alloy nanospheres, we use nitric acid to dealloy the Au-Ag alloy nanospheres. During this process the less stable Ag is etched away by the nitric acid, whereas the inert Au remains and reconstructs into abundant, highly interconnected nanopores. These nanopores enable significant coupling of the localized surface plasmon resonance. Greatly enhanced local electromagnetic fields can thus be created. These fields can also be confirmed through numerical simulations (using the finite-difference time-domain method), as illustrated in Figure 1(b). The high porosity of the nanopores in the nanoparticles therefore ensures a high density of hotspots for ultrasensitive SERS analysis, i.e., strong Raman signals can be emitted from the molecules that are absorbed in the nanopores.

With the high density of hotspots, combined with the clean metal surfaces, our porous Au-Ag alloy nanospheres exhibit excellent SERS properties for the detection of molecules of interest that are in low abundance. In particular, we can use the nanospheres in single-particle probes to detect molecules of interest in a local area (see Figure 2). To demonstrate this capability, we deposited the silica-encased porous Au-Ag alloy nanospheres on a silicon substrate, on which a dye of low concentration (10^{-6} M) was dried (i.e., as a model molecule to be analyzed). We then focused a laser on an individual nanosphere and detected intense Raman scattering signals from the dye. This confirmed the high sensitivity of the analysis with the single-particle probe. We calculated that the Raman scattering enhancement factor can be as high as 1.3 \times 10^7 for an off-resonant condition. We may be able to achieve an even higher sensitivity with an optimal experimental setup. In contrast, for a control experiment, individual Au and porous Au-Ag nanospheres (with a polymer as the capping ligand) emitted very weak Raman signals. Our results thus indicate that the porous Au-Ag nanospheres encased in ultrathin silica shells are superior single-particle probes and are thus promising for use in local analytics and in vitro/live cell biomedical applications.

In summary, we have designed and demonstrated a novel strategy for the synthesis of highly porous Au-Ag alloy nanospheres encased in ultrathin silica shells, for use as stable colloids. The nanopores within these particles act as resonators to focus the electromagnetic field and thus act as hotspots for SERS analyses. Our use of ultrathin silica shells as a pseudosurfactant means that we eliminate the need for conventional organic capping ligands, yet we maintain the colloidal property. In addition, we provide a clean surface for the porous Au-Ag alloy nanospheres for convenient access to the hotspots for analyte molecules. Both these characteristics of our nanospheres contribute to their outstanding SERS performance as single-particle probes. These nanospheres can thus be used to detect molecules of interest within a localized area, and they open up many opportunities for SERS-based analytical and biomedical applications. In the next stages of our research we plan to develop techniques that are based on these nanospheres for the quick analysis of contaminants in water or agricultural products, in vitro biomolecular sensing, and tracking of nanoparticles in live cells with Raman tags embedded in the nanopores.

**Figure 2.** (a) Raman spectra that illustrate the surface-enhanced Raman scattering (SERS) performance of an individual porous Au-Ag nanosphere encased within an ultrathin silica shell that is acting as a single-particle probe, in comparison with the SERS activity of a Au nanosphere and a porous Au-Ag nanosphere with an organic capping ligand. (b) Scanning electron microscope (left) and optical microscope (right) images in which the single particles used for the SERS analyses can be seen (indicated by the arrows).
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References