Three-Dimensional Reduced-Symmetry of Colloidal Plasmonic Nanoparticles

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ABSTRACT: Owing to their novel optical properties, three-dimensional plasmonic nanostructures with reduced symmetry such as a nanocrescent and a nanocup have attracted considerable current interest in biophotonic imaging and sensing. However, their practical applications have been still limited since the colloidal synthesis of such structures that allows, in principle, for in vivo application and large-scale production has not been explored yet. To date, these structures have been fabricated only on two-dimensional substrates using micro/nanofabrication techniques. Here we demonstrate an innovative way of breaking symmetry of colloidal plasmonic nanoparticles. Our strategy exploits the direct overgrowth of Au on a hybrid colloidal dimer consisting of Au and polystyrene (PS) nanoparticles without the self-nucleation of Au in an aqueous solution. Upon the overgrowth reaction, the steric crowding of PS leads to morphological evolution of the Au part in the dimer ranging from half-shell, nanocrescent to nanoshell associated with the appearance of the second plasmon absorption band in near IR. Surface-enhanced Raman scattering signal is obtained directly from the symmetry-broken nanoparticles solution as an example showing the viability of the present approach. We believe our concept represents an important step toward a wide range of biophotonic applications for optical nanoplasmonics such as targeting, sensing/imaging, gene delivery, and optical gene regulations.

KEYWORDS: Colloidal plasmonic nanoparticle, hybrid nanoparticles, reduced symmetry, selective overgrowth, colloidal synthesis, surface-enhanced Raman scattering

Three-dimensional plasmonic nanostructures with reduced symmetry, for example, a nanocrescent and a nanocup, support a wide range of novel optical phenomena, such as the nanoscale control of near-field enhancement within the structure and far-field scattering that for most of their counterparts with a higher degree of symmetry are difficult to possess. These unique optical properties have important implications in terms of their potential use in future biomedical applications. For this reason, extensive efforts have been devoted to the development and preparation of the reduced-symmetry plasmonic nanostructures. So far, such nanostructures have been only fabricated on two-dimensional (2D) substrates using a variety of clean room techniques. These 2D strategies suffer from low throughput and are not suitable for in vivo biological applications, which causes a serious bottleneck toward practical applications. On the other hand, the colloidal synthesis of such particles can be considered to be a solution that could overcome these limitations. Although colloidal nanoparticles with a high degree of structural complexity were successfully fabricated, the synthesis of reduced-symmetry metallic nanoparticles in a solution, for example, a nanocrescent, have been challenging, because, during typical colloidal synthetic procedures, the small nucleus formed at the early stage of nucleation becomes the starting point for further structural evolution, thus generating colloidal nanostructures with a point of symmetry (see Supporting Information Figure S1).

Here we describe a solution based on the concept of direct overgrowth of a metal on a colloidal metal/nonmetal dimer to synthesize symmetry-broken colloidal plasmonic nanoparticles. Our solution involves two consecutive steps and is outlined in Figure 1a. The synthesis of colloidal gold nanoparticles with reduced symmetry starts with the preparation of uniform colloidal gold/polystyrene (Au/PS) hybrid dimers followed by the most important step, the direct overgrowth of Au on the...
hybrid dimer, by avoiding the self-nucleation of Au in an aqueous solution with the precise control of overgrowth conditions. Upon the overgrowth, the PS part in the dimer (Figure 1b(i)) provides steric crowding, giving rise to the anisotropic evolution of the external morphology of the Au part (Figure 1b(ii)). In the course of the overgrowth, we found that three factors including the type of reducing agent, the concentration of Au precursor (i.e., HAuCl₄), and the size of PS are critical for both the success of the overgrowth reaction and the final morphology of the resulting Au nanoparticle. Therefore, the effects of the above three factors on this reaction are systematically examined.

Au/PS hybrid dimers consisting of ca. 50 nm Au and ca. 110 nm PS nanoparticles with spherical shape were synthesized by a previously reported precipitation polymerization method. The dimers are obtained in high yield (>90%). The Au/PS colloidal dimer is stabilized with negatively charged molecules (citrate (C₆H₅O(COO)₃⁻) and sulfate (SO₄²⁻) for Au and PS nanoparticles, respectively). The key to the success of our strategy is to avoid the self-nucleation of Au in a solution during the overgrowth reaction. First, we investigate the type of reducing agents that can promote the overgrowth of Au on the colloidal dimers while keeping the self-nucleation minimum. In general, reducing agents such as sodium citrate, ascorbic acid (AA), mercaptosuccinic acid (MSA), and hydroxylamine hydrochloride (HAHC) have been widely used in the reduction of HAuCl₄ (i.e., Au³⁺ → Au⁰). When using citrate (a relatively strong reducing agent), as expected, the self-nucleation in a solution preferentially occurs over the overgrowth of Au on the dimers. In cases where AA and MSA, which are mild reducing agents, are used, considerable self-nucleation along with the overgrowth is still observed (data not shown). Interestingly, it is found that only HAHC among mild reducing agents used can successfully induce the overgrowth of Au on the surface of the dimer without the self-nucleation. These results can be attributed to the electrostatic interaction between the reducing agent and the dimer. HAHC contains a positively charged amine group (H₃N⁺), whereas both AA and MSA exhibit negative charge due to carboxyl group (COO⁻). Since the Au/PS colloidal dimer is stabilized with negatively charged molecules, the positively charged HAHC could access to the surface of the dimer more easily than the others.

Having shown that HAHC can induce the overgrowth of Au on the Au/PS dimer, we next examine the degree of the

Figure 1. Schematic representation for the synthesis of reduced-symmetry colloidal Au nanoparticle. (a) Schematic illustration of direct overgrowth procedure to reduce the symmetry of Au nanoparticle in an aqueous solution. Well-defined uniform Au/PS dimer is prepared first and direct overgrowth of Au on the dimer is then achieved by adding HAuCl₄ and a reducing agent. (b) Representative TEM images of Au/PS dimer (i) and an overgrown nanoparticle (ii). All scale bars are 50 nm.

Figure 2. TEM images of the overgrown nanoparticles and their calculated percent coverage of Au on PS. The TEM images show (a) Au/PS dimers and (b−e) the overgrown nanoparticles synthesized by varying m values. All scale bars are 100 nm. Insets provide the most probable particle with a higher magnification (scale bars are 50 nm). (f) Variations of calculated percent coverage of Au on the PS part as a function of m. When m is (b) 0.2, (c) 0.5, (d) 1, and (e) 2, the coverage of Au on the PS part in each sample show 3, 16, 31, and 68%, respectively. Each of percent coverage of Au on the PS part is calculated from the average of 30−40 overgrown nanoparticles shown in TEM image. Error bars correspond to standard deviations.
overgrowth by varying the amount of HAuCl₄ added to the overgrowth solution. For convenience, m is defined by the ratio of Au³⁺ concentration used for the preparation of the Au/PS dimers to Au³⁺ concentration in the overgrowth solution. Transmission electron microscopy (TEM) image of Figure 2a shows the Au/PS dimers and Figure 2b–e shows TEM images of the overgrown nanoparticles synthesized under different m values. Morphological changes in the Au part of the dimer can be roughly quantified by measuring the coverage of Au on the PS part. The percent coverage of Au on the PS part is defined as the portion of PS surface covered with Au compared to the entire PS surface area (for more details, see Supporting Information Figure S2). Only overgrown nanoparticles clearly showing two parts of Au and PS in TEM images (i.e., 2D projection images) are taken into consideration. According to our calculation protocol, the coverage of Au in the Au/PS dimers before the overgrowth is estimated to be about 1%. As m increases, the percent coverage of Au on the PS part also increases (Figure 2f). When m is 0.2 and 0.5, the overgrowth of Au uniformly occurs over the entire surface of Au part in the Au/PS dimer and the percent coverage of Au on the PS part slightly increases to 3 and 16%, respectively (Figure 2g). At m of 1, Au starts to significantly cover the PS part, reaching the coverage of 31%, and the morphology of the overgrown nanoparticles is close to half-shell as shown in Figure 2d. When m is 2, the percent coverage increases up to 68% and the structure of the Au part evolves to crescentlike shape (Figure 2e). In the case where m exceeds 2, the PS part is completely covered with Au, forming full nanoshell. The high-resolution TEM images clearly show the existence of {111}planes of Au (see Supporting Information Figure S3).

From the TEM images of Figure 2, it is shown that overall overgrowth proceeds through two different ways. In the early stage, the overgrowth of Au on the Au part of the dimer is dominant. However, in the subsequent stage, the overgrowth leads to the wetting of Au on the PS part. On the basis of these observations, we propose a selective overgrowth mechanism for the Au/PS dimer (see Supporting Information Figure S4). Since the Au part in the dimer is negatively charged and could act as nucleation center, the overgrowth of Au occurs throughout the exposed surface of the Au part at the beginning. As the overgrowth of Au on the Au part proceeds, the surface charge of the Au part gradually changes from negative to positive due to the exchange of stabilizers (citrate to HAHC) at the initial stage. Therefore, it is difficult for positively charged HAHC to access to the Au part due to electrostatic repulsion at the later stage. Instead, HAHC could easily approach the surface of negatively charged PS part including the boundary between two parts. Owing to this, the reduction of Au ion could occur along the boundary to the PS part, allowing Au to eventually cover the entire surface of the Au/PS dimer.

The observed morphological changes of the Au nanoparticles are also correlated with UV–vis absorbance spectra (Figure 3). At m of 0.2, the redshift of the plasmon absorption peak to 560 nm with broadening of the plasmon bandwidth is observed, which can be mainly attributed to the increase in the size of the Au part. In the case where m is 0.5, the main plasmon absorption band shifts to 571 nm and a new absorption band appears around 730 nm. Further increase of m (from 1 to 2) induces the redshifts of plasmon absorption band from 573 to 581 nm. In addition, their second absorption bands are clearly observed in 757 and 794 nm, respectively. Both the increased absorption and the appearance of additional peak in near-IR range well support the symmetry breaking of the colloidal dimers during the overgrowth. It should be noted that the overgrowth on Au/PS dimer with PS of 75 nm gave broad plasmon band at longer wavelength (see Supporting Information Figure S5).

Since the size of the PS part is expected to strongly affect the morphology of the Au part, we investigate the effect of PS size on the overgrown Au nanoparticles. To test this, Au/PS dimers with three different sizes of PS (60, 110, and 200 nm) were prepared by changing the polymerization time (2, 10, and 20 min.) of PS monomers. The minimum size of PS part is found to be around 60 nm because the shape of PS is not defined as a sphere before 2 min of polymerization. Figure 4a–c shows representative TEM images of the Au/PS dimers (left) prepared with different sizes of PS particles and the resulting nanoparticles after the overgrowth (right). All scale bars are 50 nm. m is 0.5 when the overgrowth reaction is performed using the Au/PS dimers containing 60 nm of PS and m is 2 when the size of PS is 110 and 200 nm. (d) Changes of percent coverage of Au (left y-axis) depending on the size of PS (right y-axis) controlled by the polymerization time of PS (x-axis). Each of percent coverage of Au on the PS part is calculated from the average of 30 nanoparticles shown in TEM images and error bars are standard deviations.
is reduced by the two-thirds (from 100 to 68%). In the case of Au/PS dimer with a 200 nm PS part, the overgrowth of Au progresses in a manner of dewetting the PS part, which results in the significant reduction of Au coverage to 10% (Figure 4c).

To highlight the advantage of our colloidal reduced-symmetry Au nanoparticles (i.e., the potentials toward in vivo imaging probes), we measured surface-enhanced Raman scattering (SERS) directly from the Au nanoparticles solutions. SERS signals of 100 µM Rhodamine 6G (R6G) for two different colloidal Au nanoparticles were collected by illuminating 785 nm laser. The crescentlike reduced-symmetry Au nanoparticles (n = 2, with additional plasmon absorption peak at around 785 nm (see Figure 3) and 40 nm spherical Au nanoparticles (as a control) with plasmon absorption at 525 nm were used. The representative R6G Raman peaks, including 611.43, 774.45, 1188.39, 1313.91, 1365.71, and 1516.07 cm⁻¹, are marked with asterisks on the SERS spectra of Figure 5.

When illuminating the laser of 785 nm to the crescentlike Au nanoparticle solution, strong SERS signal of R6G molecule is clearly detected, as shown in Figure 5a. In the case of spherical Au nanoparticle, very weak SERS signal of R6G is observed, although the number of spherical nanoparticles in solution is 2.45 times larger than that of the crescentlike nanoparticles (Figure 5b). This weak signal is attributed to the nonmatching between the plasmon resonance wavelength of Au nanosphere and the wavelength of laser used. Note that Raman signal of pure R6G solution without Au nanoparticles is not observed (Figure 5c).

To address the main cause of SERS we observed, we additionally prepared nanoparticles with rough surfaces (via the overgrowth of Au on 50 nm spherical gold nanoparticle) under the identical overgrowth condition for our crescentlike nanoparticles and compared SERS signals of R6G (see Supporting Information Figure S6). Irrespective of no plasmon band near 785 nm, the SERS signal from the roughened nanoparticle is noticeable. Consequently, it is reasonable that the SERS enhancement obtained from our crescentlike nanoparticle is attributable to both the electromagnetic field enhancement in near IR regime due to the reduced symmetry and the surface roughness including the edge of nanocrescent.

For specific applications (e.g., optical manipulation of drug delivery), three-dimensional reduced-symmetry Au nanoparticles without PS part would be more desirable. When the particles are treated with tetrahydrofuran (THF)/ethanol mixture for 1 day, the complete removal of PS is achieved, as shown in Supporting Information Figure S7.

In summary, we have shown an innovative method for three-dimensional reduced symmetry colloidal plasmonic nanoparticles. Our concept takes advantage of the direct overgrowth of a metal on a colloidal dimer consisting of the metal and nonmetal nanoparticles. As a proof-of-concept, the selective overgrowth of Au on uniform colloidal Au/PS dimers is successfully achieved without any self-nucleation of Au in a solution by controlling overgrowth conditions such as type of reducing agents, the concentration of added HAuCl₄, and the size of PS. Type of reducing agents (charge and strength) plays critical role to avoid the self-nucleation in a solution and facilitate the direct overgrowth of Au on the dimer. In addition, 3D reduced-symmetry Au nanoparticles with different morphologies of half-shell, nanocrescent, and nanoshell are obtained by controlling the concentration of added HAuCl₄ during the overgrowth. Such morphological evolution is well correlated with the spectral change in plasmon absorption band. As one good demonstration of the potentials toward in vivo imaging probes, SERS signal of R6G with 785 nm laser can be obtained directly from the colloidal crescentlike nanoparticles. We believe that our concept provides noteworthy implications across a number of disciplines toward practical applications of 3D plasmonic nanoparticles with reduced symmetry in that it allows, in principle, for the large-scale production and in vivo application.

ASSOCIATED CONTENT

5 Supporting Information

Supporting Information includes experimental methods, calculation of the percent coverage of Au, high-resolution TEM images, description of overgrowth mechanism, morphological and optical characterization of the overgrown nanoparticles from Au/PS dimer, comparison of crescentlike gold nanoparticle with 75 nm roughened gold nanosphere, and removal of PS in the overgrown particle. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MEST) (No. 2011-0015749) and the Sogang University research grant.
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