Starfruit-Shaped Gold Nanorods and Nanowires: Synthesis and SERS Characterization

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Supporting Information

ABSTRACT: Recently, branched and star-shaped gold nanoparticles have received significant attention for their unique optical and electronic properties, but most examples of such nanoparticles have a zero-dimensional shape with varying numbers of branches coming from a quasi-spherical core. This report details the first examples of higher-order penta-branched gold particles including rod-, wire-, and platelike structures which have a uniquely periodic starfruitlike morphology. These nanoparticles are synthesized in the presence of silver ions by a seed-mediated approach based on utilizing highly purified pentahedrally twinned gold nanorods and nanowires as seed particles. The extent of the growth can be varied, leading to shifts in the plasmon resonances of the particles. In addition, the application of the starfruit rods for surface-enhanced Raman spectroscopy (SERS) is demonstrated.

INTRODUCTION

Branched gold nanoparticles have received a great amount of interest for their unusual optical and plasmonic properties. Specifically, the unique shape of these gold nanoparticles, otherwise known as star-shaped nanoparticles or nanostars, leads to strong absorptions in the near-IR regime and to extremely high electric field intensities at their tips, which, in turn, can result in very high activity in surface-enhanced Raman spectroscopy (SERS). To the point where zeptomole analyte detection is possible. Sensitive SERS detection shows great promise as an analytical platform especially in biological systems. A number of techniques can be used to synthesize nanostars in aqueous solutions with a variety of surface capping agents and gold reducing agents using both seed-mediated as well as one-pot syntheses. The seed-mediated growth of various gold nanoparticles is quite popular due to the increased degree of control and access to different morphologies. For instance, synthesis of anisotropic, one-dimensional structures such as gold nanorods with either single-crystalline or pentahedrally twinned structure proceeds via a seed-mediated growth. Although there have been many reported methods of nanostar syntheses, almost all of them form zero-dimensional structures which have a spherical base with different numbers of branches coming from the center. One-dimensional, anisotropic gold nanoparticles such as gold nanorods and gold nanowires have received a great deal of attention for their possible electronic, catalytic, and biomedical applications. Combining these properties with the unique capabilities of star-shaped particles could be beneficial, but no examples of one-dimensional structures with a star-shape cross-section have been reported. Most recently, Wu and co-workers reported the synthesis of penta-branched gold nanoparticles from pentagonally twinned bipyramids. However, the synthesis of more extended one-dimensional star-shaped particles such as nanorods or nanowires may offer anisotropic plasmonic properties.

This report describes the synthesis of gold nanorods (NRs), gold mesorods (MRs), and gold nanowires (NWs) with a well-defined pentagonal star cross-section. By applying the silver-mediated overgrowth conditions reported earlier, but changing the seed particles from spheres to gold nanorods and gold nanowires, which have been isolated and highly purified, a controlled synthesis of rods and wires with a unique, periodic starfruit morphology has been developed. The enhanced SERS activity of the starfruit structure has also been explored.

MATERIALS AND METHODS

Materials and Instrumentation. Sodium borohydride, silver nitrate, ascorbic acid, copper(II) sulfate, iron(II) sulfate, nickel(II) sulfate, and mercury(II) acetate were purchased from Sigma-Aldrich. Chloroauroic acid and cetyltrimethylammonium bromide (CTAB) were purchased from Acros Organics. Scanning electron microscopy (SEM) was performed on an FEI Quanta 400 instrument. A Hitachi SU6600 FE-SEM apparatus was used for high-resolution scanning electron microscopy (SEM). TEM images were collected on a JEOL 1230 TEM instrument. UV−vis absorbance spectra were gathered on a Cary 3000 UV−vis-NIR spectrophotometer. Raman spectra were collected on a Renishaw inVia Raman microscope.

Synthesis of Pentahedrally Twinned Gold Nanorods. Pentahedrally twinned gold nanorods (PNR) were used as the seed particles for further overgrowth in the presence of silver nitrate.

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Synthesis and purification of these particles was carried out according to a previously published procedure.35

**Synthesis of Starfruit-Shaped Gold Mesorods.** In a typical synthesis, a 100 mL Au(III) solution (0.25 mM HAuCl₄, 0.1 M CTAB) was combined with 1 mL AgNO₃ solution (30 mM). To this was added 0.55 mL of ascorbic acid solution (0.1 M) and the flask was shaken continuously in order to induce stirring of the flask’s content (hand-stirred). Immediately, 0.5 mL of PNR seed solution (c = 1 mg/mL) was added and stirred. The solution was hand-stirred several times during the first few hours and the growth was allowed to continue for 24 h. Precipitated mesorods were isolated by carefully pouring off the supernatant and redispersing the precipitate into 0.1 M CTAB aqueous solution.

**Synthesis of Starfruit-Shaped Gold Nanowires.** Gold nanowires were synthesized according to a previously published procedure.36 A 10 mL Au(III) solution (0.25 mM HAuCl₄, 0.1 M CTAB) was combined with 0.1 mL of AgNO₃ solution (30 mM). To this was added 55 μL of ascorbic acid solution (0.1 M), and the mixture was hand-stirred rapidly. Immediately, 1 mL of nanowire solution (~0.5 mg nanowires) was added and stirred. The solution was hand-stirred several times during the first few hours, and the growth was allowed to continue for 24 h. Precipitated nanowires were isolated by carefully pouring off the supernatant and redispersing into 0.1 M CTAB solution.

**Surface-Enhanced Raman Spectroscopy.** A 20 nm gold layer was evaporated onto a glass slide using an E-beam evaporator. The slide was dipped into an ethanolic solution of 1,4-benzendithiol (1 mM) for 30 min and then rinsed with ethanol and dried. A drop of starfruit mesorod solution was then dried onto the slide and rinsed multiple times with ethanol to remove any CTAB before analysis.

## RESULTS AND DISCUSSION

Recently, the synthesis of highly pure pentahedrally twinned gold nanorods was described in detail by our group.35 This procedure involves a dissolution-based purification procedure that removes nearly all morphological impurities from a nonsilver assisted gold nanorod synthesis. Figure 1 shows a TEM image of the purified nanorods and demonstrates the extremely high purity of these nanoparticles which makes them highly desirable for use as one-dimensional seed particles in a further overgrowth step.37−41 They have a length and width of about 300 and 20 nm, respectively, leading to an aspect ratio of 15 and contain the pentahedrally twinned structure which should make them amenable to the formation of pentabranched nanoparticles with a mechanism analogous to the side growth of pentagonal bipyramids described by Wu and coworkers.39

Further growth of these seed nanorods follows the general scheme shown in Scheme 1. Gold nanorods are introduced into a growth solution containing CTAB, Au⁺ ions, and silver nitrate. This solution is then allowed to grow and settle overnight, after which the resulting structures can be easily isolated by decanting the supernatant. TEM imaging revealed that the above conditions result in the formation of starfruitlike nanorods shown in Figure 2. This overgrowth step results in a significant increase in length to about 550 nm and an increase in width to 55 nm leading to an aspect ratio of 10, which is still quite high, though lower than the starting seed nanorods with an accompanying increase in roughness due to the beginning evolution of the starfruit morphology. The uniformity in shape and size of these structures has clearly been conserved from the starting nanorod seeds.

With this amount of overgrowth, it is still difficult to clearly see the penta-branched structure which is evolving. Increasing the volume of the growth solution leads to the formation of much larger rodlike structures with length approaching 1 μm and the diameter around 300 nm (mesorods) which appear to show an ordered penta-branched structure as seen in Figure 3. Most of these structures display sharp needlelike tips at the ends of the rods, but also have a core segment which contains roughened pentagonal branches. The low-magnification SEM images of these starfruit MRs shown in Figure 3A demonstrate the high yield and uniformity of this overgrowth procedure which leads to rodlike structures with starfruit morphology. Two factors are important in order to achieve this result. First, the nanorod seeds have been purified to an extremely high level leading to a uniform seed solution with almost no other shape impurities. If impurities such as platelets or spherical particles are present in the seed due to incomplete purification of the PNRs, they are carried through directly into the products, leading to the presence of various nonuniform shapes as seen in Figure S1 (see the Supporting Information). Second, the growth conditions used in this protocol do not lead to new nucleation of particles which could result in the formation of other morphologies. This is made possible by the use of the relatively weak reducing agent ascorbic acid that reduces Au(III) ions only to the Au(I) state in the presence of CTAB while further reduction is catalyzed by the surface of preformed seed nanostructures that are present in solution. Due to their size, the MRs tend to settle out of solution within 1−2 h and can be brought back into solution indefinitely as long as the concentration of CTAB in solution remains high enough. MRs can also be redispersed into pure water to reduce the concentration of CTAB in solution. Under these conditions, the rate of MR precipitation is lower but, once precipitated, may lead to irreversible aggregation if MRs are stored in this way.

It is difficult to confirm the penta-branched starfruit morphology of the MRs from particles which lay flat on a substrate. Therefore, it was necessary to achieve a standing orientation to better see the cross-section of the particles. By casting a concentrated solution of the MRs directly onto a nonuniform aluminum stub, it was possible to find areas with multiple starfruit MRs standing on their tips as seen in Figure 4. The MRs five-point star cross-section is clearly visible in these high-resolution SEM images which also reveal a higher degree
of order than is initially expected from previous images. The roughness along the tips which initially appears to be random is revealed to be the result of uniformly spaced ridges which create the impression of a “stack” of stars culminating in a uniform star-shaped “arrow head”. In addition, the surface of the MRs appears not to be perfectly smooth or faceted, instead showing a consistent roughness along the entire structure. These images, along with previous ones, also demonstrate the presence of a variety of tip structures. Many contain a broken-off tip, while some exhibit random spiky overgrowths. The amount of these spiky overgrowths can be increased greatly by

*Nanorod seeds are added to an ascorbic acid reduced gold growth solution containing silver nitrate. Growth continues for several hours, and the product is isolated after sedimentation.*

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**Figure 2.** Representative SEM image of starfruit nanorods with an aspect ratio 10. The uniformity of the sample in terms of size and shape is clearly evident.

**Figure 3.** SEM images of starfruit mesorods. The low magnification image (A) demonstrates the monodispersity of the sample. The roughened, branched structure of the MRs is visible in the high magnification image (B). Scale bars are (A) 5 μM and (B) 500 nm.

**Figure 4.** Low magnification (A) and high magnification (B) SEM images showing periodic five-point star cross section of starfruit MRs.
simply increasing the amount of reducing agent during the overgrowth process.

The previous report demonstrated that silver was the key element in the synthesis of the starfruit morphology,\textsuperscript{19} and its importance has been noted in other nanostar syntheses.\textsuperscript{18,20} By varying both the cation and anion added to the synthesis, it was confirmed that the silver cation is the crucial structure directing agent. On the other hand, varying the nature of counteranion by using silver sulfate, silver triflate, or silver acetate rather than silver nitrate showed no difference as evidenced by the SEM micrographs in Figure S2 (see the Supporting Information), indicating that the counterion is not playing an important role in this synthesis.

Various metal salts beside silver were tested including iron sulfate, copper sulfate, nickel sulfate, as well as mercury acetate, and the effects of these additives were analyzed by SEM (Figure S). The starfruit morphology is clearly not present in any of these cases, resulting in generally much smoother particles. In the case of nickel and mercury, the appearance is similar to the case when no extra metal additive is present, and more details of this synthesis will be published at a later time. Iron sulfate addition leads to highly rounded morphology which displays very little faceting, but still maintains a distinct rodlike shape. Copper sulfate addition leads to a similar rounded morphology, but the overall shape is more reminiscent of a smoothed bipyramid than a rod. On the basis of these results, it is clear that silver is unique in affecting gold nanoparticle overgrowth in this procedure even though copper and mercury should be reduced by ascorbic acid to the +1 oxidation state similar to that of silver. It may be that the specific ability of silver to undergo underpotential deposition onto or the particular binding affinity of the silver—CTAB complex with the gold particle leads to its unique structure-directing capability in this synthesis.\textsuperscript{42} In addition, determination of the silver content of

Figure 5. SEM micrographs of rods overgrowth in the presence of iron(II) sulfate (A), copper(II) sulfate (B), nickel(II) sulfate (C), and mercury(II) acetate (D). No starfruit morphology is evident. Scale bars are (A) 1 μm, (B) 3 μm, (C) 1 μm, and (D) 10 μm.

Figure 6. SEM images of plate-like nanoparticles synthesized under low silver condition (A) and starfruit gold nanowires (B). Scale bars are (A) 1 and (B) 2 μm.
the starfruit MRs by ICP-OES showed that no silver was present in the final particles, indicating its role as a structure-directing agent rather than leading to the formation of bimetallic particles.

Next, the effect of the amount of silver on the starfruit MR overgrowth was investigated by varying the concentration of silver nitrate in the growth solution from 5.9 to 590 μM. Above a concentration of about 59 μM silver cation, the starfruit morphology is completely formed with little difference between the various concentrations. Higher concentrations of silver led to its precipitation from solution. At the lowest concentration, however, a different morphology is present, shown in Figure 6A, which appears to lose the 5-fold symmetry and instead has only two major spines which appear to be fully formed, although the other spines can still be seen, resulting in a platelike morphology.

Given the success of the seed-mediated synthesis of starfruit structures from penta-twinned nanorods, it was hypothesized that this growth procedure could be applied to much longer seeds with similar penta-twinned morphology. Specifically, gold nanowires can be synthesized which have the same pentahedral cross-section as the nanorod seeds used earlier. Using nanowires as the seeds under similar silver-containing overgrowth conditions led to uniform overgrowth of the penta-branched starfruit wires (∼10 μm) with a concomitant increase in diameter from about 50 to 200 nm, as seen in Figure 6B, which is the first example of such structures. Higher magnification imaging of the starfruit wires can be found in Figure S3 in the Supporting Information. This clearly shows the versatility of the silver-mediated starfruit overgrowth procedure which appears to be applicable to any pentahedrally twinned 1D gold seeds. The presence of the starfruit morphology could have an effect on the optical and electronic properties of gold nanowires. For example, the effect of these structures on plasmon propagation along the nanowire is currently under investigation.

The starfruit particles were further characterized with UV-visible absorption spectroscopy shown in Figure 7. Amplification of PNRs with a small amount of gold in the presence of silver ions led to a change in color from brownish to reddish resulting from the red-shifting of the transverse plasmon band from 500 to 555 nm. Full growth into starfruit MRs leads to a further red-shifting of the band to 630 nm and a change to a blue-green color (Figure 7).

Finally, preliminary application of the starfruit particles to surface enhanced Raman spectroscopy (SERS) was investigated. It is expected that the increased surface roughness as well as the presence of sharp tips could lead to much higher SERS activity compared to smooth particles of a similar size and length. In general, SERS measurements can be complicated by the presence of particle aggregates which can lead to very high enhancements. In order to study the SERS activity of individual particles, a procedure was developed to image the area of analysis by optical microscopy and then locate the exact same area under SEM to ensure that each particle measured was indeed individual and sufficiently separated from all neighboring particles given the 2 μm spot size of the Raman laser. SERS measurements were obtained following a procedure similar to that of Rodriguez-Lorenzo et al. which takes advantage of electric field enhancement between a nanoparticle and a gold surface with a 1,4-benzenedithiol coating which plays the role of the SERS active molecule as well as the spacer between the gold surface and the particle. Multiple single particle measurements were performed on individual starfruit MRs as well as smooth MRs, and the average SERS spectrum shown in Figure 8 demonstrates significant enhancement of the bands at 1555, 1065, and 355 cm⁻¹. There is an approximately 25-fold signal enhancement for the starfruit MRs as compared to the smooth structures, which most likely originates from the hot spots generated between the roughened branches coming in contact with the gold surface, even though the smooth MRs likely contact more benzenedithiol molecules. This data indicate the potential utility of the starfruit morphology for SERS applications and detection of various analytes.

**CONCLUSIONS**

This report describes the synthesis of starfruit shaped gold nanostructures of various dimensions by utilizing a seed-mediated synthesis wherein the exact nature and purity of the
1D seed particles is tightly controlled. Highly purified pentagonally twinned nanorods can be amplified in the presence of silver ions to form very pure starfruit nanorods or mesorods depending on the amount of gold growth solution and using gold nanowires as a seed allows the creation of starfruit-shaped nanowires. Starfruit mesorods are shown to have enhanced SERS activity compared to similarly sized rods with smooth surface. The synthetic scheme presented here expands the types of star-shaped particles from simple spherical objects to one-dimensional particles ranging from nanorods to nanowires with lengths over 10 μm and could have applications in SERS detection and plasmonic materials.

**ASSOCIATED CONTENT**

Supporting Information
Additional SEM images. 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.

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**REFERENCES**


