Scalable Super-Resolution Synthesis of Core-Vest Composites Assisted by Surface Plasmons


Department of Electrical & Computer Engineering, University of Toronto, Toronto, Ontario MSS 3G4, Canada
Department of Chemical & Biomolecular Engineering and Berkeley Sensor & Actuator Center, University of California at Berkeley, Berkeley, California 94720, United States
Department of Physics, University of California at Berkeley, Berkeley, California 94720, United States
Department of Chemistry, University of Toronto, Toronto, Ontario MSS 3H6, Canada
Department of Materials Science & Engineering, University of Toronto, Toronto, Ontario MSS 3E4, Canada

ABSTRACT: The behavior of composite nanostructures depends on both size and elemental composition. Accordingly, concurrent control of size, shape, and composition of nanoparticles is key to tuning their functionality. In typical core–shell nanoparticles, the high degree of symmetry during shell formation results in fully encapsulated cores with severed access to the surroundings. We commingle light parameters (wavelength, intensity, and pulse duration) with the physical properties of nanoparticles (size, shape, and composition) to form hitherto unrealized core-vest composite nanostructures (CVNs). Unlike typical core–shell nanoparticles, the high symmetry of simple shapes, such as nanospheres, leaves little choice in terms of available modes that can be excited. It is known that the plasmon resonance of a complex nanoparticle is compounded from the resonances of its parts. Accordingly, the plasmonic core of the resulting CVNs selectively maintains physical access to its surrounding. Tunable variations in local temperature profiles \( \geq 50 \) °C are plasmonically induced over starburst-shaped nanoparticles as small as \( 50–100 \) nm. These temperature variations result in CVNs where the shell coverage mirrors the temperature variations. The precision thus offered individually tailors access pathways of the core and the shell.

The ability to batch-produce designer nanoparticles is severely constrained by shortcomings in scalable fabrication processes. Thermal fluctuations introduce intrinsic randomness in bottom-up approaches, while top-down methods are constrained by lithographic techniques. Thus scalable fabrication of nanocomposites has been limited to the simplest shapes, such as spherical core–shell nanoparticles. However, if energy (or matter) could be channeled with super-resolution, then more complex architectures would become possible, such as partial cladding of complex nanoparticles with nontrivial shapes (hereafter referred to as core-vest nanostructures or CVNs). We show here that surface plasmons (SPs), which result from the coupling of light with the free electrons in a metal, can be harnessed to achieve a variety of preprogrammed designer core-vest nanostructures. By localizing the energy carried by far-field radiation onto nanometer-sized regions, SPs effectively create hot blueprints that drive the self-assembly of composite structures. Here nanovests made of titania formed around gold nanostars are synthesized and characterized to illustrate the concept.

The rationale for the choice of nanostars to implement our design is that they present a variety of plasmonic modes that can be excited to create the desired heating pattern that drives the localized chemical synthesis on the nanoscale; in contrast, the high symmetry of simple shapes, such as nanospheres, leaves little choice in terms of available modes that can be excited. It is known that the plasmon resonance of a complex nanoparticle is compounded from the resonances of its parts. Accordingly, the plasmon resonance of a gold nanostar results from the hybridization of the modes of its spherical core and of the spikes, which are generally at different energies. While the coupling of light to the nanoparticle serves as the information transfer channel from the macro-world (top) to the nanoworld (bottom), these energy eigenstates allow us to direct the nanoscale heat pattern on the subparticle scale.

In the present work, we explore two essential questions: (a) Can far-field energy be directed into super-resolution SP patterns over the nanoparticles? (b) Can the resulting super-resolution SP patterns direct bottom-up self-assembly and produce novel CVN designs?

Figure 1a shows the calculated unimodal absorption cross-section for a spherical gold particle (35 nm in diameter) along
with the heat dissipation at the excitation frequency of 530 nm. In comparison, Figure 1b shows a nanostar with a spike base-to-height ratio of 1:2 and its absorption spectrum, which displays multiple resonant peaks. The three peaks clearly illustrate the unique excitation patterns (heat dissipation profiles) corresponding to the spikes and valleys that can be preferentially excited using the corresponding wavelength. This results in a controllable heat distribution over the particle through the choice of excitation wavelength. Figure 1 insets b1, b2, and b3 demonstrate that heat can indeed be concentrated in various positions over the particle, for example, in the valleys (b1) using excitation wavelength of 517 nm, as opposed to spike tips (b3), using excitation wavelength of 950 nm. This preferential excitation is a powerfully precise tool for local SP activated chemistry. Accordingly, excitation at the corresponding wavelength can lead to the synthesis of the CVNs shown in Figure 1c.

Figure 1c shows the same Au nanostar with the valleys covered with a TiO2 layer (5 nm thickness) while the tips are bare. The presence of the partial dielectric shell alters the response of the particle, whose new modes are depicted in the absorption plot with three main peaks c1, c2, and c3 and the corresponding heat dissipation patterns at 533, 800, and 980 nm, respectively. In this case, the excitation frequency of interest is now at 800 nm where the maximum field distribution is seen at the gold--dielectric interface and inside TiO2, that is, plasmonically enhanced light–matter interaction within the TiO2 shell. By way of contrast, indiscriminate coverage of the nanostar core (shown in Figure 1d) by mere heating of the entire nanostar core without wavelength selectivity results in the suppression of the peak, which yields maximum interaction with the shell. This difference in the heating pattern of a partly clad nanostar and that of a completely clad nanostar, in principle, enables plasmonic enhancement of the vest functionality. For instance, mode c2 of the core-vest particle shows that energy can be channeled to the vest rather than to the spikes.

The flexibility afforded by colloidal particle assembly and far-field excitation frequency selection allows for transfer of complex patterns of SP resonance modes. The resonant modes of nanostars with various spike-body aspect ratios are shown in Figure 2, along with their simulated absorption spectra and heat dissipation at the excitation energies shown by arrows. Unlike spherical nanoparticles, nanostars have several resonance peaks. Representative electron scanning micrographs of nanoparticles that were produced in this work are shown on the bottom row of Figure 2, and the experimental details are discussed elsewhere.15

We have used the foregoing analyses to guide the synthesis of these complex structures, as described below. First, the aspect ratios of nanostars are chosen through colloidal chemistry.15 This hard-coded or static tunability defines the set of available
resonance patterns on the subnanoparticle scale. Second, the wavelength of the excitation light determines whether heating is predominantly concentrated at the spikes or centered at the core, as illustrated in Figures 1 and 2. Because the plasmonic heating takes place on a much faster time scale than the conductive heat transport from the hotspots to cooler regions of the nanostar, the exposure time becomes a key parameter for fine-tuning the localized heat map. Experimental verification was accomplished using Au particles in a microfluidic setup containing heat-activated precursor of TiO₂, namely, liquid TiCl₄ at 1 M concentration, and directing a HeNe laser beam (633 nm) through a microscope objective (Figure 3). Controlled growth of nanostars, facilitated through colloidal chemistry, leads to various sizes, shapes, and aspect ratios, with some examples shown in the bottom left inset. The resulting shapes accordingly have different modes of interaction with light based on the light-source parameters such as wavelength, pulse duration, and intensity, as shown in the bottom middle inset. In turn, each mode of interaction results in a different temperature profile, which facilitates a different bottom-up self-assembly, leading to different designer nanoparticles. In general, the resulting nanocomposites will have selectable plasmonic modes that are accessible from the top through the light source parameters, and the plasmonic energy can be channeled toward the optimized functionality of the nanocomposites (shown in the bottom right inset). The arrows indicate an example process where suitable colloidal chemistry leads to 1:2 aspect ratio of spike height to base. These nanoparticles are then irradiated under the right light source illumination parameters to heat the valleys selectively while keeping the tips cold. This pattern, when the nanoparticles are immersed in the liquid precursor of the shell and illuminated, results in nanocomposites covered around the core, while the tips remain exposed. We note that the simulations to choose the proper aspect ratio nanostars and their corresponding super-resolution illumination patterns are conducted by taking into account the

Figure 2. Top row illustrates Au particles with the same spherical core of 35 nm but varied spike base-to-height ratios. Middle panel depicts the simulated absorption cross-section plots and the heat dissipation simulation for the modes indicated with arrows. The color bar indicates the range in temperature. Bottom panel shows the electron microscope images of the nanoparticles. (TEM for sphere, 1:1, and random geometries and SEM images of 1:2 and 1:3).
surrounding aqueous solution (refractive index and conductivity).

Experimental results corresponding to preferential heating of the valleys are shown in Figure 4a, where a gold nanostar is shown dressed in a TiO₂ vest, leaving the arms bare. The Figure inset is an enlarged image of the valley between the two spikes clearly showing the TiO₂ layer in between. Furthermore, we expect that controlling the exposure time (on the order of picoseconds) of the light source would render a more precise control over the vest formation, as predicted by theory and simulations (see SI Figure S2). Plasmonic fabrication of nanovests is largely self-limiting as the formation of the TiO₂ CVNs shifts the resonance of the composite particle outside the resonance mode with heat tightly focused within the valleys. Thus the process outlined here has the potential to be scaled up alongside the colloidal chemistry that yields a variety of nanostar shapes (Figure 3).

In a follow-up experiment, we fixed gold nanostars by drop casting on a Si substrate and immersed them in a 1 M TiCl₄ solution, which was then placed under a Raman microscope. A 2 M TiCl₄ solution was prepared by diluting the TiCl₄ (TiCl₄, ReagentPlus, 99.9% trace metals basis, Sigma-Aldrich) by introducing the pure TiCl₄ into a DI water flask cooled in an ice bath and stirred with a magnetic stirrer. The prepared solution had a yellow translucent color, was stored in the freezer for up to a week, and was used for further diluting into 1 M a solution immediately prior to experiments to minimize spontaneous hydrolysis. After placing a few drops of the 1 M solution over the gold nanoparticles, a microscope coverglass was used to cover and protect the solution from air during experiments. The actual experiment under the Raman microscope was performed in under 10 min. The partial/selective hydrolysis of the TiCl₄ into TiO₂ vests required careful tuning of the power intensity to avoid overheating. Too much power resulted in a crater of hydrolyzed TiCl₄, where entire particles were engulfed in TiO₂. The power was adjusted so as to observe the TiO₂ Raman peaks develop in real time but was turned off before thermally setting off a large hydrolysis reaction.

Figure 3. Simplified schematic illustration of the fabrication process flow of designer nanoparticles. (See also WEO 1, WEO 2, and WEO 3 for more details on the plasmonic heating and thermal diffusion processes.)

Figure 4. (A) TEM image of a gold nanostar, submersed in TiCl₄ and irradiated by a laser (excitation wavelength of 780 nm). (B) Blown up image of the resulting core-vest nanoparticle showing the selectively deposited anatase TiO₂ vest wedged in between the bases of two spikes and leaving a significant portion of the tips directly exposed to interact with radiation. (B-inset) The lattice spacing value of 0.34 nm closely matches (101) plane of anatase TiO₂. For a time-evolved simulation of the temperature distribution in aqueous environment under laser irradiation, see SI Figure S2.
Similar to the case illustrated in Figure 3, where one light source is used for CVN synthesis and another source is used for activation, here, too, the Raman laser doubles both as the source of plasmon excitation, which promotes the chemical synthesis of TiO\textsubscript{2} CVNs, and as the Raman excitation probe. The Raman shift collected in situ is a real-time indicator of the proceeding reaction, as shown in Figure 5. As the laser interacts with a cluster of nanostars suspended in TiCl\textsubscript{4}, the plasmonic activation of the nanostar “vests” them in a TiO\textsubscript{2} shell, which is immediately confirmed in real time by the Raman peaks of the anatase phase of TiO\textsubscript{2} (peaks at 149, 397, 513, and 634 cm\textsuperscript{−1}, as shown in Figure 5 bottom red plot). Further studies by transmission electron microscopy (TEM) confirm that the spacing between the crystal planes matches the anatase phase of TiO\textsubscript{2} (SI Figure S1).

We have shown that surface plasmons can be harnessed to synthesize a variety of preprogrammed designer nanostructures. As an example, surface plasmons are used to fabricate a crystalline vest covering the valleys of a nanostar yet exposing its arms (Figure 4). The most interesting activation mode of these newly formed heterostructures is near 800 nm, where the nanovest has an intense field enhancement in the vicinity of the TiO\textsubscript{2} shell shown in the inset c\textsubscript{2} of Figure 1.

This newly formed resonance peak offers a unique window of opportunity for plasmonically enhanced energetics between gold and TiO\textsubscript{2}, enhancing the catalytic properties of the TiO\textsubscript{2} vest. In addition, a host of novel interesting applications could emerge from a shift of the photocatalytic activity of titania from the UV to the visible range. The CVNs can also facilitate plasmon-assisted electron transfer from the gold cores to the conduction band of the shell and enhance the electric field at the gold–TiO\textsubscript{2} Schottky barrier. In contrast, when the nanoparticles are completely covered in a TiO\textsubscript{2} shell, as shown in inset d of Figure 1, the resonance peak of interest (∼800 nm) is suppressed, resulting in excitation modes that are minimally interactive with the shell.

Finally, we remark on the possibilities of synthesizing other CVNs. These include using other plasmonic nanostars, such as silver, as the multimodal core. Likewise, other gas- or liquid-phase precursors can result in vests such as SiO\textsubscript{2}, SnO\textsubscript{2}, ThO\textsubscript{2}, and more. CVN-forming reactions can take place either in solution or in chemical vapor deposition (CVD) setups. In addition to metal-oxide CVNs, bimetallic nanostructures can be synthesized, including hybrid silver-coated gold nanostructures, gold–copper alloyed nanostars,\textsuperscript{16} as well as other bimetallic Au-M CVNs. The superresolution synthesis of multilayer CVNs is also possible by using initial CVNs as a fabrication mask for subsequent layers. Bottom-up self-assembly has the ability to sculpt matter on length scales otherwise inaccessible from the top. This synergy is key to achieving super-resolution designs on the nanometer length scale that are not only unprecedented but also amenable to commercial scale production. What new functionalities can emerge as a result remain an exciting prospect.

## COMPUTER SIMULATION AND MEASUREMENT METHODS

The appropriate particle size and aspect ratios were determined from 3D simulations using COMSOL Multiphysics. Single physics simulation was used for determining the fields and heat dissipation rates, followed by a two-physics simulation that included solving time-domain heat diffusion equation in 3D to obtain the temperature profiles. The two-physics simulations modeled the gold nanostars immersed in water subjected to a plane-wave illumination. Data for refractive index of gold were taken from Johnson and Christy.\textsuperscript{17}

Once the optimal aspect ratios were determined through COMSOL simulations, the desired gold nanostars were synthesized following previously reported work\textsuperscript{15,18} beginning with a 10 mM stock solution of chloroauric acid (HAuCl\textsubscript{4}, 99.999% purity obtained from Sigma-Aldrich). 50 mL of the stock solution was then mixed in a 3:1 volumetric ratio with nitric acid for 15 min until the color change from light yellow to deep orange was observed. The beaker containing the mixture was then heated to 100 °C under vigorous stirring. Five mL of prepared sodium citrate solution (C\textsubscript{6}H\textsubscript{2}Na\textsubscript{3}O\textsubscript{7}.2H\textsubscript{2}O from Sigma-Aldrich) was added dropwise to the boiling solution containing chloroauric acid and mixed while boiling for 15 min. A deep-red color change followed, and the seed solution was cooled to room temperature and filtered with a nylon filter of
0.4 μm to remove any residues. The seed solution has spherical gold nanoparticles with an average diameter of 11 nm, confirmed by TEM imaging.

A 40 mL solution of 0.2 mM HAuCl₄ was prepared from stock solution. Twenty μL of 1 M HCl solution was added to the prepared chlorauric solution. While the two mixtures were being stirred, 200 μL of the gold seed solution was added to the container. Next, 400 μL of silver nitrate (AgNO₃ from Sigma-Aldrich) at 0.5 mM concentration and 200 μL of ascorbic acid (C₆H₈O₆ from Sigma-Aldrich) at 80 mM concentration were added together to the container. The solution turns from light yellow to a deep blue and suggests the formation of gold nanostars. After 30 s, the solution was centrifuged for 12 min at 6700 rpm. The pellets were dispersed in 10 mL of deionized water and sonicated.

The structure of prepared gold nanoparticles was characterized using scanning electron microscopy (SEM, Hitachi S-5200) and transmission electron microscopy (TEM, Hitachi HF-3300).

The shell formation experiment was conducted under a Raman microscope setup (Horiba LabRam) using a 633 nm laser and collimated through a microscope objective (50× and 100×). Both the plasmon-assisted chemistry and the Raman measurements of the shell formation at each point were carried out by the same light source, with Raman laser doubling as the plasmonic subwavelength heat source. This allowed the sample position to remain precisely in place, ensuring that the location of the chemical reaction and the corresponding Raman signal correspond. Real-time measurements of the Raman shift during the light-assisted plasmon chemistry of nanoshells formed were performed under the said conditions. The time evolution of the Raman shift as the TiO₂ shell formation around the gold nanostars suspended in the liquid TiCl₄ was also captured and is available in the Supporting Information. The Raman signal is measured in 0.1 s increments, while the focal point is scanned across a line that crosses a cluster of gold nanostars.

ASSOCIATED CONTENT

Supporting Information

Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.7b03288.

Additional TEM images of CVN nanostructures and additional time-evolved simulation results. (PDF)

Web-Enhanced Feature

WEO 1. Movie in AVI format showing the excitation of the spiky gold nanoparticles using a wavelength of 750 nm. When excitation light of a chosen wavelength, in this case 750 nm, predominantly interacts with the extremities (spikes) of the nanoparticles, the thermal energy is primarily channeled into the spikes whence it diffuses to other parts of the particle. As can be seen, the time of exposure, together with thermal diffusion, determines the outcome of the heat distribution. Thus a particular area of the nanoparticle, such as the valley between two spikes, can be reached from the inside out (by heating the core first and allowing the temperature to diffuse outward) or from the outside inward (by first heating the spikes and allowing the temperature to diffuse inward towards the core). WEO 2. Movie in AVI format showing the excitation of the spiky gold nanoparticles using a wavelength of 500 nm. When the wavelength of excitation predominantly interacts with the resonant mode corresponding to the body (core) of the plasmonic nanoparticle, the body becomes the heating center of the nanoparticles. WEO 3. Movie in AVI format of author description of the approach for the design and synthesis of the core-vest nanocomposites (CVNs).

AUTHOR INFORMATION

Corresponding Authors

*R.M.: E-mail: maboudia@berkeley.edu.
*N.P.K.: E-mail: kherani@ecf.utoronto.ca.
*C.C.: E-mail: carraro@berkeley.edu.

ORCID®

A. O. Montazeri: 0000-0002-6957-5211

Present Address

A.O.M.: Lawrence Berkeley National Laboratory, Berkeley, California.

Author Contributions

V. O.M. and Y.K. contributed equally. A.O.M. conceived the idea and A.O.M. and C.C. designed the experiments. A.O.M., Y.K., N.S. and G.Z. carried out the experiments while Y.S.F. and J.K.C. performed the simulations. R.M., N.P.K., and C.C. supervised the study. A.O.M. and C.C. wrote the paper while others provided feedback.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the Natural Sciences and Engineering Research Council of Canada under the aegis of Discovery and CREATE grants, Ontario Research Foundation - Research Excellence grant, Hatch Fellowship (A.O.M.), Weston Foundation Fellowship (A.O.M.), University of Toronto, and the Industrial Members of the Berkeley Sensor & Actuator Center. A.O.M. is also grateful to Mr. James Wang for his help with video production and the Productivity House.

REFERENCES


