Oxidative Etching and Metal Overgrowth of Gold Nanorods within Mesoporous Silica Shells

Tian-Song Deng,†‡ Jessi E. S. van der Hoeven,† Anil O. Yalcin,‡ Henny W. Zandbergen,‡ Marijn A. van Huis,† and Alfons van Blaaderen*,†

†Soft Condensed Matter, Debye Institute for Nanomaterials Science, Utrecht University, Princetonplein 5, 3584 CC Utrecht, The Netherlands
‡Kavli Institute of Nanoscience, Delft University of Technology, Lorentzweg 1, 2628 CJ Delft, The Netherlands

Supporting Information

ABSTRACT: Composite noble metal-based nanorods for which the surface plasmon resonances can be tuned by composition and geometry are highly interesting for applications in biotechnology, imaging, sensing, optoelectronics, photovoltaics, and catalysis. Here, we present an approach for the oxidative etching and subsequent metal overgrowth of gold nanorods, all taking place while the nanorods are embedded in mesoporous SiO2 shells (AuNRs@meso-SiO2). Heating of the AuNRs@meso-SiO2 in methanol with HCl resulted in reproducible oxidation of the AuNRs by dissolved O2 specifically at the rod ends, enabling precise control over the aspect ratio of the rods. The etched-AuNRs@meso-SiO2 were used as a template for the overgrowth of a second metal (Ag, Pd, and Pt), yielding bimetallic, core−shell structured nanorods. By varying the reaction rates of the metal deposition both smooth core−shell structures or gold nanorods covered with a dendritic overlayer could be made. This control over the morphology, including metal composition, and thus the plasmonic properties of the composite rods were measured experimentally and also confirmed by Finite-Difference Time-Domain (FDTD) calculations. The presented synthesis method gives great control over tuning over both plasmonic properties and the particle stability/affinity for specific applications.

INTRODUCTION

Gold nanorods (AuNRs) possess two different surface plasmon resonances, one associated with a longitudinal and the other with a transverse mode of oscillations of the conduction electrons. The transverse surface plasmon resonance (TSPR) is in the visible spectrum with a wavelength around 510−540 nm, whereas the longitudinal surface plasmon resonance (LSPR) can be varied from the visible (~600 nm) to near-infrared wavelength range (>1200 nm), depending on the aspect ratio of the nanorod.1−4 The tunable properties of the LSPR and the strong local electromagnetic field enhancements that can be realized close to the nanoparticle make AuNRs useful for a broad range of applications that include sensing, such as in surface-enhanced Raman scattering (SERS)5,6 or through changes in refractive index,7 plasmon enhanced fluorescence,8−10 optoelectronics,11 data storage,12 photothermal therapy,13,14 (in vivo) imaging,15−17 and biomedicine.18,19 For the present work, it is important to mention that for the different applications, sometimes even opposite requirements are optimal with respect to the plasmonic properties of the particles. For instance, excessive damping of the plasmon resonance is detrimental for many applications in optoelectronics and plasmon field enhancement methodologies (such as in SERS and plasmon enhanced fluorescence), while the generation of heat out of plasmon induced by light absorption is what makes certain imaging13,14 and medical applications13,14 possible. For some applications, like catalysis and SERS, a rough metal interface is often measured or predicted to be advantageous. For other applications like in a femtosecond-light-pulse that induces a change in the aspect ratio of AuNRs which has been used in a data storage application,12 a smooth defect free AuNR is optimal. For almost all applications, control over the actual position of the LSPR is important as well. For pure AuNRs, this tuning is possible through the aspect ratio. If composite particles, as studied in the present article, are an option, the composition in combination with the morphology provides an even wider spectrum of possibilities to tune the plasmonic properties.20

In principle, the aspect ratio of the AuNRs can be controlled during synthesis and/or via postselective-etching afterward. Presently, AuNRs are usually synthesized via a so-called seed-mediated growth method,21−23 under the influence of the shape directing and stabilizing surfactant hexadecyltrimethylammonium bromide (CTAB) and shape inducing agent Ag, whereby...
the aspect ratio of the AuNRs can roughly be controlled by tuning the acidity of the growth solution. However, selective etching\(^2^4\) after particle growth allows for more precise control of the aspect ratio. This has already been successfully shown for mild oxidation by cyanide\(^2^5\), Au(III),\(^2^6\) \(O_2\),\(^2^7\) and \(H_2O_2\).\(^2^8\) The etching preferentially takes place at the ends of the nanorods,\(^2^5\)\(^\cdots\)\(^2^8\) leaving the diameter unchanged. Thus, the AuNRs are selectively shortened, enabling more precise control over the aspect ratio. So far, these etching processes were performed in AuNRs solutions with high CTAB concentrations as stability with metal particles is always an issue at higher ionic strengths because of the large Hamaker constants and thus van der Waals forces for these systems. However, the toxicity of CTAB is problematic when using bare AuNRs for in vivo studies.\(^1^8\),\(^1^9\)

Also in applications such as catalysis, the presence of a dense surfactant layer on the particles is undesirable, for it makes the Au metal surface inaccessible for reactants.\(^2^9\) Therefore, a different stabilizing mechanism based on a nontoxic mesoporous silica layer\(^3^0\),\(^3^1\) overcomes these problems with CTAB, as the silica coating significantly reduces the van der Waals forces, and is compatible with almost any solvent by surface modification, while keeping the AuNR accessible for surrounding molecules.\(^3^2\) For example, Zhang et al.\(^1^5\) demonstrated that multilayer-coated AuNRs (with a dyed SiO\(_2\) shell and polymer layer) exhibited ultrahigh colloidal stability and excellent tunability, which makes them suitable for in vivo fluorescence imaging, SERS detection, and photothermal therapy. Apart from many developed coating schemes, an SiO\(_2\) coating has also advantages in chemical and mechanical stabilities (including increased stability against temperature induced shape changes of AuNRs\(^2^5\)), a tunable porosity, and optical transparency.\(^3^3\),\(^3^4\) A thin SiO\(_2\) shell also can act as a “spacer” to control the coupling distance between metal particles with other metal particles and molecules, and thus can be used to optimize SERS\(^3^0\) and plasmon enhanced fluorescence.\(^3^5\) In addition, the benefits of a silica shell in the growth of bimetallic nanorods were already demonstrated\(^3^6\),\(^3^7\) in at least two papers. In the first paper, Au nanoparticles grown inside empty silica shells were used to seed the growth of other metals within the rod-like silica shells.\(^3^6\) In ref 37, patchy silica layers were grown around AuNRs at the particles’ ends or midsections. Subsequently, the noncoated regions could be overgrown by another metal. Such bimetallic AuNR-metal nanostructures have unique plasmonic properties\(^3^7\),\(^3^8\) and catalytic activities,\(^3^9\),\(^4^0\) both caused by unique combinations of the properties of the two metals.

Here, we report a novel approach in which we oxidatively etched monodisperse AuNRs within meso-SiO\(_2\) shells by dissolved \(O_2\) at the tips of the nanorods only, enabling a precise control over the aspect ratio. The oxidation speed could be varied by changing the acid concentration and/or temperature. Furthermore, we show that it is possible to overgrow the resulting AuNRs by several noble metals in the mesoporous shells. The plasmonic properties of the AuNRs-metal nanostructures were studied both experimentally and by means of FDTD calculations.

### Results and Discussion

AuNRs were synthesized using a modified seed-mediated method\(^4^1\) and coated with a meso-SiO\(_2\) shell.\(^5^1\) For oxidative etching, the AuNRs@meso-SiO\(_2\) in methanol was mixed with certain amounts of HCl dissolved in water and then kept at a specific increased temperature under gentle stirring (for experimental details, see Experimental Section and Supporting Information (SI)). The etching process was monitored by measuring the extinction spectra as a function of the oxidation time after quenching the reaction to room temperature by dilution in methanol. Digital photographs and transmission electron microscopy (TEM) images were also taken at different oxidation times. Figure 1a shows the extinction spectra measured at different times after the oxidation was started by the addition of HCl solution in water. The LSPR peak of the AuNRs@meso-SiO\(_2\) before etching was found at 827 nm with intensity 1.80 in a 1.0 cm cuvette. We estimate (see SI) a particle concentration of \(2.0 \times 10^{11} \text{mL}^{-1}\). The LSPR peak was found to blue-shift, and the intensity decreases during oxidation due to “shortening” of the rods. (b) A digital photograph of the samples taken out with varying oxidation time for extinction spectra measurements. The shift in the LSPR peak caused a continuous color change during etching.

![Extinction spectra acquired with increasing etching time. The LSPR peak blue-shifts, and the intensity decreases during oxidation due to “shortening” of the rods.](image)

**Figure 1.** AuNRs were oxidatively etched by adding 0.2 mL of HCl to 10 mL of AuNRs@meso-SiO\(_2\) methanol solution at 70 °C. (a) Extinction spectra acquired with increasing etching time. The LSPR peak blue-shifts, and the intensity decreases during oxidation due to “shortening” of the rods. (b) A digital photograph of the samples taken out with varying oxidation time for extinction spectra measurements. The shift in the LSPR peak caused a continuous color change during etching.
distribution or polydispersity (see SI) and was based on 200–
400 particle measurements) is given. It can be seen in Figure 2e
that the AuNRs were etched exclusively at the ends of nanorods
(see also Figure 2b and c). After complete oxidation, only
empty meso-SiO2 shells were left due to dissolution of the
AuNR cores (Figure 2d). A full set of TEM images at different
etching stages are given in Figure S1. As mentioned, during the
oxidation process, the diameter of nanorods remained nearly
constant (Figure 2e) during the etching. Such selective etching
of bare AuNRs has been reported before, 26−28 whereby
oxidizing agents such as Au(III), O2, and H2O2 were used.
Here, we realized selective etching of the AuNRs within meso-
SiO2 shell. A plot of the aspect ratio versus the LSPR peak
shows an approximately linear relationship (Figure 2f), in
agreement with previous results. 1−4 In addition, the poly-
dispersities of the etched-AuNRs in length and diameter were
comparable to those of the starting AuNRs (Figure 2e),
suggesting fine control of the aspect ratio of AuNRs during
etching.

It was found that the oxidation speed of the AuNRs could be
controlled by the HCl concentration and/or the temperature
(Figure 3 and Figures S2–S4). In both cases, the initial blue-
shift of the LSPR peaks was approximately linear with oxidation
time. Therefore, the slope of the LSPR position with time can
be used to estimate the etching speed. At fixed temperature (70
°C), the oxidation speed was found to increase with increasing
HCl concentrations. For HCl amounts of 0 mL, 0.1 mL, and
0.2 mL, the oxidation speeds were <0.01 nm/min, 5.9 nm/min,
and 13.7 nm/min, respectively. The negligible oxidation rate in
the absence of HCl indicates that acidic conditions are required
for oxidative etching at the conditions of our experiments. The
oxidation speed could also be tuned by varying the temper-

![Figure 2. TEM images of AuNRs@meso-SiO2 at different etching stages (a) t = 0 min, LSPR = 827 nm, L = (75.3 ± 9.4) nm, D = (17.6 ± 2.1) nm, and AR = 4.3 ± 0.7; (b) t = 8 min, LSPR = 723 nm, L = (58.5 ± 9.7) nm, D = (17.7 ± 2.2) nm, and AR = 3.3 ± 0.6; (c) t = 14 min, LSPR = 661 nm, L = (44.7 ± 10.1) nm, D = (17.7 ± 2.2) nm, and AR = 2.6 ± 0.6; and (d) t = 40 min, complete etching. Scale bar for a–d is shown on the bottom-right of panel d. (e) Changes of lengths and diameters of AuNRs versus etching time. With increase of the oxidation time, the length of AuNRs decreased while the diameter of AuNRs remained nearly constant. (f) The plot of aspect ratios versus LSPR peaks during etching. The line is a linear fit.

![Figure 3. Etching rate of AuNRs@meso-SiO2 could be controlled via the (a) HCl concentration and (b) temperature. The line is a linear fit. The slopes (etching rates) are <0.01 nm/min, 5.9 nm/min, and 13.7 nm/min for 0 mL of HCl, 0.1 mL of HCl, and 0.2 mL of HCl, respectively, and 7.2 nm/min and 2.8 nm/min for 60 and 50 °C, respectively.](https://doi.org/10.1021/acs.chemmater.5b03749)
and digital photographs are shown in Figures S2–S4. As expected (results not shown in detail), the etching speed was also found to depend on the exact details (thickness and pore volume-sizes) of the mesoporous layer. However, for similar conditions etching speeds were reproducible. For this reason, the concentrations of dissolved O₂ were not determined or controlled as also these will vary with many of the parameters used in the etching solution such as amount of water, temperature, and pH. Thus, for fine-tuning the aspect ratio of a particular dispersion of AuNRs@meso-SiO₂, it suffices to determine the initial speed and from this stop at the required aspect ratio by a temperature quench (see also below).

To investigate the oxidative reaction mechanism of the AuNRs in meso-SiO₂ shells in more detail, we performed several control experiments (Figures S5–S9). First, we determined that metallic Au(0) was oxidized to Au(III) in the following way: after the reaction was completed, the solution was mixed with a certain amount of CTAB aqueous solution. The peak that appeared around 400 nm coloring the solution a clear yellow (Figure S5, inset) was caused by the metal–ligand charge transfer absorption of AuBr₄⁻, which suggests that Au was present as Au(III) (Figure S5). Second, the presence of O₂ in the air above the etching solution is required for the complete dissolution of the AuNRs. The oxidation reaction was performed under inert N₂ atmosphere, without calcination (Figure S9), most probably by a reduction of metallic Au(0) without calcination (Figure S9), most probably by a reduction of metallic Fe with a Stöber layer of similar thickness. Finally, CTAB is not required for the oxidation of the AuNRs. Before oxidation, CTAB was removed from the meso-SiO₂ shell by calcination of the AuNRs@meso-SiO₂ particles at 500 °C in air for 6 h. The AuNRs core was partially deformed to a lower aspect ratio of 1.9 ± 0.2, and the calcined particles were redispersed in methanol for the oxidation reaction. The oxidation could still be completed, but the speed was slower than the oxidation without calcination (Figure S9), most probably by a reduction in the pore volume and/or sizes. From the results obtained, we propose the following overall reaction for the oxidative etching process:

$$4\text{Au} + 16\text{Cl}^- + 3\text{O}_2 + 12\text{H}^+ = 4\text{AuCl}_4^- + 6\text{H}_2\text{O}$$

Here, H⁺ enhances the reduction potential of the O₂ half reaction from 0.401 to 1.229 V (vs a normal hydrogen electrode, NHE), while Cl⁻ acts as complexing agent, which reduces the reduction potential of Au(0)/Au(III) from 1.52 to 1.002 V (vs NHE; see SI). The etched-AuNRs@meso-SiO₂ particles were used for a second metal overgrowth. The etched-AuNRs core acts as a “seed” making the reduced metal salts specifically deposit on the AuNRs, with the meso-SiO₂ shell acting as “nanocarrier” which confines the shape and size of the final nanostructures. To illustrate the generality of this approach, we successfully completed the overgrowth of the noble metals (Ag, Pd, and Pt) on etched-AuNRs in a meso-SiO₂ shell. We found additionally that by varying the speed of growth both smooth layers and layers with very rough almost dendritic overlayers could be realized.
nanostructures were investigated by high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) and high-resolution transmission electron microscopy (HRTEM) imaging (Figure 4 and Figures S10 and S11). It is likely that part of the CTAB is removed from the mesopores in the silica shell so that precursor molecules can access the surface of the AuNRs. The openness of the pores likely influences the effectiveness of the overgrowth reaction. The meso-SiO₂ shell is accessible from all directions; therefore, a second metal can be grown on both the sides and the ends of the AuNRs. Because of the exclusive anisotropic etching at the ends only, there is more space at the ends of AuNR inside the SiO₂ shells, resulting in thicker metal overgrowth at the ends. Thus, the length was found to increase more than the diameter in the final AuNRs-metal structures. Figure 4a and f show the etched-AuNRs@meso-SiO₂ particles. The AuNRs are single crystals of face-centered cubic (fcc) structure, with one of the main cubic axes oriented along the length of the rod. In general, they are observed to lie on the grid either in a [110] or in a [100] orientation (Figure S10), in agreement with previous reports.⁴⁴,⁴⁵ The growth behavior varied for different metals. Ag could be epitaxially grown on the AuNR surface, forming an AuNRs-Ag core–shell structure with a single crystalline structure (Figure 4g). The epitaxial growth of Ag on Au is possible due to the small lattice mismatch and the low interface energy between Au and Ag. We also found line defects in some of the AuNRs-Ag structures (Figure S11), which might arise from a too fast growth speed. For Pd growth, epitaxial growth occurred only in a few atomic layers. Thereafter, Pd nanoparticles were grown on both the sides and ends of the AuNRs (Figure 4h and Figure S10c). For Pt overgrowth, the Pt layers could be either smooth or rough, depending on the speed of growth. When the growth speed is slow, the Pt layer is smooth (Figure 4i), and the morphology is similar to that of a single AuNR. The success coating of Pt was confirmed by elemental mapping (Figure S12). When the growth speed is faster, dendritic layers were obtained (Figure 4j), and the structure is similar to the AuNRs-Pt-rough nanostructure. The insets in Figure 4a–e show obvious color changes after metal growth: from brown to green after Ag growth and from brown to dark brown after Pd and Pt growth. The different color changes are due to the differences in the plasmonic properties after the second metal overgrowth.

To investigate the plasmonic properties of the AuNRs-metal nanostructures in more detail, we compared measured extinction spectra with FDTD calculated spectra for single composite rods with different geometries and compositions. Figure 5a shows the experimental extinction spectra of the etched-AuNRs@meso-SiO₂ and AuNRs-metal structures. For the LSPR of the AuNRs-Ag nanostructures, the peak blue-shifted (from 741 to 709 nm), and the peak intensity increased dramatically. The blue-shift and intensity increase arise from the higher plasmonic resonance energy and decrease in plasmonic damping of Ag compared to Au.⁴⁶ However, for the AuNRs-Pd and AuNRs-Pt-rough nanostructures, the LSPR peak red-shifted, decreased in intensity, and broadened. The red-shift is due to a slight increase in aspect ratio, whereas the intensity reduction and broadening arise from plasmon damping due to the large imaginary part of both the Pd and Pt dielectric functions.³⁷,³⁸ For the AuNRs-Pt-smooth nanostructure, the LSPR did not show an obvious shift. This unchanged LSPR band is due to nearly the same aspect ratio after the Pt overgrowth. As mentioned, we performed FDTD simulations to calculate the extinction cross-sections for different geometries of single AuNRs-metal nanostructures using the dielectric functions of the corresponding bulk materials (Figure 5b). We assumed a porosity of 63% in our mesoporous layer of silica⁷ to which we assigned a refractive index of 1.45⁴⁸ and that the pores were filled with water solvent with a refractive index of 1.33 through a volume weighed average of the pores and silica. We obtained an effective index of refraction of 1.38, which we assumed to be valid for all wavelengths. We are aware of the fact that there is a small effect on the rod resonance frequency caused by the fact that the outer mesoporous layer encounters yet another index jump to the bulk water, but earlier work has shown this effect on the metal resonances to be quite small (only several nanometer shifts for our parameters).⁴⁹ We therefore ignored this effect in the calculations. The characteristics of the plasmonic properties after the metal overgrowth in the FDTD simulations are in good agreement with the experimental data. The only important difference is the width of the peaks, which is explained by the polydispersity of our systems which was not taken into account in the single particle calculations.

■ CONCLUSIONS

In summary, we have demonstrated a relatively simple approach to selectively control the dimensions of AuNRs@
meso-SiO₂ rods after synthesis via oxidative etching. The etching speed could be precisely controlled by the HCl concentration and/or temperature but is also dependent on the mesoporous layer characteristics. Additionally, the etched AuNRs@meso-SiO₂ particles can be used as seeds for a second metal overgrowth of the etched-AuNRs in their meso-SiO₂ shells. The growth only takes place inside the mesoporous silica shell, which stabilizes the rods both mechanically, against aggregation and against deformations induced by increased temperatures, while still keeping the metal surface available for applications like catalysis and sensing such as SERS. Overgrowth was shown for the metals: Ag, Pd, and Pt, but we expect the procedure to work for other metals as well. The morphology of the additionally grown metal layers could be tuned to be both smooth and rough depending on the speed of growth. This was shown for Pt overgrowth, but preliminary results have shown these limits to be accessible for the other metals as well, and work is in progress to find the exact conditions for different metals. Depending on the intended use of these composite metal nanostructures in, e.g., plasmonics, sensing, and catalysis, the ability to also fine-tune this part of the morphology is an important extra control parameter. As expected, depending on the dielectric responses of the metals used, the plasmonic responses of the composite particles could be either increased (Ag) or decreased (Pd and Pt resulting in more dissipation). Moreover, also the catalytic properties are expected to show similarly large differences in properties depending on the reaction and metal composite as well. Finally, work is in progress to investigate whether alloy formation in the composite structures can be induced before the structures resort back to a spherical shape as the alloys of the metals used have unique properties as well and to the best of our knowledge have not yet been realized for anisotropic particles.

**Experimental Section**

**Materials.** All chemicals were used as received without further purification. Hexadecyltrimethylammonium bromide (CTAB, ≥98.0%) and sodium oleate (NaOL, ≥97.0%) were purchased from TCI America. Hydrogen tetrachloroaurate trihydrate (HAuCl₄·3H₂O), sodium hydrosulfide (98%), and polyvinylpyrrolidone (PVP, average molecular weight 58000 g/mol) were purchased from Sigma-Aldrich. Ultrapure water (Millipore Milli-Q grade) with resistivity of 18.2 MΩ was used in all of the experiments. All glassware for AuNR synthesis was cleaned with Aqua regia (HCl/HNO₃ in a 3:1 ratio by volume; caution! Aqua regia is extremely corrosive and should be handled with extra care!) and rinsed with large amounts of water.

**Oxidative Etching of AuNRs@meso-SiO₂.** The oxidative etching of AuNRs in meso-SiO₂ solution was carried out by heating the AuNRs@meso-SiO₂ solution (10.0 mL in methanol) in a 40 mL glass vial to 70 °C in an oil bath. To start the etching, 0.20 mL HCl (37 wt % in water) was added. The cap of the glass vial was closed to prevent evaporation of HCl. With the increase of etching time, the color of the solution changed from brownish to green, blue, and finally yellowish (due to the formation of Au(III)). The amount of HCl (0.10 mL, 0.03 mL) or temperature (60 °C, 50 °C) was changed to control the etching speed. The oxidation process was monitored by measuring extinction spectra as a function of oxidation time in a 1.0 cm cuvette. The spectra were measured by taking samples from the etched-AuNRs@meso-SiO₂ solutions and mixing them with the same volume of methanol to rapidly cool down the temperature. The LSPR peak of the AuNRs@meso-SiO₂ before etching was at 827 nm and had an intensity of 1.80.

**Metal Overgrowth on Etched-AuNRs@meso-SiO₂.** The AuNRs@meso-SiO₂ solution (15.0 mL in methanol) was mixed with HCl (37 wt % in water, 0.30 mL) and etched at 70 °C for 8 min. The etching was stopped by adding large amounts of cool methanol and centrifuging at 8000 rpm for 10 min. The precipitate was redispersed into PVP aqueous solution (molecular weight, 58000 g/mol, 1.1 wt %). Then, the solution was centrifuged again and redispersed into PVP solution (1.1 wt %, 10.0 mL) as a stock solution. The metals were grown on etched-AuNRs@meso-SiO₂ using the method from ref 37 with modifications. For the growth of AuNRs-Ag, AgNO₃ (0.01M, 0.03 mL) was added into the etched-AuNRs@meso-SiO₂/PVP stock solution (0.6 mL), followed by the addition of ascorbic acid (0.03 M, 0.04 mL). The mixture was gently shaken for 20 min. For the growth of AuNRs-Pd, the conditions are the same as those for the growth of AuNRs-Ag except for the use of Na₂PdCl₄ (0.01M, 0.03 mL) instead of AgNO₃. For the growth of AuNRs-Pt-smooth, K₂PtCl₆ (0.01 M, 0.03 mL) was added into the etched-AuNRs@meso-SiO₂/PVP stock solution (0.6 mL), followed by the addition of ascorbic acid (0.03 M, 0.04 mL). The mixture was gently shaken for 5 min and left undisturbed for 4 h. For the growth of AuNRs-Pt-rough, K₂PtCl₆ (0.01 M, 0.12 mL) was added into the etched-AuNRs@meso-SiO₂/PVP stock solution (0.6 mL), followed by the addition of ascorbic acid (0.1 M, 0.12 mL). The mixture was gently shaken for 5 min and left undisturbed for 4 h. Since the growth speed is much slower for the growth of AuNRs-Pt, more metal salt and ascorbic acid were added to obtain the AuNRs-Pt-rough structure. Also the reaction time was much longer for Pt overgrowth. The resulting particles were centrifuged at 8000 rpm for 10 min and redispersed in water. The results are shown in Figures 4−5 and Figures S10−S12.

**Characterization.** Extinction spectra were measured using a vertex 70 FT-IR spectrometer (BRUKER) and 1.0 cm cuvettes. To measure the Au(III) with a peak at ~400 nm, a PerkinElmer Lambda 950 spectrophotometer was used. TEM images were acquired with a Tecnai 12 microscope (FEI) operating at 120 kV. HAADF-STEM and HRTEM measurements on AuNRs-metal@meso-SiO₂ structures (Figures 4, S10, and S11) were performed using a caged Titan microscope (FEI) with spherical aberration correction for bright-field imaging, and operating at 300 kV. A camera length of 115 mm was used to limit diffraction effects in HAADF-STEM imaging. For the AuNRs-Pt-smooth@meso-SiO₂, EDX mapping was also performed. The particle sizes of etched-AuNRs were measured from TEM images, whereby 200−400 particles were measured for each sample. The mean (μ) and standard deviation (σ) of length (L), diameter (D), and aspect ratio were obtained by the following formula:

$$\sigma = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (s_i - \mu)^2}$$

$$\mu = \frac{1}{N} \sum_{i=1}^{N} s_i$$

Here, sᵢ is the length (or diameter) of measured particles or the aspect ratio obtained by (L/D), and N is the number of particles. The results shown in the article are μ ± σ.

**FDTD Simulations.** Finite difference time domain (FDTD) is a method for solving Maxwell's equations on a discretized spatial grid in complex geometries. The FDTD simulations were carried out with commercial software (Lumerical FDTD Solutions 8.11). A total field scattered field source was used to simulate a propagating plane wave interacting with the nanostructures, with a wavelength range of 450 to 1200 nm. Only LSPR was calculated by setting the polarization parallel to the long axis of AuNRs. A three-dimensional nonuniform mesh was used, and a grid size of 0.5 nm was chosen for the AuNRs-metal nanostructures and the immediate vicinity of the structures. For the dimensions of AuNRs-metal nanostructures, the average sizes as determined from TEM were used. The shape of the AuNR core was modeled as a cylinder capped with a hemisphere at each end. For the AuNRs-Ag core−shell structure, the Ag shell was modeled by wrapping the AuNR core with a Ag layer. For the AuNRs-Pd (or AuNRs-Pt) nanostructure, a few Pd (or Pt) atomic layers were epitaxially grown on the AuNR surface. Thereafter, additional Pd (or
Pt) deposition led to the formation of nanoparticles on both sides and ends of the AuNRs. Therefore, the model of AuNRs-Pd (or AuNRs-Pt) nanostructures consisted of an AuNR core wrapped by a 0.5 nm thick Pd (or Pt) layer and randomly distributed Pd (or Pt) nanoparticles (1–3 nm in diameter) on the outside. The dielectric functions of metals were obtained by fitting the points from the data of Palk, E. D. (Handbook of Optical Constants of Solids; Academic Press: Boston, MA, 1985). We assumed a porosity of 63% (f) in our mesoporous layer of silica\(^{17}\) to which we assigned a refractive index of 1.45\(^{35}\) (n_{\text{silica}}) and that the pores were filled with water solvent with a refractive index of 1.33 (n_{\text{H_2O}}) through a volume weighted average of the pores and silica. We calculated an effective refractive index by
\[
n_{\text{eff}} = \sqrt{n_{\text{H_2O}}^2 f + n_{\text{silica}}^2 (1 - f)}
\]
The obtained effective index of refraction is 1.38, which we assumed to be valid for all wavelengths.

**ASSOCIATED CONTENT**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.5b03749.

More experimental details, full set of TEM images of etched-Au@meso-SiO\(_2\), extinction spectra, TEM images and digital pictures of all control experiments, HRTEM images of AuNRs-metal nanostructures at full resolution, and EDX elemental mapping of AuNRs-Pt-smooth nanostructure (PDF)

**AUTHOR INFORMATION**

Corresponding Authors
*(T.S.D.) E-mail: dengts@pku.edu.cn.
*(A.v.B.) E-mail: A.vanBlaaderen@uu.nl.

Notes
The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

We thank Johannes D. Meeldijk and Chris Schneijdenberg for electron microscopy support, and Professor Jianfang Wang and Dr. Ruibing Jiang for help with the FDTD simulations. T.S.D. and A.v.B. acknowledge financial support from a European Research Council under the European Unions Seventh Framework Programme (FP/2007-2013)/ERC Grant Agreement no. [291667].

**REFERENCES**


(42) Stöber, W.; Fink, A.; Bohn, E. CONTROLLED GROWTH OF MONODISPERSE SILICA SPHERES IN MICRON SIZE RANGE. J. Colloid Interface Sci. 1968, 26, 62–69.

(43) Ohnishi, M.; Maiz, J. D. Surface crystallization of uniform coated inorganic colloidal particles 0.8 SILICA ON IRON. J. Colloid Interface Sci. 1993, 160, 288–292.