How Gold Nanoparticles Have Stayed in the Light: The 3M's Principle

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ABSTRACT Simultaneous advances in making, measuring, and modeling noble metal (plasmonic) particles—designated as the 3M's principle—have led to a perfect storm in discoveries and applications of gold nanoparticles. Three articles in this issue of *ACS Nano* illustrate this concept. First, exquisite control over gold nanorod length and diameter and testing of fundamental ideas are presented. Second, gold nanorods as localized surface plasmon resonance sensors to monitor the kinetics of antibody−antigen binding are reported. Third, strategies to prepare gold nanoshell substrates to enhance Raman scattering and infrared absorption are proposed. In this Perspective, we discuss how these reports fit into current challenges in plasmonics and how the prospects of localized surface plasmons will continue to shine when the right applications are revealed.

See the accompanying Article by Ni *et al.* on p 677, Article by Mayer *et al.* on p 687, and Article by Le *et al.* on p 707.

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Plasmonics—the science and application of noble metal systems that can manipulate light at the nanoscale—has attracted significant attention recently because of a combination of several factors, which we have designated as the **3M's principle:** *make, measure, model*. Advances in nanoparticle synthesis and fabrication, innovations in new analytical tools and measurements, and clever theoretical modeling have kept surface plasmons in the spotlight. The contents of this issue of *ACS Nano* are no different; three papers perfectly illustrate the 3M's principle. *Make:* Wang and co-workers exhibit control over gold nanorod diameter and length to demonstrate how large rods could scatter light more strongly than small rods with the same length/diameter ratio (Figure 1A).[1] *Measure:* Hafner and co-workers show that localized surface plasmon resonance sensors could be used to monitor antibody−antigen binding in real time and that the binding rates were consistent with literature values (Figure 2).[2] *Model:* Nordlander and co-workers propose strategies to design substrates for surface-enhanced Raman scattering (SERS) and surface-enhanced infrared absorption (SEIRA) based on "hot spots" between gold nanoshells.[3]

All three papers exploit gold nanostructures that support localized surface plasmons (LSPs), collective oscillations of conduction electrons that form when light is incident on noble metal structures. In particular, Mayer *et al.* and Le *et al.* highlight a key important characteristic of LSPs: they can amplify relatively weak processes. In this Perspective, we focus on (1) how plasmonic nanoparticles can enhance or enable the detection of molecular processes; (2) how the characteristics of nanostructures can be tuned to achieve maximum enhancement; and (3) how the prospects of LSPs can shine when the "right" application is found.

Localized Surface Plasmon Enhancement of Molecular Processes. Plasmonic nanoparticles exhibit intense electromagnetic fields that are localized within *ca.* 10 nm of the particle surface.[4] Relatively weak processes—detecting small numbers of molecules,[5–9] monitoring antibody−antigen interactions,[10–13] and SERS[3,14,15]—benefit directly from the localized fields. Gold and silver nanoparticles have found many applications for sensing, with the most common one based on LSP resonance spectroscopy, which measures shifts of the resonances to different wavelengths depending on the local dielectric environment.[16] Highly sensitive detection limits (zeptomolar concentrations) can be achieved,[5] and a comprehensive comparison of the sensitivities of different nanoparticle systems has been summarized elsewhere.[17] Besides measuring shifts in peak wavelengths from thiolated alkyl chains, LSP sensors can detect specific analytes on the basis of how the surface of the nanoparticle is functionalized.[15] What sets the work of Hafner and co-workers apart from previous studies is that specific binding events as well as the correct kinetics for the on/off rate of antibody−antigen interactions are reported.[2]

One of the first demonstrations that plasmonic nanoparticles could enhance weak molecular processes was SERS. Early work showed that molecules that were adsorbed on roughened metal surfaces exhibited unexpectedly large Raman signals.[18] Similarly, highly localized electromagnetic fields from LSPs from nanoparticles can significantly enhance Raman scattering. Moreover, by tuning the wavelength of the LSP resonance of an array of nanoparticles near the excitation wavelength, SERS enhancements can be maximized.[19] Another molecular process poised for resurgence because of metal nanoparticles is SEIRA,[20] which is highly surface sensitive and can be used to detect the reorientation and attachment of molecules on surfaces under *in situ* conditions.[21,22] In this issue, Nordlander and co-workers describe how arrays of gold nanoshells show concurrently electric field enhancements of $|E|^2$ for SEIRA and $|E|^4$ for SERS at the same spots (Figure 3A).[3]

Designing Anisotropic Plasmonic Particles. To achieve high localized electric field enhancements or desired plasmon resonances, we can take advantage of several general trends that relate the plasmon resonance to particle size, shape, and material (Figure 1).[2,23]

Size. From Mie scattering theory,[24] spherical nanoparticles have scattering and absorption[25] cross sections that scale with the diameter of the particle. In addition, as the size of the particle increases, the LSP dipolar resonance tends to broaden and shift to longer wavelengths.[26] Thus, for potential imaging applications, larger (>100 nm) nanoparticles may be desirable because they scatter light more strongly. In contrast, for biomedical therapeutic applications like photothermal therapy,[27] smaller (<100 nm) particles may be preferred since less energy is lost to scattering and more efficient heating can be expected.[25,28] In this issue, Wang and co-workers also discuss scaling factors for rod-like and other nanoparticle shapes.[2]

Shape. Anisotropically shaped particles are ideal for achieving high electromagnetic fields at specific locations on a nanostructure (Figure 3). Two examples are nanopyramids (Figure 1C and Figure 3B), which have ultrasharp tips (<2 nm radius of curvature) and well-defined facets and edges,[29] and nanostars (Figure 1D), which exhibit multiple points on a single particle.[30] Shape control can also be used to take advantage of the "lightning rod effect" in order to produce extraordinarily high electric field intensities (up to 270 times that of the incident field).[31] Hence, by tuning shape, even gold nanostars, with tip-to-tip distances less than 100 nm, can scatter strongly because light drives the localized plasmon resonance to produce high electric field intensities at the tips of the nanoparticles (Figure 3C).

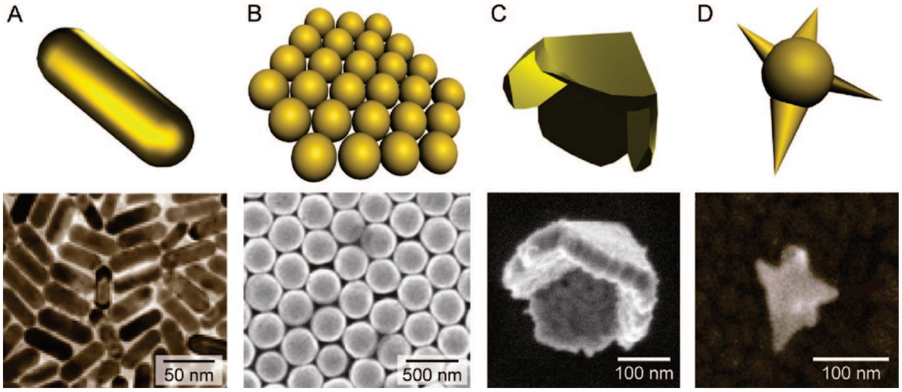

Figure 1. MAKE. Synthesized and fabricated anisotropic gold nanoparticles. (A) Nanorods.[1] (B) Arrays of nanoshells (interiors are silica).[3] (C) Nanopyramids. [Scanning electron micrograph courtesy of Jeunghoon Lee, Northwestern University.] (D) Nanostars. [SEM reprinted with permission from ref 30. Copyright 2006 American Chemical Society.]

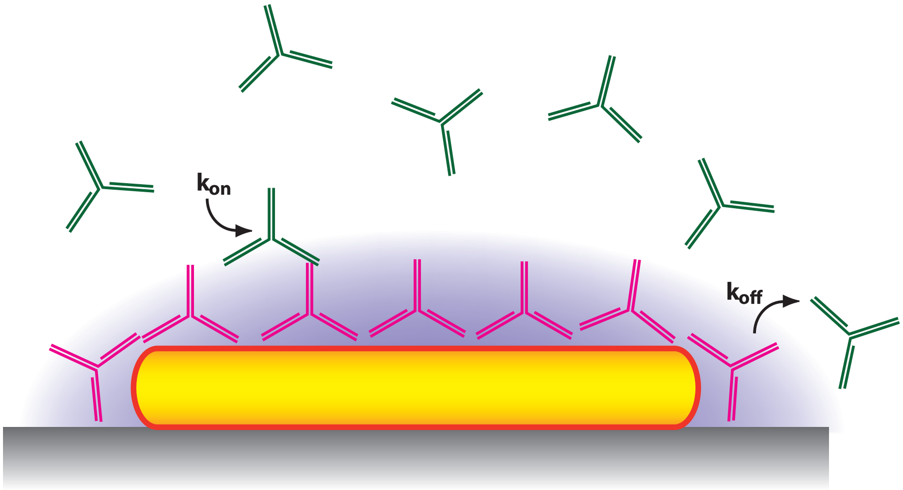

Figure 2. MEASURE. Scheme for detecting the kinetics of specific antibody−antigen binding. [Adapted with permission from ref 2.]

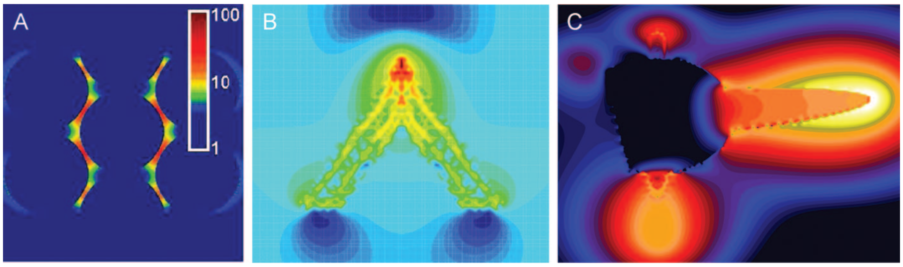

Figure 3. MODEL. Local electromagnetic field enhancements from (A) a nanoshell septamer (inner radius = 150 nm and outer radius = 172 nm) at a wavelength of 1982 nm, calculated by finite difference time domain (FDTD) methods. [Reprinted with permission from ref 3. Copyright 2008 American Chemical Society.] (B) A gold nanopyramid (base diameter = 250 nm and shell thickness = 50 nm) at a wavelength of 788 nm, calculated using the discrete dipole approximation. [Reprinted with permission from ref 60. Copyright 2006 American Chemical Society.] (C) A gold nanostar (tip-to-tip distance = 100 nm) at a wavelength of 804 nm, calculated by FDTD methods. [Reprinted with permission from ref 31. Copyright 2007 American Chemical Society.]

Materials. Noble metal particles made from silver, gold, and copper exhibit LSP resonances at visible wavelengths (400−700 nm).[25] The surface plasmon resonances of silver nanoparticles have smaller absorption components than those of either gold or copper, and thus silver nanoparticles can scatter light more strongly than gold nanoparti-

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cles of the same size and shape. Because silver surfaces are easily oxidized, however, gold has received increased attention because its surface chemistry is well-suited for attaching biomolecules for sensing. Materials that support strong plasmon resonances are limited, and thus creative *combinations* of materials can open new possibilities for tuning optical properties and for obtaining high electric field intensities. For example, bimaterial gold/silver nanoparticles,[23,32] multimaterial nanopyramids,[29,33] and metal–insulator nanoparticles[34–37] have all been prepared. An important predictive tool for determining the properties of composite nanostructures is plasmon hybridization,[38] a model that Le *et al.* use to explain the origin of the near-infrared and mid-infrared plasmon resonances from arrays of gold nanoshells.[3]

So, How Well Can We Make Them? Plasmonic nanostructures are produced through two approaches: top-down fabrication and bottom-up synthesis.[23] Chemical methods based on seed-mediated techniques have received the most attention because the synthetic procedures are relatively straightforward,[24,39] and the reactions typically occur at low temperatures (<100 °C). Breakthroughs in synthesizing some anisotropic nanoparticles (*e.g.*, nanorods,[39–43] nanoshells,[36,44] and nanocubes[23,45]) have resulted in greater sample monodispersity. However, we are not even close to achieving a mole of identical metal nanoparticles with complex shapes from a single reaction. More unusual and complex shapes do not yet have a well-defined procedure that can produce particles with uniform sizes and shapes.[17] As the applications for plasmonic nanoparticles increase in specificity and demand, complex shapes will be required, and the problem of obtaining monodisperse anisotropic particles must be solved. In this issue of *ACS Nano*, Ni *et al.* found new ways to fine-tune the length and width of nanorods.[1] Another challenge for synthesis is to create plasmonic particles composed of multiple materials. Although nanoshells are composed of a dielectric core surrounded by metal,[36,37] very few multimetal systems have been reported.[32,46]

Top-down fabrication methods offer some advantages over synthetic ones but have their own set of drawbacks. Serial techniques such as electron-beam lithography offer control over nanoparticle shape in two dimensions but are time-consuming, expensive, and not scalable to create anisotropic nanostructures. Parallel techniques can generate nanoparticles more rapidly because they rely on masks. Masks can be either *disposable*, such as close-packed arrays of sub-500 nm spheres used in nanosphere lithography[47] and colloidal lithography,[48] or *reusable*, such as those used in soft lithography[49] and microfabrication. Colloidal lithography is a simple method to create large-area arrays of truncated triangular structures, although the particles are usually not identical and are limited to a honeycomb-like lattice. The colloids can also act as a template or a shadow-mask to generate crescent shapes if the metal deposition occurs at an angle instead of at 0° (line-of-sight).[50] New nanofabrication methods, such as PEEL (which combines **p**hase-shifting photolithography, **e**tching, **e**lectron-beam deposition, and **l**ift-off) and soft-interference lithography (SIL),[34,41,51] offer scalable, accessible ways to create free-standing, three-dimensional particles at the sub-100 nm level. In these cases, the reusable mask is made from poly(dimethylsiloxane) (PDMS), and the patterns on the mask define the features' sizes and shapes in photoresist, which are then transferred into metal nanoparticles. Moreover, fabrication approaches can readily produce particles from multiple, different materials using layer-by-layer deposition.

Now, there is a perfect opportunity for the synthesis and fabrication experts to push each other to the next level, because the strengths and weaknesses of both strategies are complementary. For example, synthesis offers a facile way to generate large quantities of anisotropic, sub-250 nm (and much smaller!) metal particles.[52,53] Are there certain nanoparticles with sizes and/or shapes that show unusual optical properties and so should be pursued by fabrication routes to increase monodispersity? Also, fabrication can prototype multi-metal and metal–dielectric nanostructures easily. Are the plasmonic properties compelling enough to pursue and to scale-up by synthetic approaches? Finally, at least one other question should be raised: How "perfect" do plasmonic nanoparticles need to be for applications? Although patterned or assembled arrays of metal nanoparticles are not defect-free, as we have seen in this issue, gold nanoparticle substrates can detect specific antigen–antibody binding[2] and enhance SERS and SEIRA *via* hot spots between nanoshells.[3] In terms of fundamental properties, are singlecrystalline materials made by chemical synthesis different from amorphous, polycrystalline materials (often with large grain sizes) made by metal deposition, or is this irrelevant for first-order effects since the LSP resonances are so broad?

Future Challenges of Making and Modeling. Surprisingly, as our toolkit for creating new types of plasmonic structures has expanded, and our modeling and computational resources have improved, the applications based on localized plasmon resonances have narrowed. Why? Simply put, these noble metal nanomaterials are not yet true broadband materials. Their tunable optical properties *could* allow us to select the appropriate structure that best suits applications, but so far this has not been the case. We have chosen applications based on the nanoparticles that currently exist rather than choosing nanoparticles based on the applications that *might* exist. For example, nanoscale rods,[54] boxes,[55] and shells[56] made of gold absorb strongly at near-infrared wavelengths, and these structures are being tested for use in photothermal cancer therapy. Another example is matching the absorption of a molecular resonance with the LSP of a nanoparticle to determine the electronic structure of the adsorbed dye.[57]

One of the next challenges is to look past the nanoparticles that are already being made to nanoparticles that *could* be made for enabling new applications. To realize these prospects, we must develop methods that can screen for structure−property relations much more rapidly. Here is where theory will play an increasingly important role: instead of function following form, form can follow function. Several examples include nanorods,[39,43] nanoshells,[36] nanopyramids,[58] and arbitrary shapes,[59] where first nanoparticle sizes and shapes were calculated on the basis of desired properties and then the particles were created. Therefore, one of the next giant leaps in tailoring LSP resonances is to invert the working relationship of makers and modelers. In this way, we can think big and model desirable optical properties first, and then work on creating such particles from gold (and other noble metals) to make any application shine.

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