

Why gold nanoparticles are more precious than pretty gold: Noble metal surface plasmon resonance and its enhancement of the radiative and nonradiative properties of nanocrystals of different shapes

Susie Eustis and Mostafa A. El-Sayed*

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This *tutorial review* presents an introduction to the field of noble metal nanoparticles and their current applications. The origin of the surface plasmon resonance and synthesis procedures are described. A number of applications are presented that take advantage of the electromagnetic field enhancement of the radiative properties of noble metal nanoparticles resulting from the surface plasmon oscillations.

Introduction

This review is intended as an introduction to the concepts important in noble metal nanoparticles and their properties. Noble metal nanoparticles and their brilliant colors due to the surface plasmon resonance absorption constitute a large ongoing research field.¹ The color of the nanoparticle is found to depend on the shape and size of the nanoparticle and dielectric constant of the surrounding medium, leading to many studies on their synthesis and applications.

This review gives the researcher an idea of the field and points them to other appropriate review articles where more detailed references can be found on specific topics. The number of references has been limited to increase the

readability, but this is not intended to neglect giving appropriate credit to the researchers who did the research we present. Some specific examples are also presented to interest the researcher in this field and to show some of the newer applications of noble metal nanoparticles. Readers are encouraged to search out the review articles and the primary references therein for more detailed information. Table 1 gives recent review articles and the techniques and concepts covered in those reviews.

Nanotechnology

An atom measures about 1 ångström, or 10^{-10} meters. The study of atoms and molecules is the conventional field of chemistry as was studied in the late 19th and 20th centuries. A nanometer (nm), or 10^{-9} meters, represents a collection of a few atoms or molecules. Properties of bulk substances of micrometer sizes or larger have been studied for years by solid

Laser Dynamics Laboratory, School of Chemistry and Biochemistry, Georgia Tech, Atlanta, GA 30332
E-mail: mostafa.el-sayed@chemistry.gatech.edu



Susie Eustis

Susie Eustis obtained a BS in Chemistry from Rochester Institute of Technology (2000). She is currently a PhD candidate in chemistry with Mostafa A. El-Sayed. Her research focuses on the synthesis and optical properties of noble metal nanoparticles.

Professor Mostafa A. El-Sayed was born and received his BSc in Egypt. He received his PhD at Florida State with Professor Michael Kasha.

After doing postdoctoral work at Yale, Harvard and CalTech, he joined UCLA in 1961. In 1994, he became the Julius Brown Chair, Regent Professor and Director of the Laser Dynamic Lab at Georgia Tech. Since he moved to Georgia Tech, El-Sayed and his group became active in the study of the physical, chemical and photothermal processes of metallic and semiconductor nanostructures of different shapes. Professor El-Sayed's research



Mostafa A. El-Sayed

group is housed in the Laser Dynamics Laboratory (LDL). LDL houses the most recent lasers and laser spectroscopic equipment for time-resolved studies in the femto-to-millisecond time scale to allow study of the properties of material confined in time and nanometer space of different shapes. El-Sayed is an elected member of the National Academy of Science, Fellow of the American Academy of Arts and Sciences, the AAAS and

the Physical Society. He has received a number of national awards such as the Fersenius, the Tolman, the Richard's medal, as well as other numerous local sections ACS awards and the ACS-APS Langmuir National Award in Chemical Physics. He also received the King Faisal International Prize in Science and an Honorary Doctor of Philosophy degree from the Hebrew University.

Table 1 Some useful review articles in the field of noble metal nanoparticles

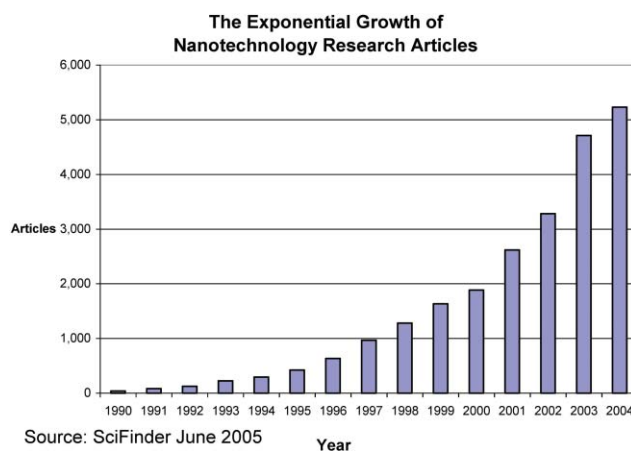
Topic	Articles					
General Reviews	Intro ¹	Intro, synthesis, assembly and applications ⁷	Shape based ¹¹	Optical and electronic ¹⁶⁻¹⁸	Photocatalytic and photochemical ²⁴	Core-shell optical properties ⁴³
Synthesis	Seeded ¹⁵	Dendrimer intro level ²⁵	Dendrimer ²⁶	Wires, rods, belts and tubes ¹²	Reverse micelle ^{13,23}	
Separation	Super critical fluid ⁴⁴					
Lithography Uses	Conventional ⁴⁵		Unconventional ⁴⁶			
Uses (cont.)	Nanosphere lithography ³⁰	Intro to Raman ³⁸	Comprehensive review of Raman ³⁹	Single Molecule SERS ⁴⁰	Biodiagnostics ²	Biological uses ^{3,4}
Assemblies	Fluorescence enhancement and quenching ³¹	Fluorescence effects ³²	Functionalization ⁴⁷	Optical componets ⁴⁸	Shape catalysis ²⁷	
Theory	Absorption and DDA of anisotropic nanoparticle ⁹	Clusters ⁵⁰	On electrodes ⁵¹	Synthesis and applications ^{52,53}	Waveguides ⁵⁴	
			Optical properties by shape and size ¹⁰	Bulk ⁵⁵		

state physicists and material scientists and are currently well understood. Materials on the 1–100 nm scale were not studied by either group in the past. It was just recently shown that on this size scale the properties of a material become dependent on its size and shape. However, the interface between substances is just now beginning to be understood. New properties develop on the nanoscale due to the lack of symmetry at the interface or to electron confinement that do not scale linearly with size. Thus, the nanometer scale (1–100 nm) incorporates collections of atoms or molecules, whose properties are neither those of the individual constituents nor those of the bulk. On this scale, many of the atoms are still located on the surface, or one layer removed from the surface, as opposed to the interior. New properties are observed on this scale due to the interface that is not observed in the bulk or individual atoms. Since the properties depend on the size of the structure, instead of the nature of the material, reliable and continual change can be achieved using a single material. Quantum dots of CdSe of different sizes have differing maximum emissions across the whole visible region, and gold and silver nanostructures have absorption across most of the visible region.

The nanometer scale is also interesting in biological systems.²⁻⁴ Many proteins are ~10's of nm in size. Since structures can be accurately designed on the nanometer scale they can be incorporated into biological systems, due to the similar size scales. Biological systems are complex, with synthesis, structure, and function all rarely understood in detail. The ability to rationally design structures on the same size as biological molecules generates the ability to probe and modify biological systems. Furthermore, biological systems are used to build up nanomaterials of specific shape and function. Nanostructures are being used as drug delivery agents, labeling agents, sensors, and to enhance electromagnetic fields.

The field of nanotechnology has received increasing attention over the last 20 years, and the number of publications of gold and silver nanoparticles has grown exponentially, as shown in Fig. 1. This review is limited to the last 10 years, with very few articles published before this time on noble metal

nanoparticles. The major publications in this area have appeared in the *Journal of Physical Chemistry B*, *Journal of the American Chemical Society* and *Langmuir*. *Nano Letters* has also published a large number of letters in this field since its conception in 2001. The number of patent applications and symposium articles for the Materials Research Society (MRS), the American Chemical Society (ACS) and *Advanced Materials* also represent a large number of the publications every year on noble metal nanoparticles. The recent growth in the number of publications observed in Fig. 1 is due to the recognition of the new and changing properties on the nanoscale. Discoveries have led to the observation that new properties exist when the size of materials is on the nanoscale due to electronic confinement in semi-conductors and surface effects in metals. The nanoparticle literature has been and continues to be dominated by synthetic papers. The difficulty in generating the desired size, shape, and monodispersity of nanoparticles continues to press the need for new and refined synthetic techniques. Generation of the desired chemical and physical interfaces to interact with target molecules also require the

**Fig. 1** Plot of the number of articles published on gold and silver nanoparticles since 1990.

need for many different synthetic techniques of generating metal nanoparticles. The percent (and also number) of papers describing the applications of nanoparticles has increased as nanoparticles are better understood and more researchers are finding useful applications for the nanoparticles. (Source: SciFinder Scholar v. 2004, accessed June 2005.) Thus, the synthesis of nanoparticles continues to be an active area of research as new and improved synthetic techniques are developed, expanding the use of nanoparticles. This increase in the available nanoparticles generates an increase in the number of applications, driving the potential for great advances in every day life due to nanotechnology. One of the hottest areas for nanoparticle use is in biological systems, owing to their potential application in medicine.

Quantum confinement in semiconductor nanoparticles

In semiconductors the nanoscale becomes important due to the quantum confinement of the electrons. As the particle size decreases below the Bohr radius of the semiconductor material used, the electron becomes more confined in the particle. This leads to an increase in the band gap energy. Furthermore the valence and conduction bands break into quantized energy levels.⁵ This is illustrated in the study by Bawendi,⁶ where CdSe spherical nanoparticles of various sizes are generated. The band gap emission shown in Fig. 2 is observed to shift through the entire visible region, from red emission for the largest particles, to blue emission for the smallest clusters.

Noble metal nanoparticles

Methods have long been known to generate beautifully colored glass by adding gold to generate burgundy, reds, or purples.⁷ Faraday attributed this color to very finely divided colloidal gold, or gold nanoparticles as known today. As the size or shape of the nanoparticle changes, the observed color also changes. Gold spheres have a characteristic red color, while silver spheres are yellow. More recent treatments have shown that the color is due to the collective oscillation of the electrons

in the conduction band, known as the surface plasmon oscillation. The oscillation frequency is usually in the visible region for gold and silver giving rise to the strong surface plasmon resonance absorption. Therefore, the origins of properties on the nanoscale are different for metal nanoparticles than for semiconductor nanoparticles. Fig. 2 exemplifies the difference in the optical properties of metal and semiconductor nanoparticles. With the CdSe semiconductor nanoparticles, a simple change in size alters the optical properties of the nanoparticles. When metal nanoparticles are enlarged, their optical properties change only slightly as observed for the different samples of gold nanospheres in Fig. 2. However, when an anisotropy is added to the nanoparticle, such as growth of nanorods, the optical properties of the nanoparticles change dramatically.

Many applications became possible due to the large enhancement of the surface electric field on the metal nanoparticles surface. The plasmon resonance absorption has an absorption coefficient orders of magnitude larger than strongly absorbing dyes. Anisotropic shapes have plasmon resonance absorptions that are even stronger, leading to increased detection sensitivity. Metal nanoparticles generate enhanced electromagnetic fields that affect the local environment. The field is determined by the geometry of the nanoparticle and can enhance fluorescence of the metal itself, the Raman signal of a molecule on the surface, and the scattering of light. The origin of the plasmon resonance and its applications will be presented in the following sections. The optical properties of noble metal nanoparticles lead to many uses as sensing and imaging techniques. Mirkin and co-workers² have pioneered the use of DNA in assembling and studying their interaction and their application in colorimetric detection of biological targets based on the binding events of target DNA. Nanoparticle use in the field of photonics⁸ is immense but is not discussed in this review owing to considerations of space and the interest of the authors.

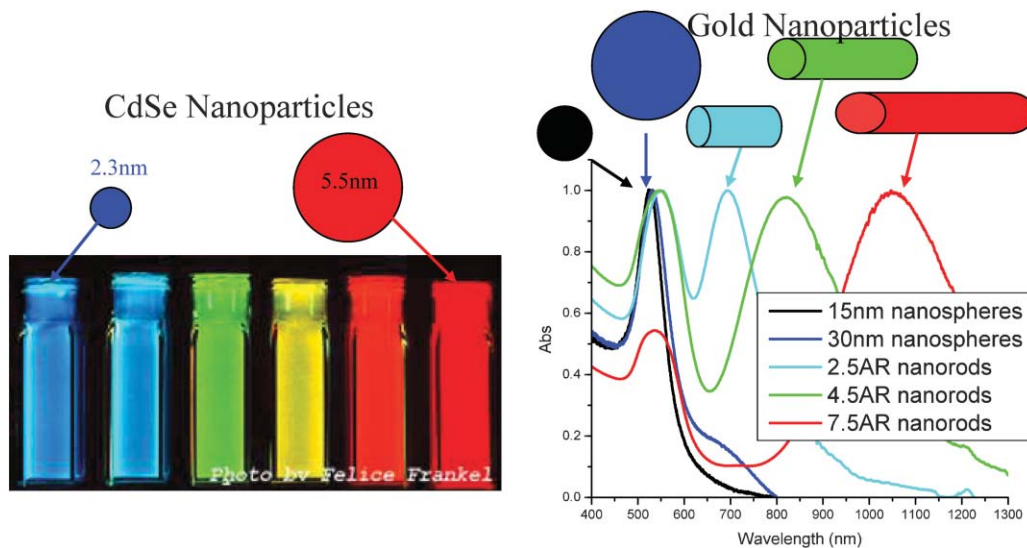


Fig. 2 Fluorescence emission of (CdSe)ZnS quantum dots of various sizes. Reproduced with permission from *J. Phys. Chem. B*, 1997, **101**, 9463–9475.⁶ Copyright 1997 American Chemical Society. Gold nanoparticles – absorption of various sizes and shapes. (Unpublished results.)

Origin of surface plasmon resonance in noble metal nanoparticles

The free electrons in the metal (d electrons in silver and gold) are free to travel through the material. The mean free path in gold and silver is ~ 50 nm, therefore in particles smaller than this, no scattering is expected from the bulk. Thus, all interactions are expected to be with the surface. When the wavelength of light is much larger than the nanoparticle size it can set up standing resonance conditions as represented in Fig. 3. Light in resonance with the surface plasmon oscillation causes the free-electrons in the metal to oscillate. As the wave front of the light passes, the electron density in the particle is polarized to one surface and oscillates in resonance with the light's frequency causing a standing oscillation. The resonance condition is determined from absorption and scattering spectroscopy and is found to depend on the shape, size, and dielectric constants of both the metal and the surrounding material. This is referred to as the surface plasmon resonance, since it is located at the surface. As the shape or size of the nanoparticle changes, the surface geometry changes causing a shift in the electric field density on the surface. This causes a change in the oscillation frequency of the electrons, generating different cross-sections for the optical properties including absorption and scattering.

Changing the dielectric constant of the surrounding material will have an effect on the oscillation frequency due to the varying ability of the surface to accommodate electron charge density from the nanoparticles. Changing the solvent will change the dielectric constant, but the capping material is most important in determining the shift of the plasmon resonance due to the local nature of its effect on the surface of the nanoparticle. Chemically bonded molecules can be detected by the observed change they induce in the electron density on the surface, which results in a shift in the surface plasmon absorption maximum. This is the basis for the use of noble metal nanoparticles as sensitive sensors.

Mie originally calculated the surface plasmon resonance by solving Maxwell's equations for small spheres interacting with an electromagnetic field. Gan was able to extend this theory to apply to ellipsoidal geometries. Modern methods using the discrete dipole approximation (DDA)^{9,10} allow one to calculate the surface plasmon resonance absorption for arbitrary geometries. Calculation of the longitudinal plasmon resonance for gold nanorods generates an increase in the intensity and wavelength maximum as the aspect ratio (length divided by width) increases. Thus, the plasmon resonance can

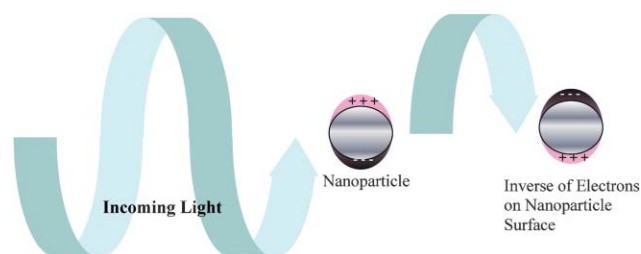


Fig. 3 Origin of surface plasmon resonance due to coherent interaction of the electrons in the conduction band with light.

be tuned across the visible region by changing the aspect ratio. The increase in the intensity of the surface plasmon resonance absorption leads to an enhancement of the electric field, as exploited in many applications described in detail in the following sections.

Many shapes of noble metal nanoparticles have been synthesized.^{9,11–15} Nanorods^{15–18} have attracted the most attention, due to the ease of preparation, the large number of synthetic methods available, the high monodispersity possible, and the rational control over the aspect ratio, which is primarily responsible for the change in their optical properties. Nanorods have been shown to have two plasmon resonances,¹ one due to the transverse oscillation of the electrons around 520 nm for gold and the other due to the longitudinal plasmon resonance at longer wavelengths as shown for various aspect ratios in Fig. 2. The transverse surface plasmon resonance does not depend on the aspect ratio and is at the same wavelength as the plasmon resonance of spheres. The longitudinal surface plasmon resonance increases with larger aspect ratios. The anisotropy has been shown to generate large control over the optical absorbance for all shapes generated.¹⁰ Triangular nanoparticles have been generated by photochemical means¹⁴ and chemical growth. Arrays of triangular nanoparticles can also be synthesized with nanosphere lithography. The edges and corners are very important with triangular nanoparticles. Snipping of the edges produces a visible blue shift in the plasmon resonance,¹⁴ which can be modeled theoretically.^{9,10} Disks also display a similar plasmon resonance absorption dependence on their aspect ratio.¹³

Synthesis

Many different techniques have been developed to generate metal nanoparticles. There are two general strategies to obtain materials on the nanoscale:³ Bottom up method where the atoms (produced from reduction of ions) are assembled to generate nanostructures, or top down method where material is removed from the bulk material, leaving only the desired nanostructures. Common top down techniques are photolithography and electron beam lithography (generation of the mask). Top down techniques suffer from the need to remove large amounts of material, while bottom up techniques suffer from poor monodispersity due to the need to arrest growth at the same point for all the nanoparticles. Photolithography is limited by the diffraction limit in the size resolution of features currently of around 60 nm, as it is based on the wavelength of the lasers available. As new techniques develop in producing laser pulses with shorter wavelengths, smaller nanostructures can be made by these techniques. Electron beam lithography is not limited by this resolution and recent instrumentation is now available that can produce nanostructures smaller than 10 nm. However, commercial instrumentation is expensive. Both of these techniques are only able to create a 2-dimensional structure in a single step. Current research in multi-photon photolithography applied to soft materials¹⁹ is working to remove both the size and the dimensional restrictions.

Nanosphere lithography,²⁰ being a bottom up technique, is an inexpensive synthetic procedure to generate arrays of noble

metal nanoparticles. A monolayer of closely packed monodisperse polystyrene spheres having sizes that are hundreds of micrometers in diameter is deposited onto a substrate that acts as a template for metal deposition. Metal is then deposited onto and in between the spheres using thermal evaporation to create particles in the voids of the polystyrene spheres. The polystyrene spheres can then be dissolved in organic solvents leaving an array of triangular shaped metal nanoparticles on the substrate as observed in Fig. 4. This generates monodisperse, uncapped nanoparticles in geometric arrays over a large surface area of the substrate. Nanosphere lithography has generated large amounts of attention due to its ease of replication and high monodispersity of samples generated, both across one sample, and multiple trials. This technique is limited in the absorption intensity due to the presence of only a monolayer of nanoparticles. However, the fact that prismatic particles have sharp corners, the absorption enhancement is so great that only ten thousand particles give excellent absorption on a microspectrometer.²¹ Recently, Haes *et al.*²² have been able to release the triangular nanoparticles into solution by adding surfactant and sonicating the sample to remove the particles from the substrate to form isolated particles or dimer pairs of triangular nanoparticles. Nanosphere lithography is being used to make sensors based on the position of the absorption maximum of the surface plasmon resonance. Due to the ease of fabrication, functionalization, and low cost per sample, this technique is useful in generating disposable units.

Other bottom up techniques include templating, chemical, electrochemical, sonochemical, thermal and photochemical reduction techniques.^{7,14,15,23} Bottom up synthesis techniques usually employ an agent to stop growth of the particle at the nanoscale.²⁴ Capping materials, such as a surfactant or polymer are used in this technique to prevent aggregation and precipitation of the metal nanoparticles out of solution. Choice of the reduction technique, time, and capping material determines the size and shape of the nanoparticles generated. Spheres,^{7,13,15,23} rods,¹⁵ cubes, disks,¹³ wires, tubes,¹² branched,⁹ triangular prisms,⁹ and tetrahedral nanoparticles

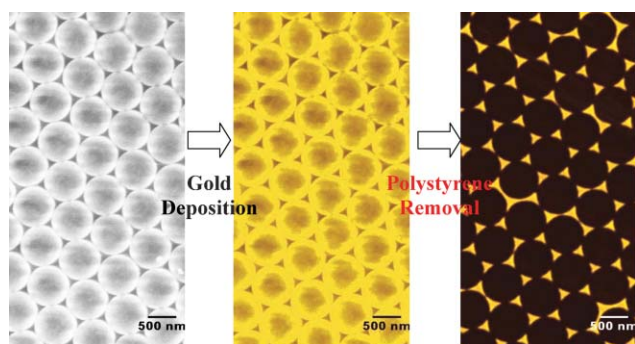


Fig. 4 Deposition of polystyrene spheres on substrate, thermal evaporation of bulk gold and removal of polystyrene spheres to leave triangular gold nanoparticles. Reproduced with permission from W.Huang, W. Qian and M. A. El-Sayed, 'Optically detected coherent picosecond lattice oscillations in two dimensional arrays of gold nanocrystals of different sizes and shapes induced by femtosecond laser pulses,' *Proc. SPIE Int. Soc. Opt. Eng.*, 2005, **5927**, 592701.⁵⁶

have been generated in gold, silver and platinum with various reduction techniques and capping materials.

Synthesis volumes are typically small and the resulting particles are slightly different on every run. Gold and silver nanoparticles are now commercially available both pre-conjugated and conjugated with popular analytes, but caution should be exercised as the samples will vary from batch to batch and could be contaminated from chemicals used in the synthetic procedure. Choice of solvent and surface chemistry often narrow the possible synthetic techniques for the desired processes.

Generation of spherical gold nanoparticles is commonly carried out by the citrate reduction method⁷ reported by Turkevitch in 1951. Gold salt and citrate are stirred in water, while the temperature, the ratio of gold to citrate, and the order of addition of the reagents control the size distribution of gold nanospheres generated. Small metal clusters have been generated in dendrimers.^{25,26}

A popular method for generation of large spherical and non-spherical nanoparticles is the seeding technique.¹⁵ A chemical reducing agent is used, where small, generally spherical nanoparticles are first generated and then added to a growth solution with more metal ions and surfactant to induce anisotropic growth. The seeds are generated with a strong reducing agent, such as sodium borohydride. The growth solution employs a weaker reducing agent (often ascorbic acid) to reduce the metal salt to an intermediate state so that only catalyzed reduction on the nanoparticle surface is allowed. Growth is believed to be due to kinetic conditions, limiting the control over size and shape. Proper seed, salt, and stabilizer concentrations are adjusted to generate nanorods. Counter ions and additives have also been found to play a role in directing growth and the final shape of nanoparticles obtained. Nanorod growth is proposed to be due to a steric interaction of the stabilizer forming bilayer structures along the long axis of the nanorod to allow growth only along the short axis.¹⁵ Having a seed with facets that are ready for growth is necessary to form anisotropic particles.

Two-phase reactions⁷ have been extensively used and studied to produce nanoparticles for generation of very small nanoparticles (1–5 nm) with narrow dispersity. The particles are stabilized by a gold–thiol bond. Samples generated with the two-phase method are stable for long periods of time when dry and can easily be redispersed in many organic solvents. In synthesis, the gold salt is first transferred to the organic phase using a suitable surfactant. Then sodium borohydride is added to the aqueous phase. The formation of nanoparticles is monitored by the generation of the orange to deep brown color in the organic phase. The ratio of gold to surfactant and the reaction temperature control particle size and dispersity. This synthetic procedure is often referred to as generating monolayer-protected clusters (MPCs) due to the monolayer coverage of the sulfur groups and the small size of nanoparticles generated. Many improvements to this synthesis procedure have been reported⁷ to generate small monodisperse gold nanoparticles.

Inverse micelles^{13,23} have been used to generate many different sizes and shapes of nanoparticles. Inverse micelles use surfactants to create small pockets of a water phase in an

organic solvent, where the surfactant has a polar group that faces the aqueous phase, and the tail faces the organic phase. Adding water will linearly affect the size of the micelle generated,²³ leading to an increase in the size of the nanoparticles generated. The key to generating single crystal, monodisperse nanoparticles in inverse micelles is to use a metal salt conjugated to the surfactant prior to the addition of the reducing agent. The inverse micelles allow for exchange between different water volumes, generating good monodispersity of nanoparticles, and can be used for many different materials.²³

Applications of noble metal nanoparticles

Catalysis

Catalysis drives many reactions, with the ability to lower the activation energy of the reaction, and thus increases the rate of reaction and the yield of the desired products. The use of nanoparticles as catalysts has increased exponentially as nanoparticle properties and reactions are better understood. The possibility of using less material and having different properties for different shapes of nanoparticles is very attractive. Nanoparticle catalysis has been investigated for both homogeneous (catalyst and reactants are both in solution) and heterogeneous (catalyst supported on a substrate) systems. A recent review has many of the references important for current research into nanocatalysis.²⁷

In homogeneous catalysis, Narayanan and El-Sayed²⁷ have shown that shapes with more corners and edge atoms have a higher reactivity than similar nanoparticles with fewer corner and edge atoms. Thus shape and crystal structure differences can lead to different catalytic rates. Research continues to observe the connection between structure and function for nanoscale catalysts.

Small clusters are also found to be very catalytically active, even for materials that display very limited reactivity on the bulk scale.^{28,29} For example, bulk gold is considered a noble metal, and is very unreactive in the bulk state. However, small clusters of gold are found to be catalytically active. Many possible explanations have been proposed^{28,29} for the difference in reactivity between clusters and bulk gold. They include the electronic and chemical properties of nanoparticles or the shape, size and oxidation state of the nanoparticles. The surface support is also suggested to be responsible for the catalytic activity.²⁸ The crystal structure of gold has also been proposed to be important in the catalytic properties. This demonstrates new properties for nanoparticles, which are unexpected based on bulk behavior since bulk gold has no catalytic activity, and clusters are efficient catalysts, generating further interest in nanomaterials as new functionality is present on the nanoscale.

Application based on the enhanced optical properties of nanoparticles

a. Absorption. Haes *et al.*²⁰ have used the surface plasmon resonance from an array of silver nanoparticles created by nanosphere lithography to detect the interaction of amyloid β -derived diffusible ligands (ADDL) and anti-ADDL

antibody, believed to be important in Alzheimer's disease. Nanosphere lithography³⁰ generates a triangular array of nanoparticles, which has a plasmon resonance whose frequency is very sensitive to the dielectric constant of the surrounding material, due to the sharp edges of the triangular nanoparticles. The gold nanoprisms were functionalized to bind to ADDLs on the exposed surface of the nanoparticles. The substrate is then exposed to varying concentrations of anti-ADDL and a shift in the plasmon resonance absorption is detected to varying degrees linked to the concentration. The binding constant of the anti-ADDL and ADDL can be determined with this technique.²⁰ Thus, the surface plasmon resonance absorption is a powerful detection technique for species of interest. The nanoparticles can be functionalized to observe only the molecules of interest³⁰ and the absorption of desired molecules can be observed by a shift in the plasmon resonance absorption (*i.e.* a change in the color).

b. Fluorescence of chromophores in close proximity. Metal nanoparticles have an effect on molecular chromophores in close proximity to the surface, as well as their intrinsic fluorescence. The effect on chromophore fluorescence in close proximity to the surface of metal nanoparticles is due to the strong electromagnetic field generated at the surface of metal nanoparticles.^{31,32} Chromophores within ~ 5 nm of the surface of the metal nanoparticle have their fluorescence quenched while chromophores at distances of ~ 10 nm or greater have their fluorescence enhanced up to 100-fold. Chromophores within 5 nm of the surface interact electronically with the surface to donate the excited electrons to the metal, thus quenching the fluorescence by non-radiative pathways available in the metal nanoparticle. However, as the distance is increased the electric field is still strong enough to enhance the fluorescence probability, but the nanoparticle is not able to interact directly with the electrons of the metal. Thus, the fluorescence of molecular fluorophores can be increased by attaching chromophores *via* long linkers to the surface of metal nanoparticles.

c. Nanoparticle fluorescence. The weak intrinsic fluorescence of noble bulk metals (quantum yield $\sim 10^{-10}$) resulting from the electronic interband transition was discovered in 1969.³³ Recent research has shown that nanoparticles have enhanced fluorescence emission over the bulk, particularly in small clusters.³⁴ Nanorods also have enhanced emission over bulk metal and nanospheres, due to the large enhancement of the longitudinal plasmon resonance.^{16-18,35,36} Clusters³⁴ and nanorods^{35,36} have an emission that shifts wavelengths as the size or aspect ratio increases, respectively. For nanorods, the longitudinal plasmon resonance enhances the radiative cross section of the interband transition of bulk gold leading to shifting emission wavelengths and intensities depending on the overlap between the two transitions.^{35,36} The observed emission of gold nanorods is presented in Fig. 5a with quantum yields of 10^{-4} – 10^{-5} .³⁵ The emission wavelength increases as the aspect ratio of the nanorod is increased.

Emission of gold³⁴ and silver clusters is highly tunable by small changes in the number of atoms in the cluster. Zheng *et al.*³⁴ characterize the gold cluster fluorescence with emission

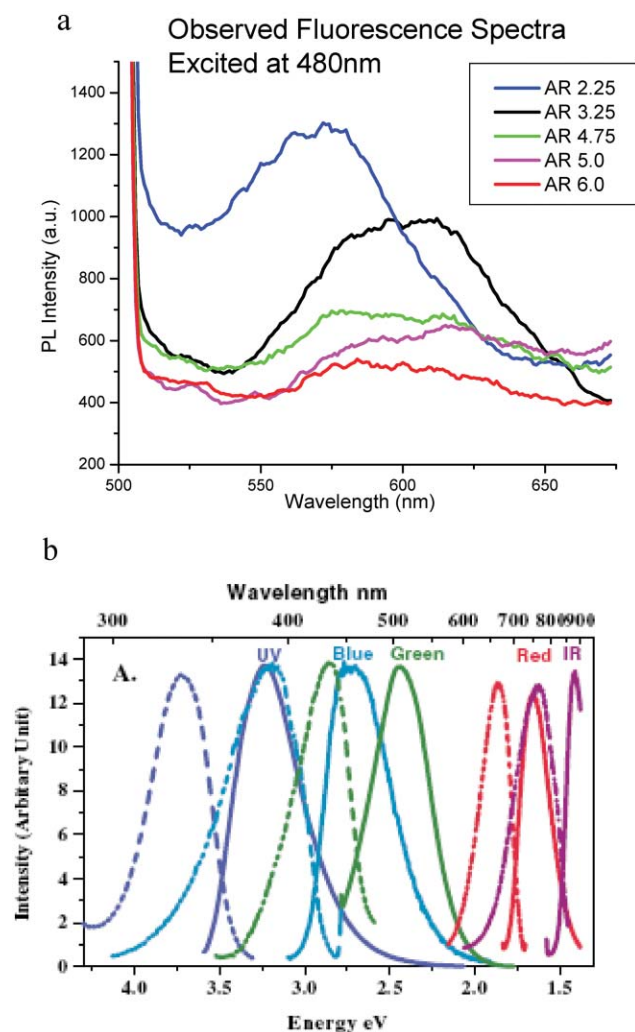


Fig. 5 Experimentally observed emission spectra from gold nanorods excited at 480 nm. Reproduced with permission from *J. Phys. Chem. B*, 2005, **109**, 16350–16356.³⁵ Copyright 2005 American Chemical Society. b) Emission from gold clusters. Reprinted Fig. 1a with permission from J. Zheng, C. Zhang, and R. M. Dickson, *Phys. Rev. Lett.*, 2004, **93**, 077402.³⁴ Copyright 2004 American Physical Society.

and excitation maxima, quantum yields, and lifetimes. The emission and excitation spectra of the different size clusters are presented in Fig. 5b. As the number of atoms in the cluster increases the emission wavelength redshifts.³⁴ High quantum yields are observed, especially for the smallest cluster (Au_5) at 70%.³⁴ The narrow and tunable emission of the gold clusters makes them attractive as energy transfer pairs used to measure distance and interactions of many types of molecules.

d. Enhanced Rayleigh (Mie) scattering. The enhanced scattering cross section due to surface field effects can be used as a powerful technique to image biological systems. Gold nanoparticle surface plasmon resonance scattering is predicted in the Mie equations and is found to increase as the size of the nanoparticle increases. By conjugating gold nanoparticles to anti-EGFR antibody, El-Sayed *et al.*³⁷ are able to distinguish between cancer and non-cancer cells from the strong scattering images of the gold nanoparticles conjugated to antibodies that

binds only to the cancer, but not to the non-cancer cells. This scattering is observed from a simple optical microscope. They obtain a 600% greater binding ratio to the cancerous cells than to non-cancerous cells, enabling detection of cancerous cells by observing the scattered light on a dark field microscope. Fig. 6 shows the scattering obtained with gold nanoparticles non-specifically adsorbed on the surface (a–c) and gold nanoparticles with anti-EGFR (d–f) antibodies specifically bound to the cancerous cells but not to the non-cancerous cells. Because of this difference the band shape and the surface plasmon absorption maximum are found to be different and this can thus be used to differentiate cancerous cells. These results show that gold nanoparticles have enormous power as a diagnostic tool. Not only can changes in the surface plasmon resonance absorbance be detected to determine the adsorbed species in chemical, biochemical, sensing, and medical fields, but also the scattering signal can be used in imaging techniques to observe different binding with functionalized nanoparticles.

e. Surface enhanced raman scattering (SERS) of adsorbed molecules. An effect was observed in the early 70's when molecules deposited on rough noble metal surfaces showed greatly enhanced Raman scattering.³⁸ Rough surfaces are decorated with nanoparticle shapes with surface plasmon oscillations. This effect has come to be known as surface enhanced Raman scattering (SERS).³⁹ Recently, nanoparticle research has shown that aggregates of nanoparticles are able to give the largest enhancement. The origin of this effect has been the subject of intense debate. Prevailing theories attribute the origin of the SERS signal as a “hot spot” at the junction of two or more particles.⁴⁰ Nanorods are observed to have higher SERS signals than spheres, due to the higher electric field generated at the tips of the nanorod.⁹ SERS is being developed as a powerful diagnostic tool.⁴⁰ Large enhancement is available along with chemical information.

There are two effects^{41,42} which have been considered to account for this enhancement of the Raman signal: chemical enhancement⁴¹ and electromagnetic field enhancement.⁴² The chemical effect states that the nature of the molecule determines the enhancement factor. Different signal strengths are observed on the same substrate with different chemicals. However, the bonding strength will affect the number of molecules bound and in contact with the substrate and the time spent in a given “hot spot.” Thus it is difficult to determine if the chemical effect is simply a bonding time in a high electromagnetic field determined by sample geometry. The electromagnetic field enhancement mechanism attributes this effect to the local field strength generated by the surface plasmon oscillations.⁴² Nanoparticles are observed to generate moderate signals, while aggregates generate much larger enhancement, suggesting that it is the interaction of multiple particles that generates large Raman enhancement. The electromagnetic field of a given geometry of the metal structures can be calculated.⁹ Large electromagnetic fields are predicted to increase at the junction of two nanoparticles or as the radius of curvature increases, such as at sharp points of a triangle. Rough surfaces have many random geometries with which to enhance Raman signals, but nanoparticles offer

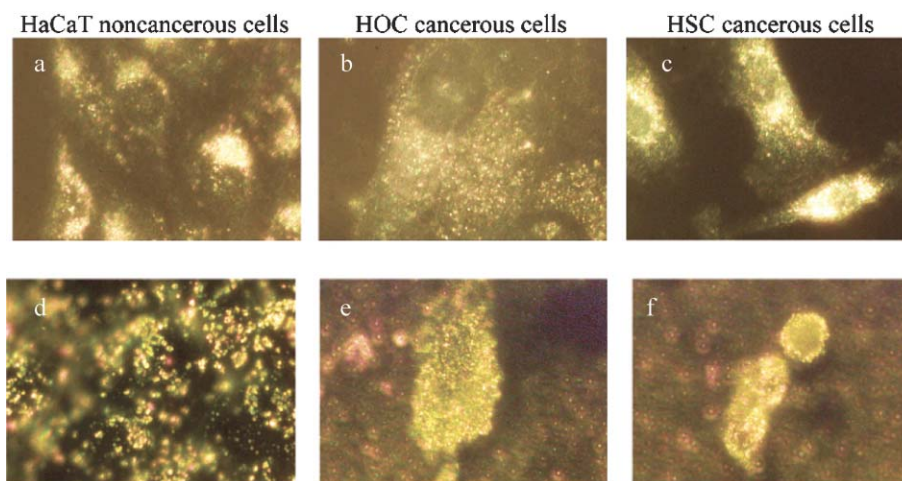


Fig. 6 Light scattering of cell labeled with (a–c) gold nanoparticles and (d–f) anti-EGFR coated gold nanoparticles. The anti-EGFR coated gold nanoparticles bind specifically to the cancerous cells, while all other gold nanoparticles are non-specifically bound. (a&d) nonmalignant epithelial cell line HaCaT (human keratinocytes), (b&d) malignant epithelial cell lines HOC 313 clone 8 (human oral squamous cell carcinoma) (c&f) malignant epithelial cell lines HSC 3 (human oral squamous cell carcinoma). Reproduced with permission from *Nano Lett.*, 2005, 5, 829–834.³⁷ Copyright 2005 American Chemical Society.

the opportunity to study the enhancement in accurately designed systems.

An intense background signal is also observed in all SERS spectra.³⁸ This background blinks with the SERS signal. This background signal has been attributed to the emission of the metal surface, enhanced by the roughness of the surface. This signal has also been attributed to a metal–substrate charge interaction leading to emission.

Summary

The field of synthesis and studying the properties of noble metal nanoparticles is presently a very active area of research. Synthetic techniques continue to evolve leading to more and improved control over the size and shape of the particles generated. The optical properties and intense electromagnetic fields generated by the nanoparticles make these particles very attractive for sensing, diagnostics, and photothermal therapeutic applications in many areas. The change in color of the nanoparticles to signal adsorption or bonding of a certain molecule to the surface can be easily detected. The enhancement of both Rayleigh and Raman signals lead to imaging and chemical information on many species of interest, previously unattainable in a diagnostic setting. Changing properties simply by changing the size or shape of the nanoparticle is attractive and will continue to be employed in new applications in the future.

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