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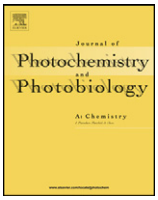

Plasmonic photochemistry and photon confinement to the nanoscale

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ABSTRACT

This account gives a simple qualitative discussion of the confinement of the motion of electrons to the nanoscale. The mechanism by which gold and silver nanoparticles confine photons to the nanoscale, resulting in both the surface plasmon resonance and strong surface plasmon fields, is mentioned. Examples of different observations and applications of the plasmonic field enhancement of light scattering, absorption, photo-thermal and nonradiative processes studied in our group are summarized.

1. Confining the motion of electrons in materials to the nanometer scale

The properties of any material are determined by the space available for its electrons to execute their characteristic motions, which in turn are determined by the balanced forces acting upon the electrons within the material [1]. This defines a characteristic length scale for the electronic motion in the material. This length scale varies between 1 and 100 nm for different materials, i.e., in the nanometer dimension [2]. In insulators the electronic motion is confined to a very small space, while in conducting material it has a much longer scale [2,3]. Reducing the size of any material below the length scale characterizing its electronic motion produces a new material with different properties [4]. These novel properties might be useful for a wide range of applications that may have far reaching effects, such as improving human life or the defenses of our country. The research developing these new materials and studying their properties will open up new industries and create new jobs, thus raising the standard of living. These are a few of the reasons behind the present interest of many governments in nanotechnology.

2. Plasmonic nanomaterials: confining photons to the nanoscale [4]

When the size of some materials, like gold and silver, is reduced to the nanometer scale, new characteristic collective motions of their conduction band electrons, which can be excited by resonant photons in the UV–visible–near infrared range, are observed [3,4]. This produces oscillating electromagnetic fields on the surface of the nanoparticles having the same frequency as the resonant light producing it, but with a reduced wavelength (on the length scale of the nanoparticle). As a result, for solid nanoparticles of different shapes, the surface electromagnetic fields produced can be orders of magnitude stronger than that of the captured photon that produced it [5–7]. Recently, we found that hollow nanoparticles can produce even stronger fields that what is possible for solid nanoparticles [8]. This ability of gold and silver nanoparticles to strongly concentrate the electromagnetic fields of absorbed photons could be used to induce photochemical or photophysical changes in another material on the surface, or very near the surface, of the nanoparticle simply by exciting the nanoparticle with a laboratory cw light source. For example, our group recently observed [9] fluorescence results that suggest exciton–exciton annihilation is occurring in a sample where π-conjugated fluorescent polymers were assembled on a monolayer of silver nanocubes and excited with a cw xenon lamp. Such annihilation events are normally only observed upon excitation with femtosecond laser pulses.

Thus, a photon with the same frequency as the surface plasmon resonance that is absorbed by the gold or silver nanoparticle will produce a strong electromagnetic surface field at the surface of the particle. This field will have an intensity corresponding to that of hundreds to thousands of photons [5]. This determines the enhancement factor of the plasmonic nanoparticle [5]. If a molecule is adsorbed on the surface of a plasmonic nanoparticle that absorbs at a frequency in resonance with the surface plasmon resonance frequency, the rate of absorption or scattering by this molecule is then greatly enhanced [10]. If the molecule undergoes photochemistry, its rate of photochemistry is greatly enhanced. New nonlinear photochemistry might even be observed upon excitation with cw xenon or mercury light sources [9]. If the adsorbed molecule is excited at a higher frequency than the nanoparticle surface plasmon resonance but its fluorescence coincides in energy with the

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nanoparticle surface plasmon resonance absorption, the fluorescence will be quenched.

3. Some important time scales that determine the properties of the plasmonic nanoparticles

3.1. The coherence decay (dephasing) time of the plasmonic collective excitation (femtoseconds)

The properties of the surface plasmon (SP) are crucially influenced by its dephasing time $T_2 = 2\hbar/T_{\mathrm{hom}}$, where T_{hom} is the homogeneous linewidth of the SP resonance. The dephasing time is proportional to the local field enhancement factor $|f|$. This relation is particularly important for nonlinear optical effects. Both the effective third-order susceptibility of metal particles [11] and the effective SERS cross section [12] are proportional to $(T_2)^4$. Microscopically, the SP dephasing time is controlled by coupling of the SP's to the electron-hole pair continuum [13] and by radiation damping, i.e., the decay of SP's into photons [11], which is important in large particles (radius larger than ca. 10 nm). The first dephasing mechanism is strongly influenced by bulk electron scattering processes [13]. In addition, electron-surface scattering is believed to contribute for small particles (sizes below ~10 nm), or for high surface state densities, where chemical interface damping is important [4]. Thus, the coherence decay time (dephasing time) of the plasmonic collective excitation depends on three factors. First, it depends on the quality of the solid-state of the gold or silver nanoparticle and its surface. Thus, single crystalline nanoparticles should have longer coherence time and thus stronger surface fields and larger enhancement factors. Second, the coherence decay depends of the size of the nanoparticle. Third, it depends on the electronic structure of the solid making the nanoparticle, e.g. for the same size and shape, silver nanoparticles should have stronger plasmon fields than those of gold nanoparticles. The reason for this is that gold has an inter-band electronic transition near the surface plasmonic transition. This could give rise to additional relaxation mechanisms to reduce the coherence lifetime. The stronger plasmonic fields of silver nanoparticles are the reason that aggregated silver nanoparticles are better to use in SERS applications. From line width measurements of the gold surface plasmon resonance band, a dephasing time of few femtoseconds was determined [3,14] as discussed above, the dephasing time determines the strength of the surface plasmonic field and thus the nanoparticle enhancement factors.

3.2. The electron–phonon relaxation time T_1 (~1 ps)

While T_2 does not involve energy exchange (but only phase change), T_1 does. In this process, electronic energy is converted into phonon excitations and consequently the nanoparticle lattice heats up. The nanoparticle can be heated to high temperatures through this decay process as the high energies of the visible light are converted into heat in such a small volume. This relaxation time is on the time scale of 1 ps [3].

3.3. Phonon–phonon relaxation time (hundreds of picoseconds)

In this relaxation, the excited phonons of the nanoparticle hot lattice are transferred to the surrounding medium. Therefore, the hot nanoparticles use their photo-thermal energy to heat the surrounding medium by converting the strongly absorbed light energy into heat. This effect can be used in many applications in material science, nano-biology and nano-medicine as we shall show later in the discussion of an application for cancer therapy [15].

4. Plasmonic field effects, Radiative or Photo-thermal?

If the rate of a chemical or photochemical reaction changes in the presence of a plasmonic field, it could be due to several different mechanisms. One possibility is that the electronic structure of the system changes upon being exposed to the enhanced electromagnetic field created by a one-photon absorption process. However, new nonlinear optical excitations under the high level of the electromagnetic flux of the plasmonic field enhancement also become possible. Furthermore, as discussed in the previous section, the rapid conversion of the absorbed light energy into heat (hundreds of picoseconds) could enhance or induce new thermo-chemical processes. In a recent study, we observed an increase in the rate of the chemical reaction between hexacyanoferrate III and thiosulfate when we photo-excited gold nanoparticles mixed in the reaction solution [16]. As the intensity of the exciting light increased, the rate of the reaction increased, but so did the solution temperature. We then determined the activation energy of the reaction by studying the reaction rate at several different temperatures. We used two separate methods to control the reaction temperature: the intensity of the light that excited the gold particles and a traditional thermostat. The activation energy was found to be the same for both heating methods, suggesting that plasmonic nanoparticles were simply heating the solution.

5. Some other studies in our laboratory

From the above discussion, it can be seen that when plasmonic nanoparticles are excited, besides enhancing photonic process like absorption and scattering (Raman and Rayleigh), they can also enhance thermally activated processes. In the following, we present results of experiments carried out in our laboratory illustrating the application of plasmonic enhancement effects on absorption, scattering, photo-thermal and nonraditive relaxation processes.

5.1. Enhancement of Rayleigh light scattering for imaging and cancer diagnosis [17]

The rates of scattering and absorption processes can be enhanced by the strong electromagnetic field at the surface of a nanoparticle caused by the surface plasmon enhancement. Our group has calculated how the ratio of the amount of light scattered to light absorbed depends on the nanoparticle size and shape [18,19]. For nanoparticles of the same shape, small nanoparticles have larger enhancement factors for the absorption processes than the scattering processes, and thus are better suited to be used for photo-thermal applications. The opposite is true for larger nanoparticles, making them better suited for imaging applications.

The detection of cancer cells based on the plasmonic enhancement of Rayleigh (or Mie) scattering by gold nanoparticles is shown in Fig. 1 [17]. Gold nanoparticles are conjugated to cancer cell antibodies (anti-EGFR) and mixed with separate solutions of living cancer and healthy cells. After 20 min of incubation, the solutions are imaged using a dark field scattering microscope. The antibodies selectively bind the gold nanoparticles to the surface of cancer cells and not to healthy cells. In Fig. 1, it is clear that the images of the four sets on the right hand side are cancer cells and the set of two on the left are healthy cells. An interesting observation is that in this figure one can see individual nanoparticles 40 nm in size each with a surface plasmon resonance wavelength of 530 nm, opposite to the diffraction limit rules in optics. This is a result of the photon confinement effect, which has greatly increased our resolution of optical imaging.

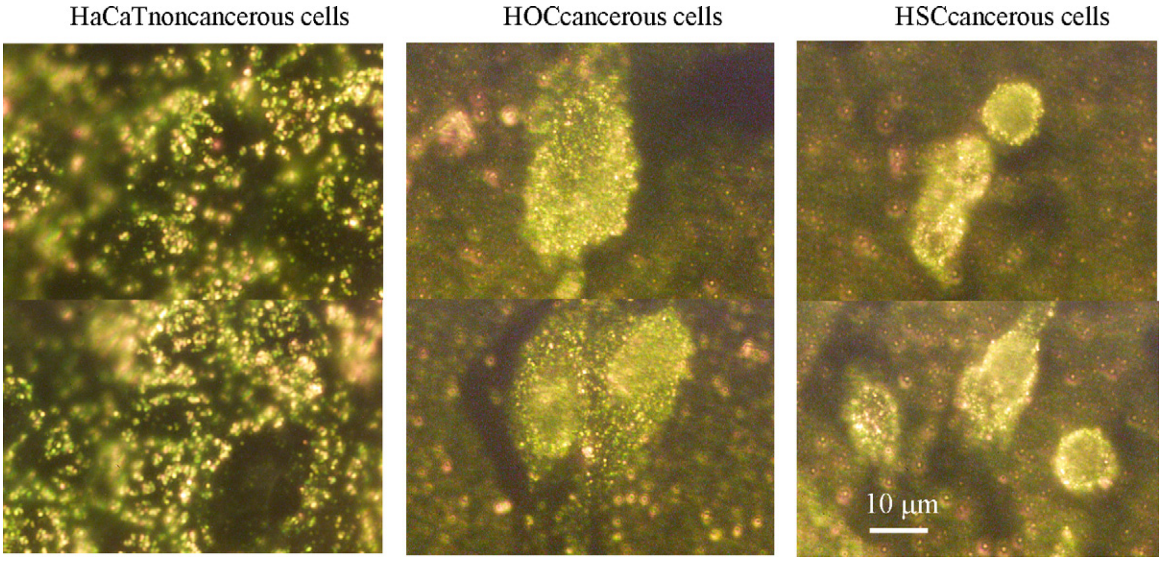

Fig. 1. Gold nano-spheres conjugated to cancer antibody and are mixed and incubated with three different solutions for 20 min, two have different cancer cells (on the right) and one has healthy cells (on the left). The dark-field images of the three types of cells are shown above. It is clear that most of the gold nano-particles are bound to the cancer cells (the two sets of images on the right but remain in solution away from the healthy cells (set of images shown in the left column).

5.2. Plasmonic photo-thermal therapy (PPTT) of cancer using gold nanoparticles [15]

In Fig. 1, it is clear that most of the gold nanoparticles have accumulated on the cancer cells and not on the healthy cells due to the antibody selectivity. A cw laser of resonant frequency with the surface plasmon resonance absorption of the gold nanoparticles is used to expose these cells for few minutes. A blue dye is then added to the solution to help distinguish the dead cells from the live ones. The live cells are able to destroy the dye; the dead cells cannot, causing the dead cells to appear blue. It is clear that at 80 mW laser power the cancer cells are destroyed while much higher energies (more than 120 mW) are required to kill the healthy cells. This is because the nanoparticles are farther away from the healthy cells, so higher energies are required to be absorbed by the nanoparticles in the solution in order to reach the temperature needed the melt the membrane of the healthy cells. Thus by keeping the laser energy below 100 mW, one can selectively destroy the cancer cells, leaving the healthy cells unaffected. This photo-thermal method was shown to work in vivo (in mice) by our group [15] (Fig. 2).

5.3. Plasmonic enhancement of the nonradiative relaxation as a result of enhancing the radiative processes in vertically aligned CdTe/Au core/shell nanorods [20–23]

The effect of nanoshell thickness and relative orientation of the plasmon field direction with respect to that of the exciton transition moment on the exciton nonradiative relaxation was investigated in arrays of CdTe-Au core-shell nanorods. To fabricate the nanorod arrays, first the CdTe nanorod cores were deposited using a vapor–liquid–solid (VLS) epitaxial growth mode. These single crystal CdTe nanorods exhibit a wurtzite crystal structure with its c-axis (long rod axis) normal to the sapphire substrate (see Fig. 3). A gold shell is sputtered onto the nanorods to the desired thickness (15 nm or 26 nm) using a sputter coater operating at room temperature.

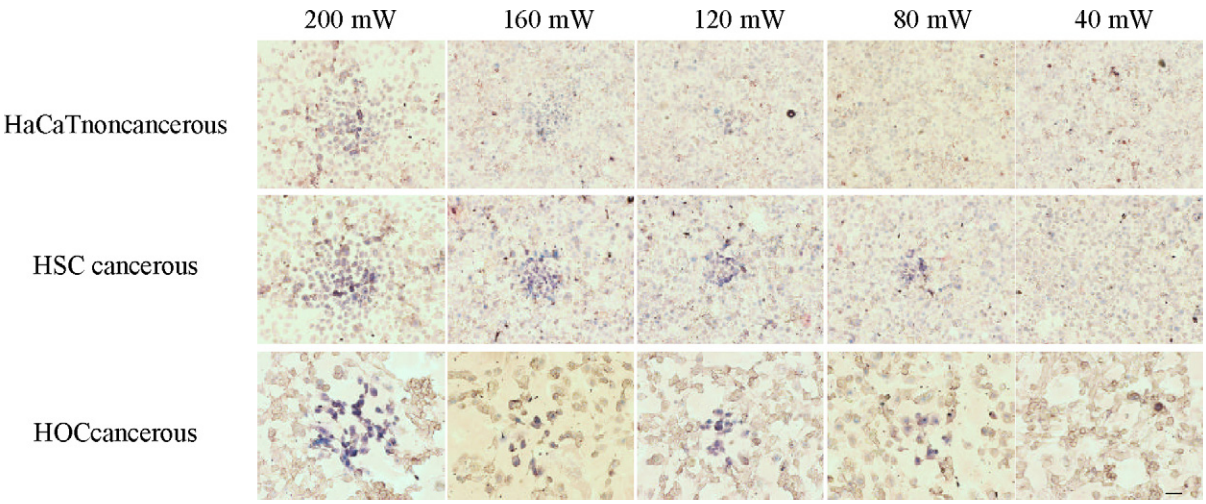

Fig. 2. Using the plasmonically enhanced absorption rate of gold nano-particles (conjugated to cancer cells) and the rapid conversion of the absorbed energy into heat to melt cancer membranes and kills the cancer cells at very low laser power (80 mW) without affecting the healthy cells. This technique (Plasmonic Photo-Thermal Therapy (PPTT)) is shown by our group to stop cancer growth in mice when using gold nanorods and near-IR cw light source capable in penetrating biological tissues [15].

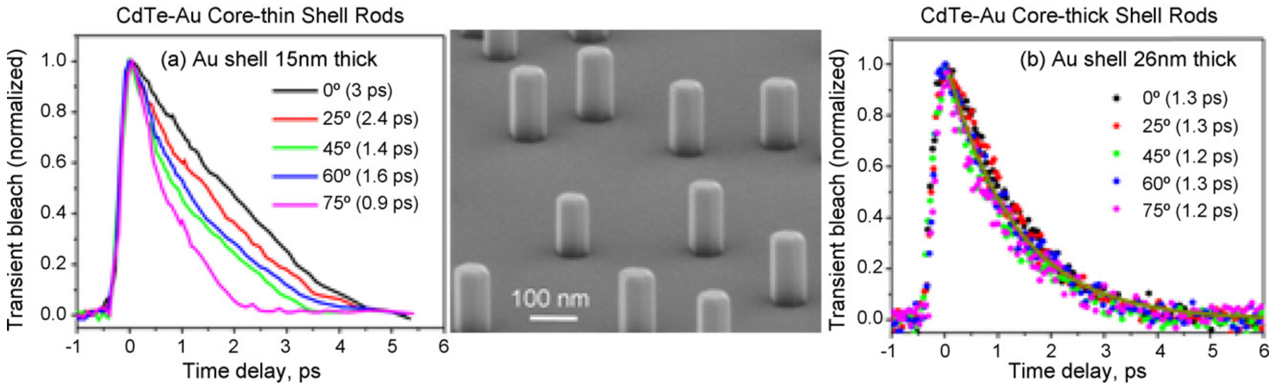

Fig. 3. The decay curves of the band gap excitation of CdTe nanorods in presence of the surface plasmon field of gold nano-shells having thicknesses of 15 nm (left) and 26 nm (right) and different angles between the rod long axis and the exciting light polarization direction.

The CdTe exciton decay was measured before and after exciting the gold shell surface plasmon as a function of the angle between the exciton band transition moment direction (the rod long axis direction) and the polarization direction of the exciting light on rods having two gold shell thicknesses, 15 and 26 nm. The following results are obtained: (1) For the thin shell, the exciton decay was non-exponential with lifetimes that were dependent on the relative orientation of the nano-rod with respect to the exciting light, with maximum effect found when the long axis of the rod (the transition moment of exciton) and the polarization of the plasmon exciting light coincide. (2) For the thick gold shell, the exciton decays were exponential and the decrease in the lifetime was independent of the exciting light polarization direction.

Two absorption mechanisms were proposed (Fig. 4a and b) that could assist the decay of the excited state of the CdTe semiconductor. Both processes involve the absorption of photons from the probe light used in the experiment that determines the transient bleach of the band gap excitation with time. The probe light is at the same frequency as that of the surface plasmon resonace and is therefore enhanced by the presence of the plasmon field. The two absorption processes involve the ionization of the excited electron. In mechanism (a) of Fig. 4, the ionization involves the absorption of one or two unpolarized photons to reach the continuum. Mechanism (b) involves an Auger process to ionize the excited electron. It requires the absorption of a photon from the plasmonically enhanced probe light to excite the ground state. This absorption is polarized along the *c*-axis (the rod long axis). The additional excited electrons are involved in an Auger process, wherein one of the excited electrons decays to the ground state by giving its energy to another excited electron for its ionization.

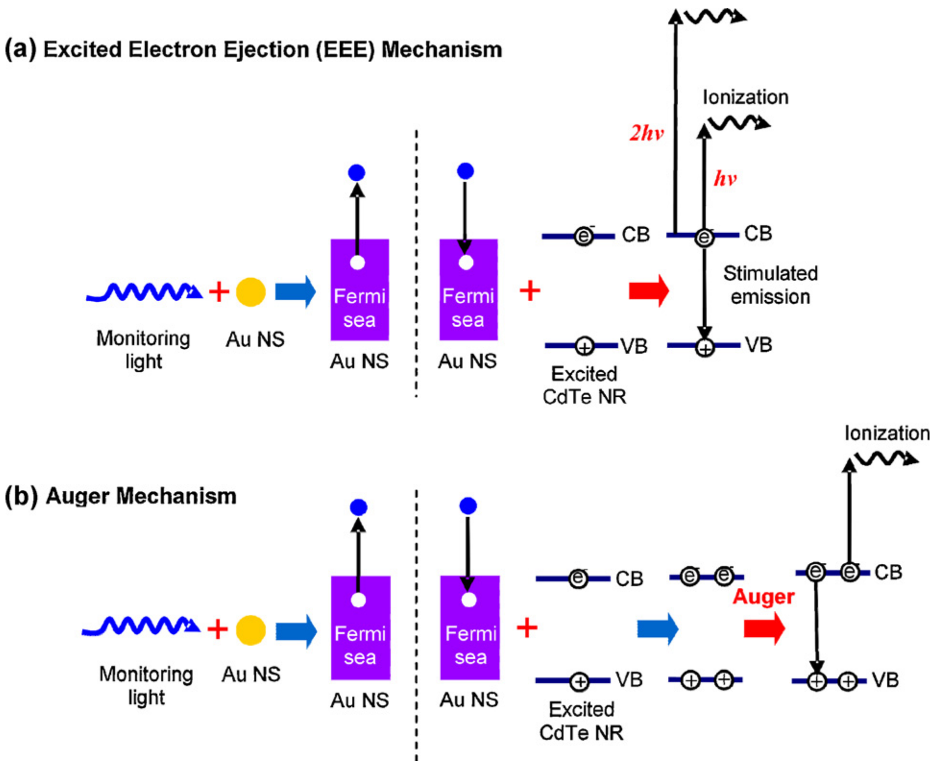

Fig. 4. Schematic diagram showing both the (a) excited electron ejection (EEE) and (b) the Auger mechanisms. For both mechanisms the incident laser light excites the surface plasmon resonance oscillations in the gold nanoshell (NS) producing strong fields which can facilitate or enhance the absorption or stimulated emission within the semiconductor nanorod (NR). Note that the excited electron ejection mechanism (EEE) involves an excited state absorption or stimulated emission while the Auger process involves ground state absorption.

The effect of shell thickness is explained as follows. The Auger mechanism is very sensitive to the relative orientation of the polarization of the light exciting the plasmon band and the exciton transition moment. It dominates when the plasmon field is dipolar in nature and polarized parallel to the exciton transition moment, i.e., parallel to the long axis of the rod. The DDA calculations showed that the plasmon of the thin gold shell was dipolar in nature. Whereas that of the thick gold shell was not [21]. Therefore, it is expected that the Auger mechanism will only dominate for the thin shell when the sample is oriented with the long axis of the rod parallel to the polarization direction. On the other hand, because the plasmon of the thicker gold shell is not dipolar in nature the lifetimes of mechanism (b) are not expected to be sensitive to the orientation, as observed. However, if both mechanisms (a) and (b) occur simultaneously in the rod with the thick shell, the lifetime decay for any nanorod orientation should be non-exponential, which was not observed. The decay was exponential, in agreement with mechanism (a) and not with (b). Thus one could conclude that the importance of mechanism (b) decreases as the shell thickness decreases. The question is why? The answer to this question was not understood when the original work was published [22]. Since then, our other groups have become interested in hollow or shell nanoparticles and how the fields of its two surfaces couple. It was previously known that when two solid nanoparticles approach one another the plasmonic field in between the particles becomes stronger due to the coupling of the fields of the individual particles [7,24,25]. Nanoshells (hollow nanoparticles) have two surface plasmon fields, one on the outer surface and one on the inner surface [8]. As the thickness of the shell becomes smaller (i.e., the shell becomes thinner), the fields of the two nanoshell surfaces are brought closer together and therefore can couple and become stronger. This gives rise to many interesting properties. Such plasmonic hollow nanoparticles as nanocages and nanoframes are found to have the strongest plasmonic fields and thus are the most useful structures for use as sensitive sensors [16,26].

The above results suggest that the thicker shell has weaker surface plasmonic field. This decreases the enhanced absorption by the ground state and thus decreases the excited state concentration. The rate of the Auger process, which decreases the exciton lifetime in mechanism (b) is proportional to the square of the excited state concentration. The rate of mechanism (a) is only linearly dependent on the excited state concentration. As a result, the relative importance of mechanism (b) is greatly reduced in the rods with thick shells and it is quite possible that only mechanism (a) is present in this rod. This explains the presence of a single exponential decay that is insensitive to orientation for rods with the thick shells, as observed.

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