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Critical Size for the Observation of Quantum Confinement in Optically Excited Gold Clusters

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New areas of research associated with monolayer protected clusters and the discovery of the extraordinary catalytic activity of nanostructured gold have emerged recently.[1] Metal nanoparticles that approach the size of their electron Fermi wavelength possess unusual properties and functionalities important for applications.[1d−f,2] The great complexity in the structural and electronic properties of these clusters becomes more apparent as their size decreases, leading to an intense interest and debate regarding the predictions of their properties. Due to the lack of systematic detailed investigations over a broad range of cluster sizes and utilizing the same cluster surface conditions, the ability to fully grasp the science of nanometer-size metal clusters is limited. Gold clusters can be stabilized to a remarkable degree by a monolayer of ligands[2a] offering the exciting possibility to fabricate building blocks for potential applications in catalysis,[1d,e] biolabeling,[1f] memory, and electronic effects based on single electron charging processes[1a,2] as well as exceptional optical properties.[3−5]

For gold nanoparticles with diameters less than 3 nm (∼1000 atoms) the surface plasmon resonance (SPR) feature gradually disintegrates and discrete peaks emerge in the UV−vis−NIR spectra for gold clusters which are less than 1.1 nm (∼50 atoms).[1a,5,6] Optical properties of nanoparticles with $N > 1000$ can be described by a bulk dielectric function with appropriate corrections associated with electron scattering at the surface.[7] However, the sharpness of this transition (as it relates to the physical properties of the metal cluster) for particles between ∼25 and ∼1000 atoms is not well understood. Careful analysis of absorption spectra for thiolate monolayer protected clusters (MPC) indicated that an HOMO−LUMO gap remains very large as compared to room temperature energy k_BT for sizes up to ∼300 gold atoms.[1a,6] It remains unclear whether there is a gradual transition from metallic behavior to the appearance of molecular-like features or if there is a sudden change with a band gap opening near the Fermi level for a particular size. Accurate knowledge of the size where the band gap opening occurs is important for many important issues such as an extraordinary rise in the catalytic activity for gold nanoclusters as the metal particle size was decreased,[1d,e] the electron self-exchange rate in thin MPCs films.[8] Here we have systematically investigated the femtosecond optical excitation dynamics in gold clusters capped with hexane thiolate as a function of the particle size in the range 1−4 nm.

The organic-soluble nanoclusters were synthesized according to a modified Brust reaction.[8,9] The isolated MPC core diameters were estimated from transmission electron microscopy (TEM) images which showed pretty narrow core size distributions: 1.1 ± 0.2, 1.7 ± 0.2, 2.2 ± 0.2, 3 ± 0.3, and 4 ± 0.1 nm.[8] The clusters were assigned to $Au_{25}(SR)_{18}$, $Au_{144}(SR)_{60}$, $Au_{309}(SR)_{92}$, $Au_{976}(SR)_{187}$, $Au_{2406}(SR)_{326}$, respectively[8] (Supporting Information (SI)). The absorption spectra of these MPCs in hexane show a decrease of the SPR band at 520 nm with decreasing core size down from 2.2 nm (SI, Figure S2). When the core size is further decreased to that of Au_{25} (1.1 nm), distinct spectral structures emerge, indicative of molecule-like properties with discrete energy levels.[1a,5,6,10]

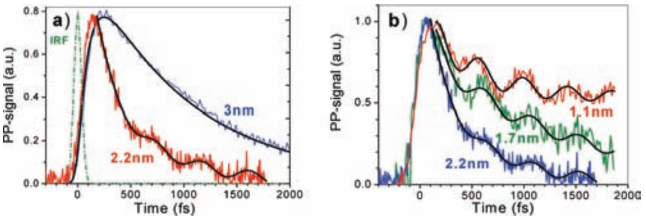

Figure 1. (a) Demonstration of different transient absorption dynamics for MPCs of 2.2 and 3 nm size particles. Instrument response function profile (IRF) is also shown. (b) Decay profiles with oscillatory feature for small MPCs (solid lines - best fits, SI).

Time-resolved degenerate transient absorption studies have been carried out utilizing a pump−probe setup based on a cavity dumped femtosecond Ti:sapphire laser system[11] (SI). We have investigated the degenerate transient absorption dynamics at 415 nm as a function of the gold cluster size. For larger size clusters exhibiting an SPR band (3 nm, 4 nm), the pump probe profile showed a rise-time feature followed by the decay. This profile was nearly the same as that of much larger 25 nm nanospheres.[11] A very different behavior in transient absorption dynamics and spectra has been observed for 2.2 nm clusters and smaller when compared to 3 nm clusters. A much faster initial decay was detected for the cluster size 2.2 nm (Figure 1a). This decay profile is qualitatively similar to that previously observed in much smaller clusters.[12] In addition, an interesting subpicosecond oscillatory feature has been detected in the transient absorption profiles for small gold clusters. For relatively large gold nanoparticles a coherently excited "breathing" vibrational mode was previously observed in the transient signal.[13] The suggested mechanism should not allow the vibrations to have a period shorter than a picosecond (which is expected for small particles) due to a relatively slow (∼1 ps) electron−phonon relaxation process which is responsible for the impulsive lattice heating[13] (SI). Indeed, in the present investigation we did not observe any oscillatory features for particle sizes greater than 2.2 nm. Surprisingly, we did detect distinct oscillations with a period of 450 fs (∼75 cm^{-1}) in smaller clusters (less than 2.2 nm) (Figure 1). Analysis of these oscillations[14] suggests a displacive excitation mechanism of coherent phonons, similar to the phenomenon observed in femtosecond transient absorption signals of semiconductors and semimetals.[15] For this mechanism the excited state electron configuration lives much longer to maintain a new equilibrium position for many periods of vibrations as it takes place in semiconductors and molecular systems.[15] Hence, the appearance of the oscillations for small MPCs can be correlated to the emergence of an energy gap in smaller clusters.

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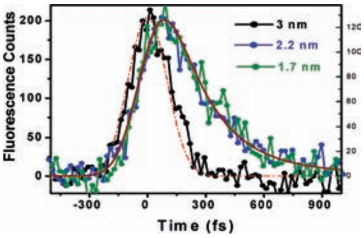

Figure 2. Time-resolved fluorescence profiles for different cluster sizes measured at 530 nm. Excitation wavelength is at 400 nm. Solid line - best fit exponential decay for MPCs 2.2 nm; decay time - 220 fs. Dash-dot line - instrument response function.

The luminescence of metals is normally very weak due to ultrafast nonradiative decay and the absence of a band gap (ref 11 and references therein). However, the near-infrared (IR) fluorescence with a relatively high quantum yield (as compared to larger nanoparticles and bulk metal) has been previously observed for small thiolate-coated Au MPCs.[3−5] In addition to the near-IR fluorescence at ∼830 nm in small gold MPCs, we have also detected a fast visible fluorescence which has a broad spectral distribution and is centered at ∼550 nm for all the gold clusters.[3]

Using a femtosecond time-resolved up-conversion setup, we measured the time-resolved visible fluorescence (∼530 nm) for MPCs of different sizes (SI). The size dependence of the dynamics of the fluorescence lifetimes is shown in Figure 2. For relatively large MPCs (>3 nm), the fluorescence decay was found to be shorter than the instrument response function and similar to what we have previously observed in much larger gold nanospheres (25 nm).[11] However, we found quantitatively different fluorescence dynamics for smaller clusters (Figure 2). The change in dynamics with size is consistent with the transition taking place at ∼2.2 nm. For smaller clusters demonstrating a molecular-like discrete energy level structure,[5,6] the visible fluorescence dynamics is fast (∼220 fs) but well resolvable with a fluorescence upconversion setup (Figure 2). This fluorescence may be due to a LUMO+1−HOMO or LUMO−HOMO-2 transition according to recent TDDFT calculations for Au_{25} which revealed the energy level structure of the Au_{25} MPC.[16] We have also measured two-photon absorption cross sections with the aid of one- and two-photon fluorescence upconversions.[3] A break in the trend as a function of size was observed at 2.2 nm consistent with the femtosecond transient absorption and fluorescence upconversion result.[3]

Figure 3 shows the trends in the mean transient absorption, mean fluorescence lifetimes, and TPA cross section for cluster sizes decreasing from 25 to 1.1 nm. The lifetimes and TPA cross section are plotted as functions of the inverse cluster diameter *D*. In this representation the band gap within a simple spherical oscillator model E_j for metal clusters[10a] or within a semiclassical circulation frequency resonance model[6] is a linear function of the inverse diameter

Considering these experimental findings we propose a relatively abrupt optical gap opening at ∼2.2 nm (∼300 atoms). The existing information about a possible structural motif change in the range of sizes 100−1000 atoms is not conclusive enough to relate the observed transition to the particular structural rearrangement in the gold core.[17] Recent structural determinations for MPCs Au_{102},[1c] Au_{25},[16] and Au_{144}[18] have provided new insights to the organization of the MPCs. However, a particular composition for larger structures remains largely unknown.

We conclude that an abrupt change in the optical properties (fluorescence, transient absorption, two-photon absorption) is observed once the diameter of the cluster is smaller than 2.2 nm. Displacively excited vibrations for smaller MPCs which are associated with the presence of the band gap have been detected for only particles smaller than 2.2 nm. With this information, scientists and engineers may be able to tailor the small clusters to optimize specific properties (electric or optical) for particular applications.

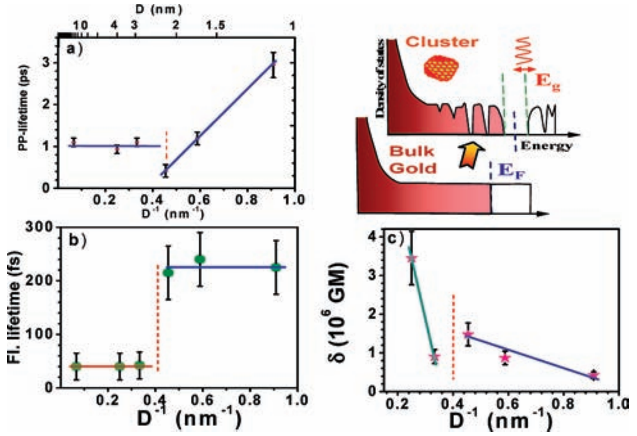

Figure 3. Transient absorption mean decay time (a), visible fluorescence decay time (b), and two-photon absorption cross section (c) as a function of MPC size. Schematic illustration of the gap opening in the gold density of states is also shown.

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Supporting Information Available: Experimental procedures and characterization results. This material is available free of charge via the Internet at http://pubs.acs.org.

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