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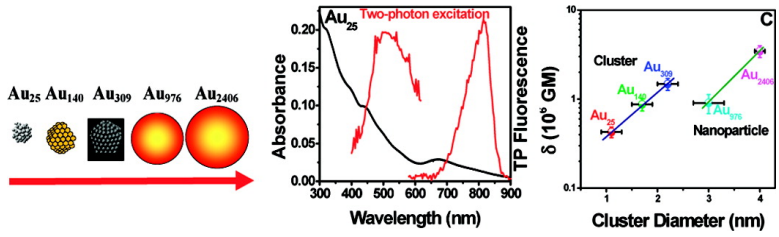

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Quantum-Sized Gold Clusters as Efficient Two-Photon Absorbers

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Metallic nanoscale materials with a size close to the Fermi wavelength of an electron (less than 1 nm) tend to show quantum size effects and have received great research attention in the past decade.[1–3] The research in this size regime has been sparked by their appeal in technological applications as well as for a fundamental scientific understanding of the behavior of nanoscopic materials.[1–3] Among several metal clusters, gold clusters have been extensively investigated where researchers have observed a transition from bulk-like properties to molecular-like regimes leading to quantum confinement effects.[3–8] Gold clusters comprising tens of atoms to several hundred atoms have been synthesized by stabilizing them with alkyl or aryl thiolates, and they are often referred to as monolayer protected gold clusters (MPC).[3–8] Quantization of energy as well as charge was observed for small size metal clusters, and the electrochemical measurements have shown the size-dependent oxidation and reduction peaks.[3–6] Although there has been extensive research on the electrochemical and electron-transfer properties on the small sized MPCs, research concerning the optical effects, excited-state dynamics and in particular the nonlinear optical properties are quite unexplored. Optical absorption and steady-state luminescence on the MPCs has been investigated by Murray and co-workers[3,4,6] as well as Tsukuda and co-workers[7] with several thiolate capped MPCs. Luminescence mainly in the near-infrared region has been observed for several small sized MPCs.[4,7] The nonlinear optical properties such as two-photon absorption (TPA) of these luminescent MPCs may give rise to potential applications in two-photon biological imaging, optical power limiting, and nanolithography.

Materials with the luminescence in near-infrared region have found applications in biological imaging of breast-cancer tissue.[9] Since small-size metal clusters such as Au_{25}* have decent luminescence efficiencies ($\sim 2.5 \times 10^{-4}$) in the near-infrared region, they can be made useful for two-photon imaging with infrared light. In this context, we have investigated the two-photon emission and cross-section of Au_{25} clusters with infrared light. In addition, the present investigation is aimed at understanding the scaling laws of TPA cross-section as the cluster size is decreased from a gold nanoparticle (4 nm) down to Au_{25} clusters (1.1 nm).

Shown in Figure 1A are the optical absorption and steady-state emission spectra obtained for Au_{25} clusters capped with hexane thiolate and dissolved in hexane. Absorption spanning the visible to near-infrared region is seen for Au_{25} with distinct maxima around 675 and 410 nm and the ultraviolet region. The observed absorption spectra matched well with the previous reports and are ascribed to the quantized nature of the gold clusters.[5,6] Also shown in Figure 1A is the emission spectrum obtained after excitation at 1290 nm from the output of an optical parametric amplifier which shows the emission with a maximum at 830 nm. The corresponding pump-power dependence of the fluorescence at 830 nm is shown in Figure 1B which

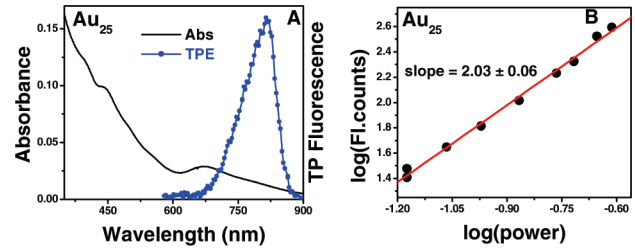

Figure 1. (A) Optical absorption of Au_{25} and two-photon emission spectrum after excitation at 1290 nm for Au_{25} clusters. (B) Power dependence of fluorescence obtained at 1290 nm suggesting it is a two-photon process.

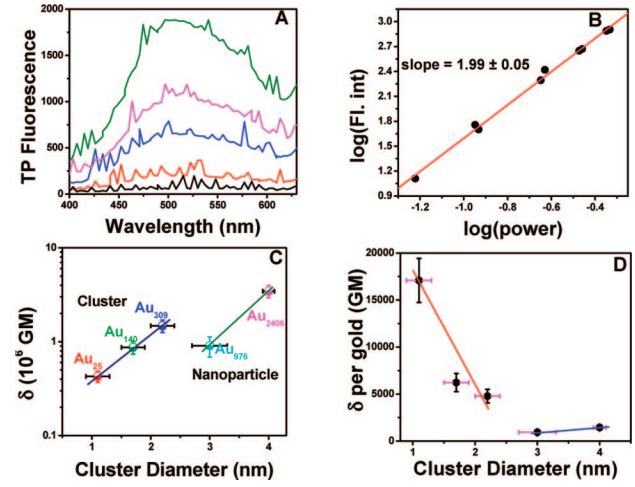

Figure 2. (A) Two-photon excited fluorescence spectra of Au_{25} at different pump powers after excitation at 800 nm. (B) Power dependence of emission at 510 nm. (C) Absolute TPA cross-sections obtained by one and two-photon excited fluorescence upconversion measurements for different gold clusters. (D) TPA cross-section per gold atom as a function of cluster size. TPA results shown in panels C and D are obtained with 800 nm excitation. Solid lines in panels C and D are guides to the eye.

gave a slope of ~2 indicating that it is a two-photon excited emission. Comparative TPA cross-section measurements have been carried out using the two-photon excited fluorescence method[10] with H_2TPP in toluene[11] as the standard. From these measurements, TPA cross-section at 1290 nm for Au_{25} in hexane was determined to be 2700 GM which is superior to the TPA cross-sections of many organic chromophores with emission in the near-infrared region.[11] Present measurements on Au_{25} gold clusters suggest that they can be used as multiphoton imaging agents with near-infrared luminescence.

Apart from the near-infrared luminescence for Au_{25} clusters, additional luminescence in the visible region with maximum around 510 nm has been observed. Interestingly, such fluorescence is also two-photon allowed and Figure 2 A shows the fluorescence spectra obtained after excitation at 800 nm and at different pump-powers for

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Au_{25} clusters in hexane. Pump-power dependence of the fluorescence at 510 nm is shown in Figure 2B which gave a slope of ~2 suggesting also that it is indeed a two-photon excited emission. Fluorescence in the visible region was observed for gold nanoparticles in our earlier work for spherical gold nanoparticles, dendrimer gold nanocomposites and gold nanorods which have surface plasmon absorption in the visible region.[12,13] The emission spectrum of the gold nanoparticles tend to follow the surface plasmon absorption band and has very short lifetime which was ascribed to the intraband d to sp electron–hole recombination via the Auger process.[13] In an effort to understand the cluster size-dependence on such luminescence and on the nonlinear optical properties (especially on TPA), studies of gold clusters with increasing size have been carried out. In the present investigation, we have carried out TPA measurements on gold clusters comprising 25 (1.1 nm), 140 (1.7 nm), 309 (2.2 nm), 976 (3 nm), and 2406 (4 nm) gold atoms synthesized using well-established procedure[5] and passivated with same hexane thiolate capping agent. Absorption measurements on these clusters have shown surface plasmon absorption in the visible region for Au_{976} and Au_{2406} gold clusters while it is found to be absent for Au_{309}, Au_{140}, and Au_{25} gold clusters (Supporting Information). Discrete spectral features are observed for Au_{25} as shown in Figure 1A.

Two-photon excited fluorescence in the visible region with excitation at 800 nm has been observed for all gold clusters with different sizes though with different fluorescence maxima and spectra (Supporting Information). However, the fluorescence quantum yield of the visible emission is quite small (in the order of 10^{-7} to 10^{-8}) for all gold clusters and is difficult to be measured with a standard Spex-Fluorolog fluorimeter. Thus, it is not easy to determine the TPA cross-sections of these gold clusters with relative TP excited fluorescence method which needs the exact measure of one-photon quantum yield and a standard whose TPA cross-section with similar fluorescence quantum yields as that of gold clusters. Because of the experimental difficulties for measuring relative TP cross-section of gold clusters, efforts have been made here for absolute measurement of TP cross-sections with a technique of combined one and two-photon excited femtosecond time-resolved fluorescence upconversion (details are furnished in Supporting Information).

The fluorescence kinetic decay traces for all gold clusters were measured with one and two-photon excitation and by taking the ratio of the relative counts per second at 100 fs time delay for one and two-photon excitation, the TPA cross-sections for all the gold clusters were determined. The corresponding cross-sections are plotted as a function of cluster size in Figure 2C. The cross-section of Au_{25} in hexane was found to be around 427 000 GM and it is increased to 1 476 000 GM for Au_{309} in hexane. There is an increase in cross-section from Au_{25} to Au_{309}. However, the TPA cross-section for Au_{976} was around 905 200 GM and it is increased for Au_{2406} cluster which has a cross-section of 3 452 000 GM. Obviously there is a singularity in the TPA cross-section plot as a function of cluster size when the it is increased from the Au_{309} (2.2 nm) to Au_{976} (3 nm). This can be ascribed to the transition of the cluster behavior to a gold nanoparticle behavior possessing strong surface plasmon absorption.

Absolute TPA cross-sections observed for the gold clusters are very high and are much larger than any of the experimentally investigated organic macromolecules (typically ~1000 GM at 800 nm for some of best organics) or semiconductor nanocrystals. Such large TPA cross-sections are useful in several applications such as optical power limiting, nanolithography, and as labels for multiphoton biological imaging. In addition, an interesting trend is observed in the plot of the TPA cross-section per gold atom as a function of cluster size shown in Figure 2D. δ per gold atom decreases drastically with increasing the cluster size and there is a saturation-type of behavior for large gold nanoparticles. The results can be explained by the evolution and involvement of interband transitions in smaller clusters. Even the TPA cross-section per gold atom is as high as 17 080 GM for Au_{25} and taking in to account the number of valence electrons in gold atom, the observed cross-sections per gold are approaching the theoretical limit predicted for TPA cross-sections[14]

In summary, our results have shown that the Au_{25} cluster is a very good TPA material with a cross-section of 2700 GM at 1290 nm with luminescence in near-infrared region making it a good biological label for multiphoton imaging. In the near-infrared region (800 nm), TPA cross-sections in the region of half-million to a few million GMs has been observed for gold clusters which make them efficient TP absorbers for applications in optical power limiting, nanolithography. An interesting trend of singularity in TPA cross-section has been observed indicating a transition from cluster to nanoparticle behavior in gold clusters.

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Supporting Information Available: TEM images of clusters, optical absorption, two-photon luminescence spectra, and details of the one and two-photon excited fluorescence upconversion are furnished. This material is available free of charge via the Internet at http://pubs.acs.org.

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