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Near-Infrared Luminescence from Small Gold Nanocrystals

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A novel photoluminescence is reported for small metal nanocrystals in the near-infrared region (1.1−1.6 μm). Near-infrared photoluminescence spectra were measured at room temperature for 1.1 and 1.7 nm Au nanocrystals using a 1.06 μm excitation source. This photoluminescence is attributed to sp to sp-like transitions, analogous to intraband transitions in bulk gold; however, the exact mechanism is unknown. A conservative estimate for the quantum yield for the 1.7 nm gold nanocrystals is $(4.4 \pm 1.5) \times 10^{-5}$ at room temperature, more than 5 orders of magnitude greater than that of bulk gold.

1. Introduction

Luminescence from metal surfaces has received only a limited amount of attention.[1−5] The process has a very low efficiency and has not proven to be important technologically. The reason for the rarity of luminescence from metals is quite simple: metals do not have band gaps. In a simple model of a semiconductor, an electron excited from the valence band into the conduction band continuum will initially decay through phonon-mediated nonradiative processes until reaching the bottom of the conduction band. A transition across the gap, in general, will leave too much energy for a phonon to dissipate; therefore, it will be radiative if it is allowed. In metals, the nonradiative decay can proceed all the way back down to the ground state, making luminescence exceedingly improbable. For example, the quantum yield for photoluminescence from bulk gold and copper films is on the order of 10^{-10}.[1]

It is clear that if an energy gap was present among the higher lying states, one could expect to see an appreciable amount of photoluminescence from a metal. The most natural regime where one can find large energy gaps between electronic states is that of molecules. Indeed, the most active area of gold luminescence research has been in the field of gold-centered organometallic compounds, where a large number of photoemissive gold(I) compounds have been discovered and studied.[6,7] These compounds consist of mono-, di-, and trinuclear gold complexes. On the same size scale, other workers have studied the emission of light from silver clusters in matrices. They have observed chemiluminescence during deposition into the matrix,[8,9] due to the reactive combination of two small clusters of one to three silver atoms. On a larger scale, photoluminescence studies have been conducted on nanometer-sized gold clusters in the visible region of the spectrum,[10] where chromatographically separated gold clusters <5 nm in diameter were shown to be luminescent while larger 15 nm clusters were not. Photoluminescence near

440 nm was measured for most of the clusters after exciting at 230 nm, which was attributed to sp to d interband transitions with a quantum yield of $\sim 10^{-4}-10^{-5}$. The most impressive photoluminescence seen thus far, however, involves field-enhanced emission at 548−598 nm from 20 nm diameter Au nanorods with a quantum yield in the $10^{-4}-10^{-3}$ range.[11] This emission is visible to the naked eye and has also been attributed to interband transitions.

The present work describes photoluminescence experiments that establish the emission properties of small gold nanocrystals in the near-infrared (IR) region of the electromagnetic spectrum. The gold nanocrystals studied herein consist of 1.1 and 1.7 nm nanocrystalline gold cores, of about 38 and 145 atoms, respectively, surrounded by a passivating layer of dodecanethiol molecules.[12−14] These two gold nanocrystals are discrete members of a family, each member having a unique set of properties. This family of nanocrystals has been extensively studied and characterized over the past several years,[13,15] which has included structural,[16,17] optical,[18,19] electrochemical,[19,20] and electronic[21] measurements.

This initial study of photoluminescence from these gold nanocrystals has been done in the near-IR part of the spectrum, since optical absorption measurements indicated an electronic energy gap of 0.9 eV and near 0.5 eV for the 1.1 and 1.7 nm nanocrystals, respectively.[19,22] Such energy gaps are consistent with the anomalous stability of these core sizes.[15,19] Considering that the energy of a bulk gold phonon is on the order of 10 meV, an energy gap of 0.5 eV or more should provide sufficient decoupling from phonon-mediated nonradiative processes for radiative processes to become significant, enhancing the luminescence quantum yield. This effect should be even more pronounced for smaller nanocrystals with larger energy gaps, the limiting case being that of the above-mentioned gold(I) compounds.

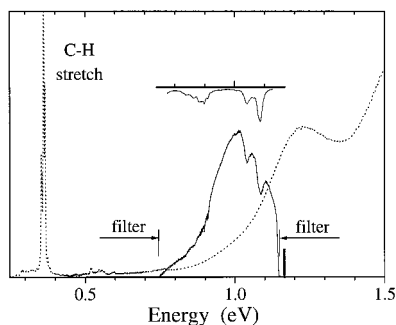* To whom correspondence should be addressed. E-mail: whetten@chemistry.gatech.edu.

Figure 1. Intraband photoluminescence of 1.1 nm gold nanocrystals is shown with respect to its absorption spectrum (dotted line). Notches in the emission spectrum are attributed to the solvent, whose transmission spectrum is shown above it. Note the rapid decrease in nanocrystal emission intensity with decreasing energy. The laser power was 90 mW, and the excitation energy is indicated by the vertical bar at 1.165 eV. (Relative intensities are not to scale.)

2. Methods

Given an energy gap in the near-infrared, it was expected that there could be strong emission in this region. Photoluminescence spectra were therefore recorded using a Bomem MB-157 Fourier transform Raman spectrometer with an InGaAs near-IR detector. The light source was a Spectra Physics diode-pumped Nd:YLF laser, emitting at 1.16 eV (1064 nm) with a 350 kHz repetition rate. Spectra were recorded in 180° back-scattering mode for laser powers ranging from 35 to 550 mW. A notch filter transmitting between 1.15 eV (1100 nm) and 0.75 eV (1600 nm) was used to discriminate against elastic scattering.

As synthesized nanocrystal raw mixtures were purified by repeated recrystallization. Sizes were then separated by fractional recrystallization, where this fractionation of the mixture of sizes was monitored by mass spectrometry.[13] Impurities for our nanocrystal samples typically consist of only undesired nanocrystal sizes that have not been rigorously removed.[23] The concentration of 1.7 nm nanocrystals in the sample used for quantitative measurements was 4.76×10^{-4} M, but spectra were also recorded for higher and lower concentrations. The concentration of the 1.1 nm sample was similar but not accurately known. All measurements were performed at room temperature on samples dissolved in toluene or dichloroethane.

3. Results

The first measurements were performed on a sample consisting predominantly of 1.1 nm nanocrystals dissolved in toluene. A small quantity of 1.3 nm nanocrystals may be present as an impurity, however, as determined by mass spectrometry.[13] The gold nanocrystal solution was excited using the 1064 nm Nd:YLF laser line and a luminescence spectrum was recorded, as shown in Figure 1. The overall shape of the luminescence is not unexpected. The emission begins just below the excitation energy of 1.16 eV and peaks somewhat higher than the gap energy of 0.9 eV, falling off rapidly below it. The gradual falloff of the intensity past the 0.9 eV energy gap may be exaggerated by the presence of impurity 1.3 nm nanocrystals in the solution. The precipitous drop at 1.15 eV is due to the high energy cutoff of the filter. Convolution of the emission spectrum due to solvent absorption bands resulted in notches in the spectrum. The transmission spectrum of the solvent is given in Figure 1 for comparison.

Although the spectral region near the suspected energy gap of the 1.7 nm nanocrystals was excluded by the low-energy cutoff of the instrument's filter, measurements on this species
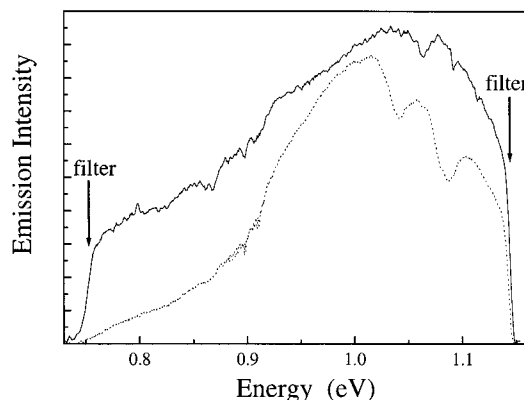

Figure 2. Emission spectrum of a 4.76×10^{-4} M solution of 1.7 nm nanocrystals in dichloroethane, also showing signs of absorption due to the solvent. Note the high emission intensity at the low-energy cutoff, compared with that of the 1.1 nm nanocrystals (dotted line). Laser power was 35 mW. Emission intensities are not to scale.

were made in the same manner. The measured luminescence was relatively strong considering that excitation was at an energy much higher than the HOMO−LUMO gap. The shape of the emission is similar to that of the 1.1 nm nanocrystals at high energies, as shown in Figure 2; however, the intensity falls off more slowly toward the low-energy cutoff of 0.75 eV. The intensity of the emission falls to only about 35% of its maximum value by this cutoff, while in comparison it falls to virtually zero for the 1.1 nm nanocrystals. This is quite consistent with the smaller 0.5 eV energy gap for the larger nanocrystals.

Quantitative measurements were performed on the 1.7 nm nanocrystals in order to estimate their luminescence quantum yield, although the filter imposed some limitations. The quantum yield was calculated by comparing the emission with that of Q-switch 5, an IR dye of quantum yield 5×10^{-4}.[24] This dye was ideal since it has been well studied, it has an absorption maximum very close to the 1064 nm excitation source and its emission spectrum falls almost entirely within the notch filter. Considering the missing part of the gold spectrum, the approximate treatment of the calculation, and the reabsorption of emitted light by the nanocrystal solution, we can conservatively estimate the quantum yield of 1.7 nm gold nanocrystals to be $(4.4 \pm 1.5) \times 10^{-5}$. This is approximately an order of magnitude less than that of the laser dye Q-switch 5, but more than 5 orders of magnitude greater than that of bulk gold. Although the 1.1 nm nanocrystals have not been quantitatively examined, they are expected to have a quantum yield of similar or larger magnitude.

4. Discussion

We do not believe that the mechanism for the observed photoluminescence involves the ligand shell. Electronic transitions in an alkanethiol are in the deep-ultraviolet region of the spectrum, far from the excitation energies used.[22] Ligand vibrational modes are also an unlikely source since these transitions are of very low energy, as is the Au−S linkage. Combination bands such as those seen in the transmission spectrum of the solvent are of the correct energy; however, these transitions are typically quite discrete and unique to the molecule.[25] In contrast, the recorded emission is quite broad and depends on the size of the nanocrystal core. Also, other measurements have been made on glutathione-encapsulated gold nanocrystals in water, showing a similar spectral envelope for a very different ligand and solvent. Unfortunately the spectrum is truncated by solvent absorption below 0.9 eV.
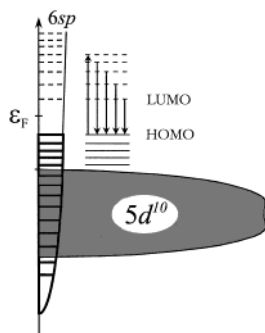
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Figure 3. Schematic of the energy level diagram for intraband excitation and emission for small gold nanocrystals.

Other surface-related mechanisms such as those involving charge transfer or localized states may also be ruled out. X-ray photoelectron spectroscopy on thiol-passivated gold nanocrystals show that the atoms in the core are all metallic (Au^0).[22] Thiol adsorption on Au surfaces is currently thought to occur by dimerization of thiols, satisfying the valence of sulfur by forming a disulfide linkage rather than oxidizing the gold.[26] This leaves no localized states on the surface that are related to the metal core. The states on the ligand are also too high in energy to be occupied. Charge transfer from metal to ligand (or vice versa) is very unlikely due to the inaccessibility of states on the ligand. In fact, tunneling spectroscopy measurements clearly show that the addition or removal of charge is reversible and involves only the metal core, similar to the charging of a classical metal sphere.[21] These results are also borne out by theoretical calculations.[27] We therefore believe that the photoluminescence mechanism involves only gold core electronic states.

Unlike other recent work on luminescence from metal nanocrystals, we do not attribute this photoluminescence to sp to d transitions.[10] Since the onset for such interband transitions in bulk gold occurs at approximately 1.6 eV,[18,28] it is clear that the optical transitions leading to the observed spectra are too low in energy and must be attributed to intraband transitions. However, this does not necessarily mean that the transitions would be forbidden. In bulk gold, intraband transitions are weak due to the large change in momentum necessary. For metal clusters, however, there are no good linear momentum eigenstates due to the absence of an extended lattice. The prevalent model for the electronic structure of metal clusters near the Fermi level is based upon the particle-in-a-box-like nuclear shell model,[29,30] not the bulk band structure. According to such a picture, direct optical transitions between states arising from the Au 6s electrons would be allowed.

It was expected that the photoluminescence mechanism for these nanocrystals would involve relaxed luminescence across the HOMO−LUMO gap. In this picture, the photoexcited electrons and holes decay nonradiatively through the manifold of excited states. Once there, the electrons would have too much energy to give up to phonons and thus be forced to radiatively decay back to the ground state. This decay pattern, however, would not lead to the observed envelope of emission between the excitation energy and that of the energy gap. This is most apparent for the larger of the two nanocrystals. Rather than being peaked near the excitation energy, one would expect for such a relaxed luminescence scheme that the emission would be strongest near the HOMO−LUMO gap. The observed emission envelope is more indicative of hot luminescence, in which the intrinsic radiative rate is faster than the nonradiative decay rate. This scheme is shown in Figure 3. It is somewhat unusual for the radiative decay rate to exceed the nonradiative decay rate,

especially at room temperature. Although we are confident that these transitions are occurring between discrete electronic states in the gold cores, the precise luminescence mechanism remains unclear. Also, the role of the HOMO−LUMO gap in the photoluminescence process is not fully understood.

The quantum yield for emission was relatively low, given the observed energy gaps. In order for transitions across the gap to be quenched, there must be another mechanism for energy transfer. Two possibilities for this mechanism lie in the molecular vibrations of the solvent or the thiols. Although the C−H stretching mode is about 0.35 eV in energy, there are higher order modes in the solvent that absorb in the heart of the emission. Thus far, attempts to eliminate the solvent by performing experiments on films have been unsuccessful due to the extremely high molar absorptivities of the nanocrystals, leading to thermal decomposition of the sample.

It is worth noting that while emission in the visible part of the spectrum can have a myriad of sources other than the analyte, thereby complicating the interpretation of the spectra, emission in the near-infrared does not. Even though a great variety of species absorb in the near-infrared, it is quite easy to couple to vibrational modes in order to quench emission. Since emission in this region is quite uncommon, the analysis of the data is more straightforward and it would seem that the assignment of the gold sp to sp-like transition is unambiguous.

5. Conclusions

In summary, we have demonstrated for the first time near-infrared photoluminescence from metal nanocrystals. Near-infrared luminescence spectra were measured for 1.1 and 1.7 nm nanocrystals using a 1064 nm excitation source. This photoluminescence has been assigned to sp to sp-like transitions, analogous to intraband transitions in bulk gold; however, the exact mechanism is unknown. We have established a conservative estimate for the quantum yield of the 1.7 nm gold nanocrystals to be $(4.4 \pm 1.5) \times 10^{-5}$, which is more than 5 orders of magnitude greater than that of bulk gold.

Note Added in Proof. Since this work was completed, we[31] have found a much stronger NIR luminescence from somewhat smaller Au:SR nanocrystals (0.9 nm core size), of the type described by Schaaff et al.[32]

References and Notes

(1) Mooradian, A. *Phys. Rev. Lett.* **1969**, *22*, 185−187.
(2) Boyd, G. T.; Yu, Z. H.; Shen, Y. R. *Phys. Rev. B* **1986**, *33*, 7923−7936.
(3) Apell, P.; Monreal, R.; Lundqvist, S. *Phys. Scr.* **1988**, *38*, 174−179.
(4) Gimzewski, J. K.; Sass, J. K.; Schlitter, R. R.; Schott, J. *Europhys. Lett.* **1989**, *8*, 435−440.
(5) Reihl, B.; Coombs, J. H.; Gimzewski, J. K. *Surf. Sci.* **1989**, *211−212*, 156−164.
(6) Gade, L. H. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1171.
(7) Fu, W.-F.; Chan, K.-C.; Miskowski, V. M.; Che, C.-M. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2783−2785.
(8) Konig, L.; Rabin, I.; Schulze, W.; Ertl, G. *Science* **1996**, *274*, 1353.
(9) Rabin, I.; Schulze, W.; Ertl, G. *J. Chem. Phys.* **1998**, *108*, 5137−5142.
(10) Wilcoxon, J. P.; Martin, J. E.; Parsapour, F.; Wiedenman, B.; Kelley, D. F. *J. Chem. Phys.* **1998**, *108*, 9137.
(11) Mohamed, M. B.; Volkov, V.; Link, S.; El-Sayed, M. A. *Chem. Phys. Lett.* **2000**, *317*, 517−523.

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(12) Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R. *J. Chem. Soc., Chem. Commun.* **1994**, 801−802.

(13) Whetten, R. L.; Khoury, J. T.; Alvarez, M. M.; Murthy, S.; Vezmar, I.; Wang, Z. L.; Stephens, P. W.; Cleveland, C. L.; Luedtke, W. D.; Landman, U. *Adv. Mater.* **1996**, *8*, 428−433.

(14) Hostetler, M. J.; Wingate, J. E.; Zhong, C.-J.; Harris, J. E.; Vachet, R. W.; Clark, M. R.; Londono, J. D.; Green, S. J.; Stokes, J. J.; Wignall, G. D.; Glish, G. L.; Porter, M. D.; Evens, N. D.; Murray, R. W. *Langmuir* **1998**, *14*, 17−30.

(15) Whetten, R. L.; Alvarez, M. M.; Bigioni, T.; Khoury, J. T.; Salisbury, B. E.; Schaaff, T. G.; Shafigullin, M. N.; Vezmar, I. "Giant gold-cluster compounds−Gaps in optical and charging spectra, and an electronic origin of abundance anomalies." Electronic Properties of Novel Materials; presented at the XII International Winterschool, Kirchberg, Tyrol, Austria, 1998.

(16) Cleveland, C. L.; Landman, U.; Schaaff, T. G.; Shafigullin, M. N.; Stephens, P. W.; Whetten, R. L. *Phys. Rev. Lett.* **1997**, *79*, 1873−1876.

(17) Whetten, R. L.; Shafigullin, M. N.; Khoury, J. T.; Schaaff, T. G.; Vezmar, I.; Alvarez, M. M.; Wilkinson, A. *Acc. Chem. Res.* **1998**, *32*, 397−406.

(18) Alvarez, M. M.; Khoury, J. T.; Schaaff, T. G.; Shafigullin, M. N.; Vezmar, I.; Whetten, R. L. *J. Phys. Chem. B* **1997**, *101*, 3706−3712.

(19) Chen, S.; Ingram, R. S.; Hostetler, M. J.; Pietron, J. J.; Murray, R. W.; Schaaff, T. G.; Khoury, J. T.; Alvarez, M. M.; Whetten, R. L. *Science* **1998**, *280*, 2098−2101.

(20) Ingram, R. S.; Hostetler, M. J.; Murray, R. W.; Schaaff, T. G.; Khoury, J. T.; Whetten, R. L.; Bigioni, T. P.; Guthrie, D. K.; First, P. N. *J. Am. Chem. Soc.* **1997**, *119*, 9279−9280.

(21) Bigioni, T. P.; Harrell, L. E.; Guthrie, D. K.; Cullen, W. G.; Whetten, R. L.; First, P. N. *Eur. Phys. J. D* **1999**, *6*, 355−364.

(22) Khoury, J. T. Colours of Nanometric Gold. Ph.D. Thesis, UCLA, 1999.

(23) Schaaff, T. G.; Shafigullin, M. N.; Khoury, J. T.; Vezmar, I.; Whetten, R. L.; Cullen, W. G.; First, P. N.; Gutierrez, C.; Ascensio, J.; Jose-Yacaman, M. J. *J. Phys. Chem. B* **1997**, *101*, 7885−7891.

(24) Seilmeier, A.; Kopainsky, B.; Kaiser, W. *Appl. Phys.* **1980**, *22*, 355−359.

(25) Goddu, R. F. *Near-Infrared Spectrophotometry*; Wiley-Interscience: New York, 1960; Vol. 1.

(26) Fenter, P.; Eberhardt, A.; Eisenberger, P. *Science* **1994**, *266*, 1216−1218.

(27) Hakkinen, H.; Barnett, R. N.; Landman, U. *Phys. Rev. Lett.* **1999**, *82*, 3264.

(28) Johnson, P. B.; Christy, R. W. *Phys. Rev. B* **1972**, *6*, 4370−9.

(29) Mayer, M. G.; Jensen, J. H. D. *Elementary Theory of Nuclear Shell Structure*; John Wiley & Sons: New York, 1955.

(30) deHeer, W. A. *Rev. Mod. Phys.* **1993**, *65*, 611−676.

(31) Link, S.; El-Sayed, M. A.; Schaaff, T. G.; Whetten, R. L., to be published.

(32) Schaaff, T. G.; Whetten, R. L. *J. Phys. Chem. B* **2000**, *104*, 2630−2641.