Temperature- and Magnetic Field-dependent Photoluminescence of Metal Nanoclusters

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Introduction

Quantum- confined thiolated gold nanoclusters represent a class of nanomaterials that recently has become recognized for its potential application across a wide range of fields (e.g. fluorescence imaging, energy conversion, and catalysis). The optical properties of these clusters depend critically upon structural properties (e.g. size, composition, and charge state) [1,2]. Our work has focused on describing the charge-state-dependent electronic structure and optical properties of $Au_{25}(SR)_{18}^{q}$, and its influence on photocatalysis.

Experimental

Experiments were performed at the NHMFL DC field facility utilizing a 17.5 T superconducting magnet (SCM-3) with temperature control from 4.5 K to ambient temperature. The 800 nm output of a regeneratively amplified Ti:Sapphire femtosecond laser system was frequency doubled to 400 nm and attenuated to 1 µJ/pulse to provide an excitation source. Photoluminescence was collected in transmission geometry and coupled to a spectrometer via optical fiber. The spectrally resolved signal was collected with a liquid N_2-cooled CCD. Photoluminescence lifetime data were collected using time-correlated single-photon counting.

Results and Discussion

We investigated the temperature dependence of the photoluminescence (PL) of $Au_{25}(SR)_{18}$ in both the anionic and neutral charge states. Analysis of the global PL as a function of temperature revealed strikingly different behavior for the two charge states. In the neutral system, the high-energy portion of the PL spectrum diminishes in relative contribution as temperature increases. The shape of the spectrum for the anion is much less sensitive to temperature. To understand this behavior, the spectrum was decomposed into individual peaks. The best fit for both charge states contained three Gaussian peaks. Analysis of the temperature-dependent energy and peakwidth for the neutral cluster revealed two vibrational components (2.1 THz, and 13 THz) that assist photoluminescence. Theoretical work suggests there is a ~2 THz vibration in ultra-small gold nanoparticles that arises from a thin surface layer of gold atoms [3]. The 2.1 THz mode in this system can be interpreted as a vibration between gold atoms in the semirings and those in the core. This is significant because while the HOMO and LUMO in these clusters are predicted to be core-localized states [4], the NIR PL originates from semiring states [4]. A manuscript describing these findings is in preparation. Temperature-dependent PL lifetime measurements revealed an energy barrier of approximately 1.4 meV in the both cluster charge states. Lifetimes collected at 4.5 K were found to decrease as the magnetic field was increased from zero to 17.5 T. The sensitivity of the lifetime to field was reduced as temperature was increased, and at 20 K there was no resolvable difference in lifetimes at 0 T and 17.5 T. These data suggest this 1.4 meV energy barrier (equivalent temperature 16.5 K) reflects non-degenerate states involved in the relaxation dynamics. At low temperature the applied field mixes the states, which modifies the lifetime. As the temperature increases above the energy barrier, thermal energy mixes the states and no effect is observed in the presence of the applied field. These quantitative results will also be published.

Conclusions

Temperature- and field-dependent PL measurements have been made on $Au_{25}(SR)_{18}$ nanoclusters, and these data have provided significant new insights into the electronic structure and electron dynamics of gold nanoclusters. Energy resolved data suggests two vibrational components assist in electronic energy relaxation. This research, and its continuation are critical to providing a predictive understanding of the role of hot electron dynamics in photocatalysis by metals.

Acknowledgements

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References

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