Exploring the Oxidation States of Optically Active Silver Nanoclusters for Biological Applications

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Water soluble silver nanoclusters capped with DNA have been shown to emit visible light upon photoexcitation showing considerable promise as potential biological sensors and detectors, yet the mechanism of photoluminescence in these systems is not well understood.[1] In this work we use density functional theory with Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional under the generalized gradient approximation (GGA) in the Vienna ab initio simulation package (VASP) framework to examine the optical and electronic properties (i.e. total energy, electronic density of states and absorbance) of an icosahedron silver nanoclusters capped with twelve cytosine molecules representing DNA scaffolding [Figure 1(a)] with varying electronic configurations.[2-5] We found that all configurations exhibit high absorption yet only a select few have a band gap conducive to emitting light [Figure 1 (b)]. We then turned our attention to one specific silver nanocluster with a charge of 5+ and singlet spin configuration to further investigate the origin of photoluminescence. For the most probable electronic transitions across the band gap of this model it turned out that the electron resided in the silver nanocluster core. Yet upon excitation, the electron is promoted to Kohn-Sham orbitals residing in the cytosine scaffold, indicating the importance of DNA to the experimentally observed photoluminescence. Finally, we explored the dynamics of the photoexcited electron and hole as they thermalize to their respective band edges prior to exciton recombination.[6] We found that the electron thermalization rate exponentially decreases as a function of the initial energy difference between electron and hole [Figure 1 (c)], in agreement with the empirical band gap law.

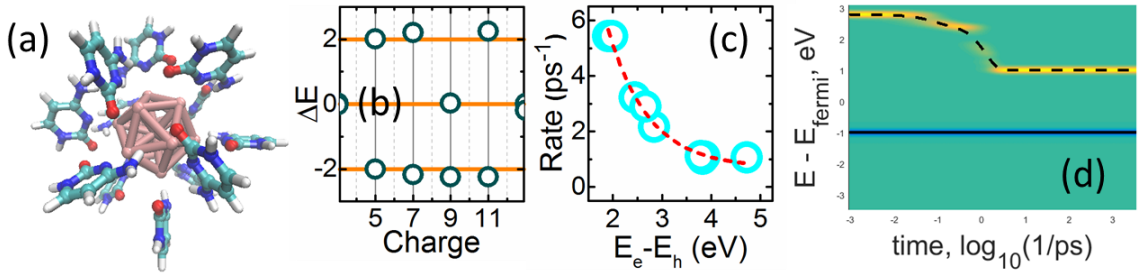

Figure 1: (a) Silver nanocluster model (b) Band gap of silver nanocluster with zero spin as a function of charge where the band gap for beta electrons was multiplied by -1. (c) Electron thermalization rate as a function of the energy difference between the photoexcited electron and hole. (d) Typical electron hole thermalization dynamics (yellow = electron, blue = hole).

References

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