Optical Properties of Colloidal Atomically Precise Semiconductor and Noble Metal Nanostructures by Computational Analysis

Kiet Nguyen, Paul Day, and Ruth Pachter
Air Force Research Laboratory, Materials and Manufacturing Directorate
Wright-Patterson Air Force Base, Ohio 45433-7702

To gain an understanding of the structure and optical properties of colloidal 2D nanoplatelets (NPLs) that are grown from atomically precise semiconductor nanoclusters, and which exhibited large optical nonlinearities, we systematically examined structures and absorption spectra for CdS NPLs. Nanoplatelet model systems, passivated with formate and acetate ligands, were used to analyze the effects of quantum confinement in the lateral dimension within an extended monolayer and the effects of thickness. Based on computed structures using density functional theory (DFT), we found good agreement between observed and time-dependent DFT (TDDFT) calculated spectra. As the structures are extended laterally to eight and seven monolayers for two-monolayer and three-monolayer (3ML)-thick systems, respectively, ligand participation to influence the color and intensity of low-energy absorption bands was found to be small. The spectral red-shift for 3ML CdS NPLs is attributed to the electron delocalization from expansion of both the short and long axes in a NPL.

Although the prediction of the optical excitations of ligated gold clusters by TDDFT is well-established, limitations still exist, for example in the choice of the exchange-correlation functional. In aiming to improve on the accuracy of the calculated linear absorption, we report a theoretical study on phosphine-ligated gold clusters, specifically $Au_9(PR_3)_8^{3+}$ and $Au_8(PR_3)_7^{2+}$, which were characterized by highly resolved UV/Vis spectra using mass-selective electronic absorption photofragmentation spectroscopy (Cirri, A.; Hernández, H. M.; Johnson, C. J. *J. Phys. Chem. A* **2020**, *124*, 1467−1479, and references therein). The optical absorption of $Au_9(PR_3)_8^{3+}$ and $Au_8(PR_3)_7^{2+}$ were calculated using TDDFT and the many-body GW-BSE (G-Green's function, and W-screened Coulomb interaction)-BSE (Bethe Salpeter Equation) method, and compared to the experimental measurements. Results with the GW-BSE method at the evGW level demonstrated good agreement with the experimental data, comparable to the best TDDFT results, but with less dependence on the reference exchange-correlation functional.