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Silver Adsorbates on Pure and Doped Silicon Quantum Dots: Optical Absorbance Calculated by Time-Dependent DFT

David Stewart, Michael Mavros, and David A. Micha
Departments of Chemistry and of Physics
Quantum Theory Project, University of Florida
Gainesville, Florida 32611, USA

A recent paper on light absorption by model surfaces of Si have shown that Ag adsorbates increase the intensity of photoinduced electronic transitions at lower photon energies [1]; another set of recent results for Si quantum dots (QDs) have shown that P and Al dopants also shift the absorbance toward lower photon energies [2]. The present contribution deals with the combined effects of both adsorbates and dopants in Si QDs, and how the joint effects can be used to increase absorption intensities in desired regions of the solar spectrum. The optical absorbance of the Si QDs with P and Al dopants and either one or three Ag adsorbed atoms has been calculated with TD-DFT using the PW91/PW91 density functionals, to compare with our previous results. Trends have been compared first for adsorbates without dopants and then with both adsorbates and dopants. Generally, the presence of Ag adsorbates shows both a decrease in the HOMO-LUMO gap and a drastic increase in the absorbance below 4 eV. The addition of dopants leads to a combined effect where the energy gap is further decreased and absorbance below 3 eV is increased, though substantially less so than the increased absorbance due to Ag adsorbates. The molecular orbitals for the initial and final states involved in transitions with large oscillator strengths were also calculated, and they qualitatively show the excited electrons moving towards the Ag during excitation, with larger Ag clusters causing a more pronounced motion. The excited state lifetime of an undoped Si QD with a Ag adsorbate was found to be shorter than that of a pure Si QD; however, when both a dopant and a Ag adsorbate were present, the lifetime was found to be longer than that of a pure QD. This study indicates that stronger absorption in the visible, near UV, and near IR parts of the spectrum can be achieved with a combination of Ag adsorbate clusters and doping.

1. LaJoie, T. W, Ramirez, J. J, Kilin, D. S, Micha, D.A. Int. J. Quant. Chem. 2010, 110, 3005-14.
2. Mavros, M. G, Micha, D. A, Kilin, D. S. J. Phys. Chem. C. 2011, 115, 19529-37.

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