Relaxation of Photoexcited Electron-Hole Pairs at Nanostructured Si(111) Surfaces from Quantum Dissipative Dynamics and Deep Neural Network Analyses

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The efficiency of silicon solar cells is affected by light absorption and recombination losses. One possible way to improve the efficiency is through the deposition of transition metal nanoparticles onto Si surfaces. Group IB elements (copper, silver, and gold) are of particular interest, because they are among the best conductors of electricity and heat, have closed *d* shells, and are widely studied in laboratories. Studies have shown that the deposition of silver nanoparticles onto Si surfaces can lead to stronger absorption of light and additional pathways for charge transfer compared to pure Si surfaces. Here, we first carry out density functional theory (DFT) calculations to obtain electronic structures for Ag_n (n=0, 3-7) monolayered-clusters adsorbed on Si(111)/H surfaces. Results are presented in the form of density of states, band gaps, and light absorption, which allow for the investigation of the interaction of Ag clusters with Si. Different behavior can be expected depending on the size of the deposited Ag clusters. Overall, the deposition of Ag clusters leads to smaller band gaps, redshifts, and large increases in light absorption compared to pure Si slab. We then study relaxation dynamics of electron-hole pairs for slabs based on nonadiabatic couplings using the reduced density matrix approach within the Redfield formalism.[1,2] Moreover, we employ a deep neural network (DNN) using the Redfield tensors as the inputs to predict relaxation rates of electrons and holes. The DNN predicted relaxation rates agree well with results obtained from direct calculations using the Redfield formalism. One observes smaller relaxation rates for surfaces with adsorbates than for pure Si surfaces, due to charge transfer events involving Ag orbitals. We also compute emission spectra from the excited-state trajectories. It is found that slabs with silver adsorbates show bright bandgap emission. However, the bandgap emission is dark for pure Si due to the indirect nature of its bandgap. The introduction of adsorbates is advantageous for applications to photovoltaics and photocatalysis.

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References

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