559h Multiscale Modeling of the Synthesis of Quantum Semiconductor Nanostructures in Templated Media

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A lattice-based stochastic simulation technique has been developed to describe the formation of ZnSe quantum dots inside the spherical nanodroplets of a microemulsion formed by self-assembly of a ternary system consisting of an amphiphilic block copolymer, a polar continuous phase (formamide) and a non-polar dispersed phase (heptane) [1]. The stochastic model describes diffusion of diethylzinc molecules in heptane, nucleation of ZnSe through a fast reaction between dielthylzinc and hydrogen selenide taking place at the interface, as well as diffusion and coalescence of ZnSe clusters inside the nanodroplet leading to the formation of a single nanocrystal. The simulation is calibrated to real time by using a diffusion-reaction model describing diethylzinc depletion due to a fast interfacial reaction at sufficiently high concentrations. The motion of molecules and clusters in the lattice is programmed according to their diffusivity, which is estimated by using the Stokes-Einstein equation. At the beginning of the process the slow diffusion of hydrogen selenide through the block copolymer layer is the rate determining step. As the zinc precursor gets depleted inside the nanodroplet, its diffusion to the interface becomes the rate controlling step. The formation of stable “magic” clusters of ZnSe with a fullerene-like close-caged structure has been tracked in the simulations and the predicted size variation of the final nanocrystals due to the random formation such clusters is recorded. A thermal analysis of cluster-cluster coalescence was also performed using dynamic models accounting for the: (1) energy release due to surface area reduction, (2) energy accumulation in the coalescing particles, (3) energy dissipation to the surrounding medium, (4) the melting of coalescing particles when the local temperature exceeds their size-dependent melting point. The simulations reveal the possibility of melting and recrystallization of nanoparticles, as well as surface melting phenomena, thus explaining the formation of single crystals in a medium that is at room temperature. The detailed nanodroplet-level models of quantum dot formation are connected to reactor-level operating conditions through the interfacial flux of hydrogen selenide. The results are compared to experimental observations with the purpose of optimizing the quantum dot synthesis process in the experimental system. Extensions of this work to the modeling of nanowire growth in lyotropic liquid crystalline templates will be discussed.

[1] G.N. Karanikolos, et al., Langmuir, 20(3), 550-553 (2004).