

LATTICE KINETIC MONTE CARLO SIMULATIONS OF QUANTUM DOT SYNTHESIS IN MICROEMULSION TEMPLATES

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Summary

A Lattice kinetic Monte-Carlo model was developed to study the reactive synthesis of a single quantum dot inside a microemulsion droplet. The simulations describe the diffusion of molecules of a reactant dissolved in the droplet, particle nucleation by an irreversible reaction at the interface, diffusion of nuclei into the droplet and coalescence into clusters, and diffusion and coalescence of clusters to form a single particle. A generalized dimensionless equation was obtained for the formation time of a single particle as function of its size. Parametric studies were performed and scaling laws for coalescence of particles in confined domains were developed.

Keywords

Novel Functional Materials, Nanotechnology Applications, Materials for Energy Applications, High Value Added Products.

Introduction

Semiconductor nanocrystals (quantum dots or QDs) are an interesting class of materials exhibiting size-tunable optical and electronic properties that make them attractive for applications in biosensors, high-efficiency solar cells, and high-density optoelectronics^{1,2}. The use of templates in the synthesis of semiconductor nanocrystals allows precise control of their shape and size³⁻⁵. It also enables easy scale-up for commercial production. Modeling of this process enables studies of the particle synthesis kinetics that are difficult (or impossible) to track experimentally. It also enables parametric studies that can elucidate the effects of operating conditions on cluster-cluster coalescence and the time required to form a single particle in each dispersed domain of the template.

Model Description

A Lattice kinetic Monte-Carlo (LkMC) model was developed to describe the formation of a single QD inside a droplet of a microemulsion. The operating conditions used in our modeling study are similar to those used for experimental synthesis of ZnSe QDs inside the droplets of a microemulsion formed by self-assembly of a tri-block copolymer at the interface between a polar solvent (formamide), that forms the continuous phase, and a non-polar solvent (heptane), that forms the dispersed phase³. In this system, the concentration of diethylzinc in each

heptane droplet determines the final size of the ZnSe QD formed in the droplet. The conversion of diethylzinc to ZnSe nuclei takes place at the interface by an irreversible reaction with hydrogen selenide. The hydrogen selenide gas is diluted with hydrogen and is bubbled through the microemulsion. It subsequently dissolves in the formamide continuous phase and diffuses through the interface formed by the block copolymer layer to undergo a spontaneous and irreversible reaction with diethylzinc that forms ZnSe nuclei. The ZnSe nuclei diffuse inside the droplets of the microemulsion and coalesce into clusters which in turn coalesce to form a single QD in each droplet.

The LkMC model describes the diffusion of diethylzinc (A) molecules, their reaction with hydrogen selenide (B) molecules at the interface to yield AB nuclei, diffusion and coalescence of nuclei into clusters, and diffusion and coalescence of clusters into a single QD. The cluster-cluster interactions are modeled by a hard sphere potential. The simulation is performed in a spherical domain that is discretized using a cubic lattice.

The A molecules, AB nuclei, and clusters formed by coalescence can occupy a lattice point placed at the center of each unit cell. Multiple occupancy by A molecules is allowed as long as the particle volume fraction does not exceed the value corresponding to random packing of

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equally sized spheres. Larger clusters can occupy a volume that is larger than that of a single unit cell and may render neighboring lattice points inaccessible to other particles to prevent particle overlap.

The LkMC model was validated by simulating the diffusion of solute molecules dispersed in a spherical droplet consisting of a solvent under conditions involving a fast reaction at the interface, where the solute molecules are converted to an immobile species. The LkMC predictions for the evolution of solute concentration were compared to the analytical solution of a continuum (PDE-based) model. The optimal lattice spacing was selected by employing progressively smaller lattice sizes until the LkMC predictions became lattice-independent. We found that a lattice spacing equal to the diameter of an AB nucleus makes the LkMC predictions to be lattice-independent for all cases considered in this study.

Results and Discussion

LkMC simulations were performed to predict the time required for forming a single QD inside a microemulsion droplet. A variety of initial precursor (A) concentrations and droplet sizes was studied. In all cases, the predicted final particle formation time initially increases with particle size, reaches a maximum corresponding to the formation of an $(AB)_5$ final particle, and subsequently decreases as the particle size increases. This behavior was explained by the formation of large “sweeper” clusters during the synthesis of particles larger than $(AB)_5$. Large clusters are more efficient collision targets for smaller clusters because of the large volume that they occupy. As a result, they accelerate the coalescence of all clusters into a single final particle, despite the fact that their diffusivity is low.

The time required to form a single final particle was scaled using the characteristic time for diffusion of the final particle over a distance equal to the droplet radius. The final particle diameter was scaled with the droplet diameter.

A series of LkMC simulations was performed by varying the initial concentration of diethylzinc in the droplet to yield a final ZnSe QD with size ranging from 0.6 to 7nm. The droplet diameter was also varied from 10 to 40nm. For final particles with sizes larger than $(ZnSe)_5$, we found that, for a wide range of operating conditions, the scaled final particle formation time, τ_p , can be correlated to the scaled final particle diameter, δ , by the equation:

$$\tau_p = 0.064\delta^{-1.13}$$

Parametric studies were performed to elucidate the effects of cluster coalescence efficiency and nucleation rate on the evolution of cluster sizes and the time required for the formation of a single QD inside the droplet. The final particle formation time was found to be relatively insensitive to the rate of the nucleation reaction because the cluster-cluster coalescence process takes much longer to be completed than the consumption of precursor A by the nucleation reaction. For nucleation reaction

probabilities between 1 and 10^{-2} , the LkMC simulations predict no significant change in the final particle formation time. When the probability of the nucleation reaction was reduced to 10^{-3} , the final particle formation time exhibited a significant increase. For a spontaneous irreversible reaction, like the one taking place between the precursors of the ZnSe QDs, the reaction probability can be manipulated directly by restricting the supply of hydrogen selenide to the system, which reduces the interfacial flux of that precursor to the dispersed phase, thus limiting its availability for reaction with diethylzinc to form (ZnSe) nuclei.

The final particle formation time was found to be sensitive to changes in the probability of cluster-cluster coalescence. The particle formation time increases as the value of this parameter decreases and this effect is more pronounced for smaller particle sizes. For large particles, the higher rate of collisions due to the higher concentration of clusters in the droplet tends to partially alleviate the adverse effects of a smaller coalescence probability.

The LkMC predictions of particle coalescence rates inside a spherical droplet were compared to theoretical and LMC predictions of scaling laws for particle coalescence in an infinite domain^{6,7}. Corrections to the scaling parameters were obtained to describe coalescence kinetics in spherical domains of finite size.

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