Understanding the Self-Assembly Behavior of Nanoparticles and Polymers

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Inorganic Nanoparticle/Polymer Hybrid Materials for Alternative Energy

CdSe nanocrystals
Overview

1. Cooperative Assembly of Nanoparticles and Block-Copolymers
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2. Self-Organizing Organic Electronic Materials
Cooperative Assembly of Nanoparticles and Block-Copolymers

Random Incorporation of Nanoparticles as Simple Solutes

Interfacial Assembly of Nanoparticles

1) DMF

2) H₂O

3) Dialysis
Interfacial Assembly of Quantum Dots in Discrete Block-Copolymer Aggregates

Co-assemblies of PAA$_{41}$-$b$-PS$_{193}$ and CdSe nanocrystals in water

Cavity-like Structure of Nanoparticles

- Polymer shell: A monolayer of block-copolymers with PAA at the exterior
- Polymer core: Reverse micelles of block-copolymers
- QDs arranged at the interface between the polymer core and the polymer shell.

Origin of the Interfacial Assembly

- **Enthalpic Effect**

- **Entropic Effect**

![Enthalpic Effect Diagram](image1)

![Entropic Effect Graph](image2)

![Experimental Images](image3)
Control of the Location of Nanoparticles

Polymer/QD = 100  Polymer/QD = 400

[Images of nanoparticles with varying Polymer/QD ratios]

Graphs showing:
- Radius (nm) vs. \( \Phi_{\text{QD}} \)
- Shell thickness (nm) vs. \( \Phi_{\text{QD}} \)
- \( r_c/r \) vs. \( \Phi_{\text{QD}} \)

Legend:
- \( r_c \)
- \( r \)

# of QDs
Distance Dependence Studies Using the Controllable Shell Thickness

No silver: $84.38 \pm 50.66$ cts/ms
with silver: $281.59 \pm 126.01$ cts/ms
What Controls the Structural Parameters?

$\text{PAA}_{38}^{\text{--}}\text{b-PS}_{108}$

$\text{PAA}_{38}^{\text{--}}\text{b-PS}_{154}$

$\text{PAA}_{38}^{\text{--}}\text{b-PS}_{189}$

$\text{PAA}_{38}^{\text{--}}\text{b-PS}_{247}$
Nanoparticle Size Determines the Size of Co-assemblies

- 25 nm iron oxide particles
- 4 nm iron oxide particles
The Incorporation of Nanoparticles Reduces the Size Distribution.

- Nanoparticles narrow the size distribution of the assemblies formed.
- As the concentration of nanoparticles is decreased, the size distribution gradually gets larger.
Nanoparticle-Induced Morphological Changes

- Nanoparticles play an active role in the block-copolymer assembly processes rather than simply being incorporated passively in the hydrophobic domain as solutes.
- Nanoparticles cause a drastic morphology change of block copolymer assemblies.
Morphological Transition Induced by Nanoparticle Clustering
Membrane Curvature Change Induced by Nanoparticle clustering

Figure 2: Clathrin-coated vesicle budding where yolk protein is being incorporated into vesicles in oocytes. *Taken from McMahon et al. Nature, 438, 590 (2005).*
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2. Self-Organizing Organic Electronic Materials
Self-Organizing, Optically Active Organic Materials

\[ \text{CHCl}_3 \rightarrow \text{CH}_3\text{OH} \rightarrow \text{H}_2\text{O} \]

A \rightarrow B \rightarrow C

D \rightarrow E \rightarrow F

IR
Reversible Morphology and Emission Color Changes

![Graph showing PL intensity and wavelength changes with different solvent concentrations.](image)

100% CH₃OH
67% CHCl₃
75% CHCl₃
100% CHCl₃

Wavelength (nm)

PL wavelength (nm)

CHCl₃  CH₃OH  CHCl₃  CH₃OH  CHCl₃  CH₃OH
Fine Tuning of Emission Colors: Salt Effect
Self-Assembled Building Blocks for Inorganic/Organic Hybrid Materials

Nanotubes wrapped in conjugated block-copolymers

Polar solvent → Conducting Nanowire
Nonpolar solvent → Conducting Nanotube

Spin-coating → Annealing
Summary

- Nanoparticles play an active role in the self-assembly process of block-copolymers, and they can drastically alter the behavior of polymers and the co-assembly structure.

- Cooperative self-assembly of nanoparticles and block-copolymers offer a facile way to control the arrangement of nanoparticles in discrete block-copolymer assemblies.

- We developed conjugated block-copolymers that can self-assemble into various morphologies including core-shell particles, rods, nanowires and layered structures.

- Their band gap and the photoluminescent properties are highly tunable by simply controlling their assembly structures.
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