Asymmetric Dumbbells from Selective Deposition of Metals on Seeded Semiconductor Nanorods

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Introduction

- Integration of multiple materials into same nanostructure has been a major challenge in nanocrystal research.

- Hybrid metal-semiconductor nanocomposites contain a metal and its semiconductor counterpart closely coupled to each other and already known for various applications.

  Anchor point for self-assembly

  Photocatalytic process

- Seeded semiconductor nanorod have attract considerable interest for generating hybrid metal-semiconductor nano-heterostructure as their chemical and optical properties can be tuned by changing both the core and the shell.

- Such nanorods carrying Pt, Au, Co nanoparticle has already been synthesized.
In this paper...

- Good control over deposition of Au on Seeded CdSe/CdS nano-heterostructure have been achieved by varying the concentration of Au-precursor.

- Morphology of Ag$_2$S- CdSe/CdS hybrid nanorod heterostructure has been controlled.

- It has been found that exposure of seeded CdSe/CdS nanorod to different Ag$^+$ concentration leads to similar morphological changes as in case of Au- CdSe/CdS system though they have different mechanisms of formation.

- “Janus-type” dumbbell structures were prepared by sequential deposition of Au and Ag precursors to seeded CdSe/CdS nanorods.
Experimental Section

- CdSe cores of 2.5 nm diameter were synthesized following a reported procedure.
- Growth of CdS shell around CdSe core was achieved following the protocol of Manna et al.

- CdSe/CdS nanorods were separated and dispersed in a mixture of toluene and ODPA.
- Gold growth proceeded after injection of a mixture of AuCl$_3$, TOAB and DDA into the rod solution.
- All these reactions were carried out under inert (N$_2$) atmosphere and at room temperature.
- Amount of Au precursor was varied.

Absorption (black), PL (red) spectra of toluene solutions of 40 nm long CdSe/CdS NRs grown from 2.5 nm CdSe seeds. The gray line is a part of the absorption spectrum. The inset is a TEM image of the nanorods, showing their uniformity. The scale bar is 100 nm.

- ODPA (n-octadecylphosphonic acid)
- TOAB (tetraoctylammonium bromide)
- DDA (dodecylamine)
Observation and discussion

Selectivity of growth of Au at one end, both ends and throughout the rod with increasing concentration of Au precursor proves the presence of hierarchical order of reactivities between the facets at the tips and sides of the nanorods.

Earlier report of selective growth of Au on top of CdSe core was observed rarely and this has been attributed to the presence of ODPA which binds selectively to the \{100\} facets of CdS and thus reduces the surface defects and sterically hinders the process of Au deposition on the side faces of the nanorods.

Au deposition first occurs on the end away from CdSe core which is known to be sulphur-rich from earlier reports and then Au deposition starts on the facets present on the other end of the nanorod which are cadmium-rich.

- TEM images of CdSe-seeded CdS nano-heterostructures with controlled, varying degrees of Au deposition
  - a) one end, b) both ends, and c) throughout the rod
  - d) HRTEM image showing a gold nanoparticle at the apex of the nanorod. The measured d-spacing values from the visible lattice fringes 0.24 nm and 0.34 nm are assigned to Au (111) and CdS (002) respectively.
a) HAADF-STEM image of seeded CdSe/CdS “lance” shaped rods with a CdSe core size of 3.6 nm.

b) EDX data taken from the encircled area. Proves the presence of CdSe core

c) TEM image of “lance” shaped nanorod with Au at the end of the rod furthest from CdSe core.
Ag$_2$S- CdSe/CdS hybrid nanorod

Uniform CdSe/CdS nanorods were reacted with AgNO$_3$ in a solution containing toluene, ethanol and DDA under ambient light at room temperature. Concentration of AgNO$_3$ was the only variable parameter.

A significant number of rods were also found to have Ag$_2$S located specifically above the location of the CdSe seed, as expected from the occurrence of more surface defects there.

Exclusive formation of Ag$_2$S at the tips of the nanorods was obtained at low concentrations of Ag$^+$ ions.

Visible lattice fringes in HRTEM correspond to the $\{121\}$ plane of Ag$_2$S and are consistent with a cationic exchange process.

The distinction between relative populations of rods with Ag$_2$S at one end and two ends was not as pronounced as in the case with Au, where selective deposition at one end versus two ends can be precisely controlled.

TEM images illustrating the morphology evolution of seeded CdSe/CdS nanorods with the concentration of Ag$^+$ ions as the only variable parameter. Exposure to (a) low and (b) high concentrations of Ag$^+$ ions resulted in the formation of Ag$_2$S nanoparticles exclusively at the tips and throughout the nanorod respectively. The inset in (a) is a HRTEM image showing the visible lattice fringes of the Ag$_2$S $\{121\}$ and CdS $\{002\}$ planes with measured d spacings of 0.26 nm and 0.34 nm, respectively. Scale bar (inset): 5 nm.
Absorption spectra of starting seeded CdSe/CdS nanorods (violet) red trace- rods shown in figure a [previous slide] and black trace- rods shown in figure b [previous slide]

- Progressive decline in number of observable spectral features in absorption spectra has been linked with the variation in the extent of Cd\textsuperscript{2+} ion exchanged from rod to rod leading to a wider size/ shape distribution
Asymmetric Dumbbells

a) TEM image of seeded CdSe/CdS nanorods with Au nano-particles at one end and Ag₂S nanoparticles at the other end.

b) HRTEM image showing the visible lattice fringes of the Ag₂S {121} and Au {111} planes with measured d spacings of 0.26 nm and 0.24 nm, respectively.

EDX of seeded CdSe/CdS NRs having different nanoparticles at either end. The red lines show the standard positions of each element.
This phenomena also has been attributed to the presence of DDA which can act as a mild reducing agent as well (besides it’s role as capping agent for the rods) and can reduce excess Ag⁺ ions onto Au or Ag₂S surfaces.

This can be controlled by the right choice of Ag⁺ concentration and controlling the reaction time.
Thanks