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# Editorial: The molecular underpinnings of nanoscale semiconductor synthesis

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nanocrystal, quantum dot, cluster, precursor conversion, molecular understanding

## Editorial on the Research Topic

[The molecular underpinnings of nanoscale semiconductor synthesis](#)

Colloidal semiconductor nanocrystals have attracted considerable attention over the past several decades due to their size-dependent optoelectronic properties, which have driven their integration into cutting-edge applications ranging from LEDs and displays to quantum computing and biosensing. The utility of these materials stems from their solution processability, broad absorption profiles, narrow photoluminescence emission, and surfaces that can be easily modulated. Wet chemical synthesis of these materials provides a versatile space for development of new compositions, morphologies, heterostructures, and coordination environments simply by changing precursors, ligands, concentrations, and temperatures. Mechanistic studies into molecular and cluster intermediates during formation can direct researchers towards better control over synthetic outcomes. Furthermore, the high surface to volume ratios inherent to nanocrystals makes the study of their surfaces and their stabilizing ligands particularly important, with surface accessibility controlling reaction and charge transfer rates in catalytic applications and photovoltaics.

We organized this Research Topic to highlight some of the recent advances in the field of nanocrystal synthesis. We are particularly interested in understanding the reactions that make and modify nanocrystals at the atomic level, including precursor conversion, ligand exchange, and cluster formation and dissolution. By understanding the molecular underpinnings of nanoscale semiconductor synthesis, it becomes possible to control end products and their properties.

Precursor reactivity gates the nucleation and growth of nanocrystals in colloidal syntheses. In the synthesis of WSe<sub>2</sub>, tungsten hexacarbonyl is often used as the metal precursor, which typically requires high reaction temperatures to force the cleavage of the strong W–CO bond. Schimpf and colleagues demonstrate that W–CO bond labilization, and hence the availability of tungsten metal for subsequent monomer formation, can be tuned through the inclusion of common ligands such as trioctylphosphine (TOP) and trioctylphosphine oxide (TOPO) (Geisenhoff et al.). Using IR spectroscopy for reaction monitoring in the presence of TOPO, the authors noted W(CO)<sub>6</sub> rapidly decomposes into W(CO)<sub>6-x</sub>(TOPO)<sub>x</sub>, which promoted rapid nucleation of WSe<sub>2</sub> nanocrystals and lower reaction temperatures. The structural assignment of this intermediate was corroborated through the growth of a diffraction-quality single crystal of the triarylphosphine analogue W(CO)<sub>5</sub>(TPPO) (TPPO = triphenylphosphine oxide). On the other hand, the use of strongly coordinating triphenylphosphine (TPP) was found to sequester tungsten as W(CO)<sub>5</sub>(TPP),

requiring higher nucleation temperatures. This work demonstrates that tuning precursor identity through the inclusion of coordinating ligands can affect subsequent reactivity towards nanocrystal formation.

Highly reactive precursors also play a significant role in the nucleation of much smaller nanocrystals called magic-sized clusters (MSCs). MSCs are kinetically stable, atomically precise nanocrystals often found as intermediates towards the synthesis of colloidal quantum dots. Jeong and coworkers review the current understanding of structure, composition, and surface chemistry of these nanocrystals and make a case for their use as reagents (Shin et al.). In particular, the authors document several protocols for the synthesis of InP or InAs quantum dots that utilize MSCs as a monomer source.

Clusters can serve as single-source precursors of nanocrystals through dissolution or as catalytic sites for growth, allowing formation of larger structures at temperatures much lower than commonly employed in hot-injection syntheses. Snee and coworkers leveraged this in their microfluidic setup to study in-depth the formation of CdSe NCs at low temperatures (<200 °C) using MSCs of  $(\text{NMe}_4)_4 [\text{Cd}_{10}\text{Se}_4(\text{SPh})_{16}]$  and  $(\text{NMe}_4)_4 [\text{Zn}_{10}\text{Se}_4(\text{SPh})_{16}]$  as nucleation sites (Kim et al.). The microfluidic setup allowed fine control over reaction parameters (e.g., reactant concentration, temperature) and enabled two growth stages by incorporation of a second heating block.

Seed-mediated growth is common in the synthesis of metal nanocrystals, oftentimes using small pre-formed particles (as opposed to MSCs) whose surfaces enable growth of larger crystals. Ye and colleagues analyzed the effects of modulating surface chemistry on Au seeds for growth of Au-Cu alloyed and bimetallic nanocrystals (Jeong et al.). When weakly coordinated ligands such as oleylamine and pentaethylenhexamine-terminated-polystyrene were coordinated to the surface the resulting particles were one-dimensional Cu nanorods. In contrast, when a strongly coordinating ligand such as dodecanethiol was used, heterodimers with composition  $\text{Au}_{0.2}\text{Cu}_{0.8}/\text{Cu}_{2-x}\text{S}$  formed. Similar differentiation was observed when the crystallinity of the Au-seed was

tuned. CTAB-capped single crystalline Au resulted in heterostructured Au/Cu nanocrystals while pentatwinned Au formed Cu nanorods.

Semiconductor nanocrystals are complex systems that are vastly tunable beyond size and composition. The work highlighted by this Research Topic covers many exciting areas of synthesis in nanoscale colloidal materials. Each article emphasizes the importance of understanding colloidal nanocrystals at the atomic level, with growth rates, reaction mechanisms, size, structure, and morphology all tunable through small molecule chemistry. We hope that it promotes further development of new compositions, new techniques, and modifications that push the boundaries of our understanding of semiconductor nanocrystals and their synthesis.

## Author contributions

HR and SH drafted the editorial with input and editing from BC. All authors contributed to the article and approved the submitted version.

## Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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