Enabling nanocrystal science and applications with WANDA, a custom robotic laboratory

Emory Chan[1], Gang Han[1], Shiwei Wu[1], Bruce E. Cohen[1], P. James Schuck[1], Jonathan S. Owen[2], A. Paul Alivisatos[2], Delia J. Milliron[1]

[1]The Molecular Foundry, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA 94720; [2]Department of Chemistry, University of California, Berkeley, CA 94720. Correspondence to DJM: dmilliron@lbl.gov.

Scientific Thrust Area

This project is lead by the Molecular Foundry's Inorganic Nanostructures Facility, in collaboration with the Biological Nanostructures and the Imaging & Manipulation Facilities.

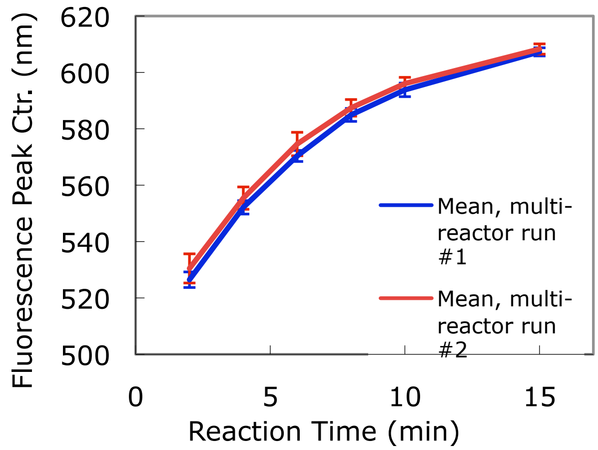
Research Achievement

From 2007 to 2008, the Molecular Foundry took on the challenge of enabling automated synthesis of colloidal nanocrystals. Symyx Technologies built and tested the product of a collaborative design process over the course of 7 months and installed the Workstation for Automated Nanomaterials Discovery and Analysis (WANDA) at the Molecular Foundry in October 2008. Although WANDA has been operational for only six months, it is already facilitating nanoscience in unprecedented ways. The custom low-thermal-mass reactor bay at the heart of WANDA's core module has performed impeccably, synthesizing colloidal nanocrystals ranging from semiconductors to metals, and characterizing their growth processes using high-throughput optical spectroscopy.

Colloidal nanocrystals are a centerpiece of modern nanoscience, investigated worldwide for their size-dependent properties and their potential applications in catalysis, photovoltaics, light-emitting diodes, and bio-imaging, among others. Nanocrystal synthesis is conventionally carried out in a round bottom flask which is stirred magnetically, heated by an electric mantle, and connected to a Schlenk line to prevent inadvertent oxidation. Using this approach, a tremendous diversity of size-controlled nanocrystals have been synthesized including metals, and oxide, chalcogenide, and pnictide semiconductors with rounded, faceted, anisotropic, or even branched shapes. Nonetheless, the conventional flask makes synthetic development slow and reproducibility challenging, especially as the product can be highly sensitive to synthetic variables such as heating and cooling rates, or the rate of reactant addition. Problems with batch-to-batch reproducibility limit the systematic investigation of size-dependent properties, typically making it necessary to perform all measurements on a single batch of nanocrystals. By developing an automated synthesis platform, we seek to a) accelerate the rate of synthetic development and the investigation of synthetic pathways and b) produce completely reproducible nanocrystals to facilitate property assessments and applications of all kinds.

The result of our development effort, WANDA, contains eight custom reactors, which can be operated in parallel and which are capability of executing the extreme thermal profiles required for nanocrystal synthesis, including reaction temperatures up to 350 °C and rapid, active cooling at the reaction end point. Aliquots collected by a sampling needle are characterized in a 96-well plate reader by photoluminescence and absorption spectroscopy. In addition, a quartz plate can be automatically spotted for x-ray diffraction analysis by the Facility's existing diffractometer.

Nanocrystals of the semiconductor CdSe have been extensively investigated and are still the subject of active research for optoelectronics applications and as bio-imaging probes. The synthesis of monodisperse CdSe nanocrystals with exceptionally reproducible growth kinetics has been demonstrated using WANDA. We have taken advantage of this reproducibility, and the high-throughput capabilities of WANDA to optimize the CdSe synthesis with respect to size distribution. Then, varying reactant concentrations, temperature, and time over 160 samples, we were able to determine kinetic rate orders, activation energies, and pre-exponential factors for nanocrystal growth. These results demonstrates the power of automation to enable rapid refinement and detailed investigation of synthetic methods.



Critical to facilitating the diverse internal and user projects at the Molecular Foundry, WANDA's reactors are designed to switch instantly between different nanocrystals chemistries. For example, lanthanide-doped $NaYF_4$ nanocrystals are being developed as next-generation single-biomolecule probes. When co-doped with lanthanides which undergo efficient energy transfer, such as Yb^{3+} and Er^{3+}, these nanocrystals efficiently up-convert NIR excitation to visible emission, avoiding autofluorescence interference. Because up-conversion utilizes a real, long-lived intermediate state, the efficiency is orders of magnitude higher than two-photon excitation. We have recently investigated the single-particle photophysical properties of these materials to evaluate their potential as single-molecule probes. The ensemble of emitters in each particle eliminates the emission intermittency characteristic of organic probes and semiconductor nanocrystals alike, and they are extremely photostable. These attractive properties are maintained when an amphiphilic polymer coating is used to transfer the up-converting nanocrystals from organic to aqueous solution.

Future Work

Already, WANDA is synthesizing and characterizing nanocrystals of semiconductors (CdSe, CdTe, PbTe), metals (Co, Te), and up-converting materials, with new capabilities being developed to support internal and user projects. We plan also to implement synthetic methods in which previously synthesized nanocrystals are further modified in subsequent reactions. This will include the synthesis of nanocrystal heterostructures, whose nanoscale interfaces are the subject of a collaborative theoretical and spectroscopic investigation at the Foundry. Core/shell heterostructures with high luminescence quantum yield are of keen interest for optoelectronic and bio applications, yet are challenging to prepare reproducibly by conventional methods. Finally, post-synthetic ligand exchange will be carried out to investigate the role played by the organic-inorganic interface in determining nanocrystal properties and energetics.

Publications

S. Wu, G. Han, D.J. Milliron, S. Aloni, V. Altoe, D.V. Talapin, B.E. Cohen, P.J. Schuck, "Non-blinking and photostable upconverted luminescence from single lanthanide-doped nanocrystals," *PNAS*, in press.