COLLOIDAL PEROVSKITE HALIDE EXCHANGE OPTIMIZATION VIA REAL-TIME MACHINE LEARNING INTEGRATED WITH AUTOMATED MICROFLUIDIC SAMPLING

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Abstract Overview

Detailed herein is a discussion of the integration of machine learning algorithms with microfluidic optical sampling strategies towards, continuous, real-time optimization of colloidal semiconductor nanocrystals. We have developed an automated, gas-liquid segmented flow platform which collects inline UV-Vis absorption (A) and photoluminescent (PL) spectra on equilibrated, continuous flowing systems with set reactant compositions. Using a novel, reduced pathlength tube-based optical flow cell and dynamic spectra processing algorithms we may derive, in real-time, the peak emission energy (PE), full width at half maximum of the emission spectra (FWHM), and photoluminescent quantum yield (PLQY). These measurements are integrated into an off-set feedback system paired with a machine learning algorithm, which controls the proceeding flow conditions to test. Using this device, we have optimized the composition of the reactive phase in the post-synthesis halide exchange of cesium-lead-trihalide perovskite quantum dots (PQDs) in real-time. Through the direct control of PQD, exchanging zinc halide (ZnX_2), zinc bromide ($ZnBr_2$), oleic acid (OA), and oleylamine (OLA) concentrations as well as the exchanging halide (X=Cl or I) a weighted three-parameter optimum was obtained within 238 samples.

Keywords

Microfluidics, Perovskites, Quantum dots, Optimization, Machine learning

Introduction

In the past decade PQD electronic devices have seen a sudden emergence in their study and application due to their favorable electronic properties in photovoltaics, photocatalysis, and light emitting diodes as well as their accessibility towards low-cost solution phase processing strategies. These materials could very likely produce the next generation of many commercial devices invoking lower costs and greater efficiencies as well as proliferating the availability of harnessed solar energy. However, among the inherent issues of these materials is the difficulty that comes with controlling the complex reaction space associated with PQD syntheses. Even after choosing a single reaction pathway among the thousands of different perovskite compositions and methods, the end product remains heavily dependent on the relative precursor ratios in the reactive solution, which itself encompasses an inaccessibly large environment – as illustrated in Figure 1.

In response to this inherent need in the study of the material group, many microfluidic strategies have been developed to evaluate *in situ* colloidal growth of semiconductor nanocrystals. These systems enable high-throughput reaction screening at low chemical costs and are

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inherently more accessible to automated reaction control through inline flow measurement methods. These techniques reduce the labor costs, variability, and sampling time and consumption over batch screening strategies, allowing more comprehensive studies of the materials. Our prior work has established effective methods for carrying out these reactions in flow as well as using optical flow cells for inline synthesis monitoring. The work reported here marks the first integration of these strategies with intelligent, real-time optimization methods.

Microfluidic Design

The microfluidic system used in this study – shown in Figure 2 – consists of off the shelf tubular components, which allow for modular control of the reactor configuration and low-cost replacement of the various components. The flow in the system is driven by three continuous flow positive displacement (CFP) pumps and three syringe pumps. Note that syringe pumps are used for precursors that either require lower flow rates or have viscosities that are not conducive to accurate CFP driven flow. The ZnX_2 is chosen with a binary channel selector valve and all precursors are fed into a series of cross-junctions to combine. They are then mixed in a braided tubing micromixer, combined with the PQD stream in a tee-junction, mixed again, then segmented into gas-liquid flow in a final tee-junction connected to an argon mass flow controller (MFC). The segmented slugs move in the coiled reactor tubing for 90 seconds before inline PL/A sampling. The automated reactor controls also feature a toluene flush between each condition, a halide purge stage when transitioning to a different source, and a delayed start for the PQD CFP to reduce chemical consumption. The process is carried out at a sampling rate of 10 samples/hr and requires approximately 0.4 mL of reagents per sample.

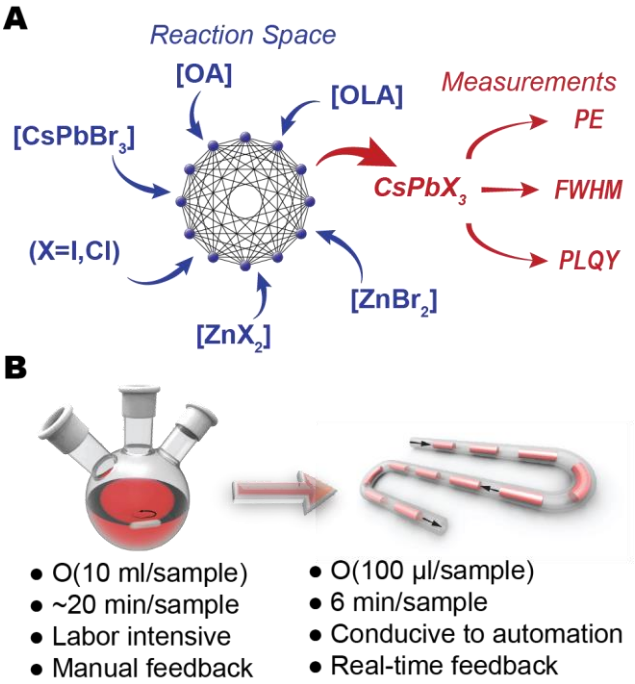

Figure 1. (A) Illustration of six-dimensional sampling space with three detectable outputs for the post-synthesis halide exchange of PQDs and (B) comparison chart between batch and microfluidic reaction screening

Inline PL/A sampling is performed with a custom reduced pathlength flow cell, which compresses the reactor tubing at the sampling point to allow for an ~100 µm pathlength between the spectrometer and deuterium halogen light source for A spectra collection. PL spectra are subsequently collected by shining a 365 nm high powered LED onto the center of the flattened tubing at a 50^{O} angle to the spectrometer. This modified flow cell design allows for inline reaction studies without reducing overall reactant concentrations.

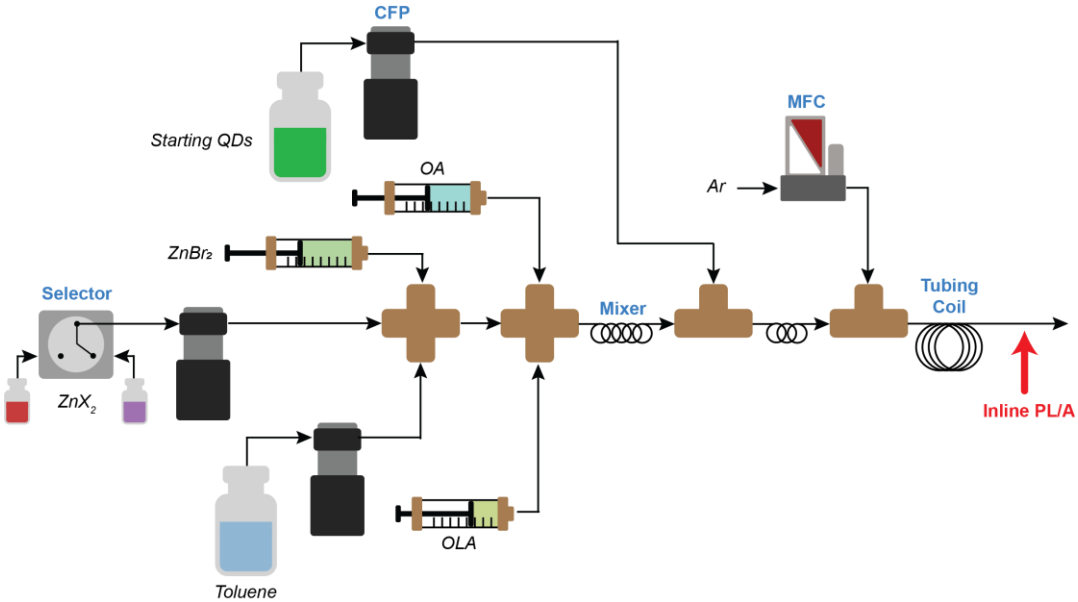

Figure 2. Schematic of custom microfluidic system

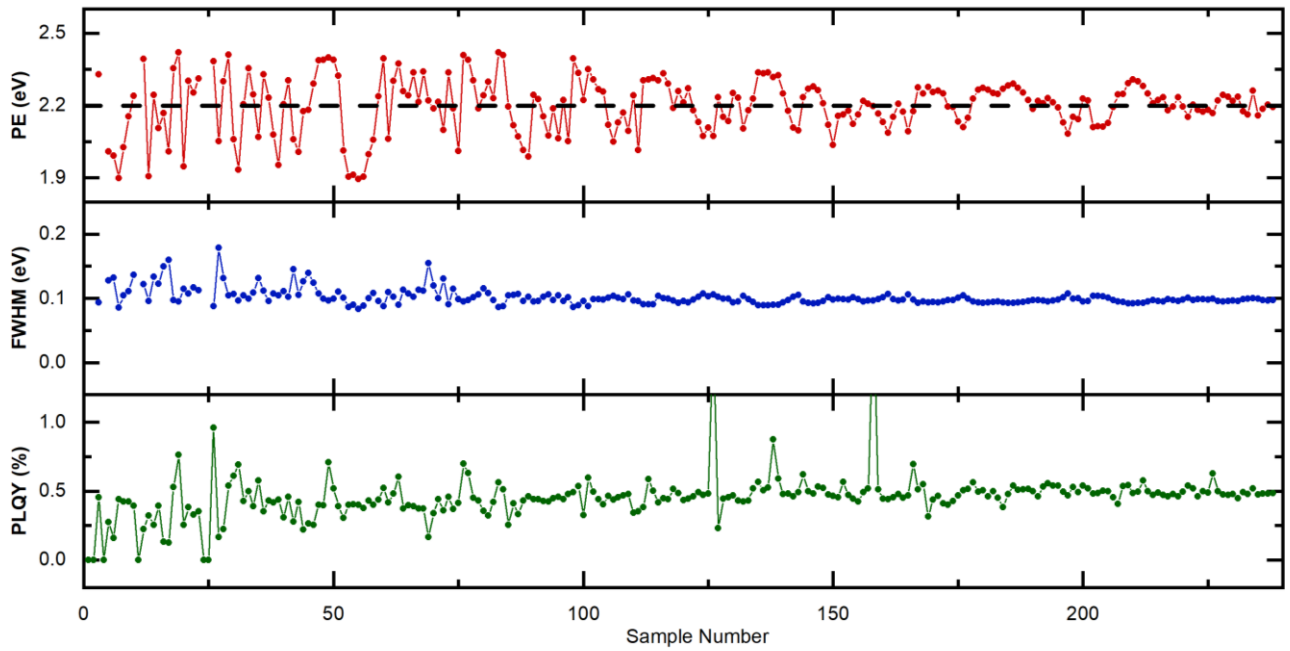

Figure 3. Blind optimization results of the bracketing algorithm using a PE setpoint value of 2.2 eV

Machine Learning Method

The optimization strategy applied in this study was a custom neural network (NN) bracketing algorithm. This program randomly creates a list of 2^{12} input sets with values within the previously determined bounds of the system. These sets are then paired up and scored using a sequence of neural networks, the size and accuracy of which is correlated with the size of the test and training sets. The scores are determined by comparing the predicted output with a previously stated target value. The quality of an output value set is quantified through a weighted average of the proportional distance from the set-point values of PE, FWHM, and PLQY (90, 5, and 5% respectively). Maxima (minima) are found by raising (lowering) the target value if a trial run produces a value over (under) the target. Next, the scores of paired sets are compared, and the less accurate set is removed from the system. This process is repeated until only one data set remains, at which point its contents are passed along for testing. Each replication produces larger training data sets, leading to more accurate measurements and guesses. This procedure is carried out for each round of sample collection with an offset sampling time between the optimization algorithm and microfluidic device (i.e. where the microfluidic device is sampling the n^{th} condition while the optimization algorithm uses data from the n^{th}-1 samples to select the conditions for the n^{th}+1 sample).

Result

Using this NN bracketing algorithm with the integrated microfluidic sampling device, a setpoint PE value of 2.2 eV yielded an equlibrated result in 238 samples within one day without any prior training – as shown in Figure 3.

Conclusions

The success of this platform and strategy in the blind optimization of a single setpoint value lays out an opportunity for future work with more comprehensive and varied data availability and more advanced machine learning systems. A systematic study of the influence of NN pretraining and optimization methods will not only unlock the optima of post-synthesis halide exchange but also reduce the development time for many other future colloidal semiconductor nanocrystal synthesis strategies.

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