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THERMAL STABILITY AND CHEMISTRY OF FLUORESCENT NANOCRYSTALS FOR USE AS A NOVEL GEOTHERMAL TRACER

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ABSTRACT

Fluorescent nanocrystals are promising candidates for a range of applications, ranging from biomedical imaging and sensing to solar energy conversion and lighting. Recently, these nanometer-sized semiconductor crystals (also referred to as "quantum dots") have shown potential to be used as novel geothermal reservoir tracer particles. Quantum dots have size-dependent, tunable electronic and optical properties that make them promising candidates for use as tracers in geothermal fields. In this study, organic molecules were investigated as quantum-dot-surface-stabilizing ligands in order to create water-soluble nanocrystals that behave as conservative tracers in geothermal media. More extensive modification of the surface chemistry of nanocrystals could also make them attractive materials for reactive tracers. The thermal stability of organic-ligand-stabilized core/shell quantum dots under simulated geothermal conditions was studied through autoclave experiments at temperatures exceeding 150 ºC. These tests looked for degradation, agglomeration, and solubility, all of which would alter the optical properties of the tracers. Quantum dot behavior and response was also tested in flow-through reactors packed with geothermal media using in-line fluorometers, and compared to conventional tracers.

INTRODUCTION

Quantum dots (QDs) are colloidal nanocrystals that are between 2 and 20 nm in diameter. They can be made from various semiconductor compounds and exhibit electronic and optical properties that differ from those observed in the bulk form, representing a transition into quantum mechanically-defined physics. Confinement of an exciton within each nanoparticle cause the QDs to fluoresce when exposed to incident UV light. Furthermore, QDs show quantum size-effects and small changes in the QD diameter result in dramatic changes in the fluorescent emission behavior (wavelength position). This property has made QDs attractive for many fields including bio-imaging, solid-state lighting, and solar cells.

The field of semiconductor QDs and the subsequent study of nanoscale optoelectronic properties has grown fantastically since the development of a rigorous, high-temperature synthetic method by Murray *et. al*. that allowed for size monodisperse samples to be synthesized and studied, and correlations between QD diameter and band-gap energy to be determined. The development of low-temperature, aqueous synthetic methods have led to an increase in high-quality, water soluble quantum dots, properties that are crucial for geothermal tracer particles. The size of QDs can be determined by semi-empirical relationships between QD diameters measured via electron microscopy and their corresponding optical absorption wavelength positions.

Recent synthetic approaches allow for the creation of hydrophilic QDs with emission peak wavelength positions between 450 nm (blue) and 800 nm (near-IR). This precise control of the optical properties can be used to create a family of tracers each with a characteristic absorbance and emission properties. Geothermal reservoir waters need to have very little baseline concentrations (either from nature or previous tracer tests), low limits of detectability, and high degrees of stability. The ability to tune the emission wavelength of the QDs essentially provides a different tracer with little spectral interference while maintaining the exceptional brightness that is typical of high quality QDs.

Furthermore, extensive research efforts have focused on the surface chemistry of QDs in order to customize and control how they interact with their environment. It has been well-established that organic ligands are important factors in creating high-quality QDs due to surface passivation, their roles in preventing QD interaction, and binding with unoccupied valences in the crystal surface. Manipulation of functional groups on QDs has been

proposed to create both conservative (nonreactive) and reactive (interactive) tracer families for use in fracture surface area quantification, either in conjunction with classic conservative tracers or novel QD tracers. Colloid transport faces different challenges than solute transport, such as the physical entrapment of particles in narrow pore throats, and must be addressed in initial benchtop experiments.

As with all geothermal tracers, QDs must be very stable at high temperatures and pressures for extended periods of time. Ideal stability is represented by the absence of particle agglomeration and the maintenance of bright fluorescence following exposure to geothermal-type conditions. The highest quality tracers undergo minimal optical property changes when subjected to high temperatures and pressures for extended periods of time. The effect of high temperatures on QD stability is a largely unstudied property, but previous work by Rose *et. al.* has established an outline for testing tracers in geothermal reservoir conditions.

Transport of colloids through porous media is a well-studied phenomenon due to applications in viral and environmental contamination of groundwater. Due to their relatively new discovery, the health effects and environmental impact of QDs are largely unknown, spurring studies of QD breakthrough in groundwater systems. As previously noted, the migration of colloids is subject to a wide variety of physics including adsorptive and desorptive effects, physical filtration and hydrodynamic. Initial tests of QD samples will be geared towards proof of concept and demonstration of successful QD transport through columns packed with geothermal reservoir analogues.

QUANTUM DOT SYNTHESIS

Synthesis of aqueous colloidal nanocrystals occurs in batch processes under a variety of possible conditions, and can utilize different precursor materials or surface ligands. The method used here was modified from work originally done by Rogach *et. al* and low-temperature synthetic procedures developed by the Bartl group to synthesize CdSe/CdS core-shell QDs. The goals of the aqueous synthesis are two-fold: first, to create highly stable, brightly fluorescing QDs that can withstand exposure to geothermal conditions; and second, to scale up the synthesis in order to provide the large amount of tracer particles required for field-scale single-well tracer tests. Low temperature synthetic routes are advantageous due to amount of control they allow over the size (and subsequently, emission wavelength) of the QDs, which is imperative in their use as tracer particles.

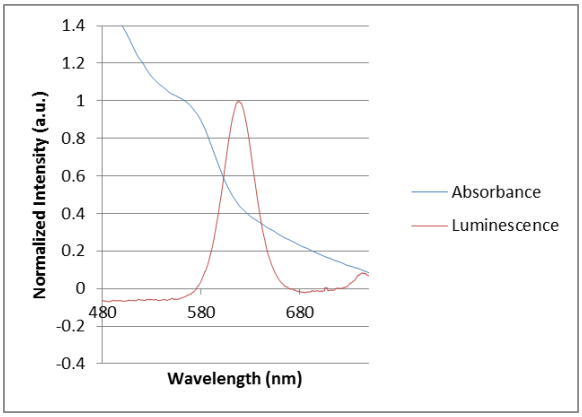

Figure 1 – Absorbance and luminescence of a quantum dot sample

Furthermore, in looking to the future, these low-temperature procedures would greatly simplify the scale-up of synthetic processes by preventing large temperature gradients, which would result in larger variation of growth rates and produce highly disperse crystal size populations.

The QD synthesis method used here is based on the nucleation of nanocrystals at low temperatures (50-100 □C) followed by slow, uniform crystal growth driven by optimization of precursor injection volumes and concentrations. Initial injection of cadmium and selenium precursors in the presence of sodium citrate ligand and an alkaline pH facilitates growth of CdSe core crystals. Core growth is still fairly rapid at the low temperatures of this study, reaching average diameters of 2.2 nm within 5 minutes and 2.3 nm within 10 minutes, corresponding to a 5 nm redshift in the absorbance peak. After ten minutes the growth rate declines due to exhaustion of selenium precursor, and a sulfur precursor is introduced to initiate a CdS shell to grow around the CdSe core crystal. The shell addition adds approximately 0.2 nm to the diameter of each core crystal, represented by a 30 nm redshift of the absorbance peak. The growth of the shell is a significant aspect in the development of high quality luminescence. Over time, as the shell forms the QD luminescence becomes more distinguished from the trap state emission, as seen in figure 2. In this example, the characteristic peak falls in the 530-600 nm range, while the trap emission peak is the broader peak from 630-780 nm.

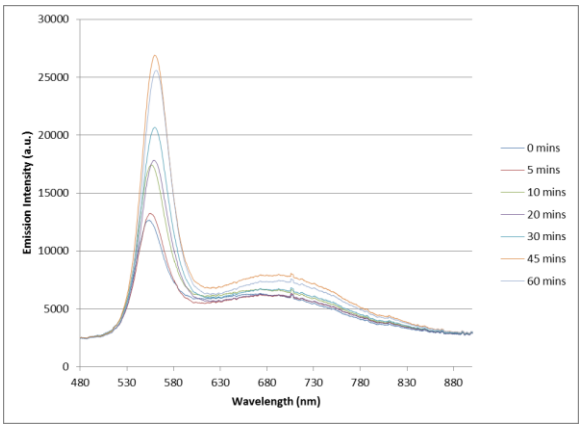

Figure 2- QD sample luminescence increases in the time following the addition of sulfur precursor material. At approximately 45 minutes, the luminescence maximum begins to change very little.

Core/shell QDs have demonstrated greatly increased optical properties due to the confinement of the generated exciton to the core, driving the recombination of charge carriers and resulting in increased emission intensities over the sample. Agglomeration of the crystals during and after synthesis is prevented due to charge repulsion and steric effects caused by the citrate ligands covering the surface of each nanocrystal. By altering temperature, pH, and injection concentrations and volumes, samples with a range of emission wavelengths spanning the visible light spectrum can be created, seen in figure 3.

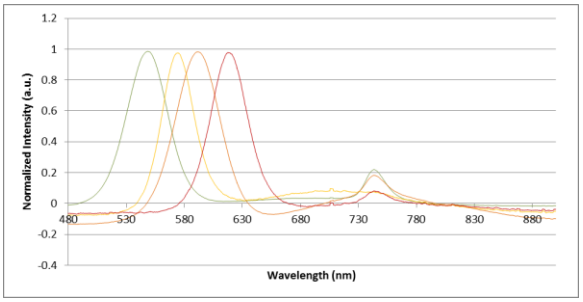

Figure 3- Characteristic emission of various quantum dot samples

The ease and tunability of the QD synthesis along with the modest reaction conditions made the batch process a reasonable candidate for scale-up. The primary goal was to establish comparable optical properties and stability in each sample using identical chemical environments as those used in the small-scale synthesis. Temperature gradients, large volume precursor injection rates, and mixture homogenization were identified as primary problems that might result in increased size dispersity or decreased quality. In order to attain enough tracer particles for transport experiments, either an increased reaction volume or nanocrystal concentration must be obtained. Rogach *et. al.* observed that increasing the ratio of cadmium to selenium and sulfur resulted in higher concentrations of QDs, due to the greater number of possible nucleation sites for new crystal growth. The large emission intensity gain was successfully demonstrated in the small-scale synthesis, shown in figure 4.

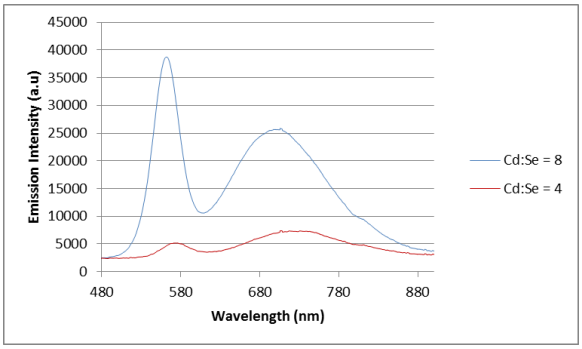

Figure 4- Result of increased cadmium molar ration on quantum dot sample luminescence

The increased amount of cadmium led to the formation of impurities, seen by the broad emission peak centered around 700 nm. The conditions described in the 50 mL reaction volume were implemented in a 500 mL batch process, a ten-fold increase from the smaller scale. It is clear from figure 5 that high quality luminescence can be obtained when the reaction conditions (precursor molar ratios, injection volumes, etc) are also increased proportionally.

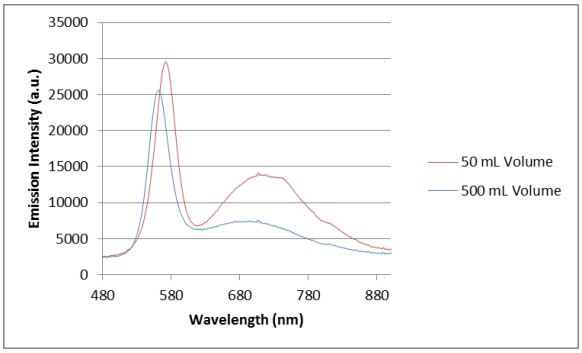

Figure 5- Luminescence of quantum dot samples synthesized in two different reaction volumes

These results even suggest that the large-scale synthetic products have smaller trap states, representing more complete conversion of precursor material into luminescent nanocrystals. The larger reaction volume results in higher concentrations under the identical reation conditions (alkaline pH, Cd:Se:S = 8:1:1) as opposed to the smaller volume, seen in figure 6. This could be a direct result of the increased amount of precursor material that is consumed in primary reactions, observed in the smaller trap state emission peak in figure 5.

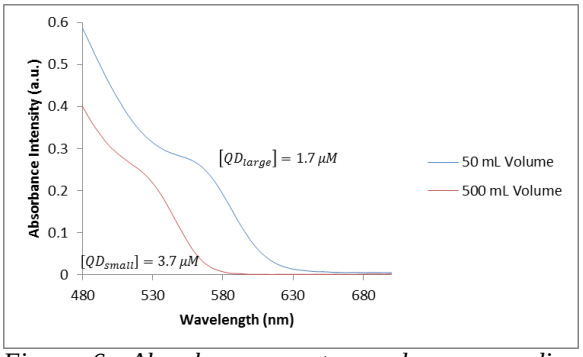

Figure 6- Absorbance spectra and corresponding molar concentrations of two different reaction volumes

AUTOCLAVE TESTING

Thermal stability is a crucial property of any geothermal tracer and must be extensively studied to predict the behavior and potential thermal decay of tracer characteristics. Rose *et. al.* established experimental methodology to test thermal stability of optical properties and establish thermal decay kinetics of various families of fluorescent molecules. The geothermal conditions are simulated using autoclave batch reactors at temperatures up to 300 □C and time scales up to one week. Tracers stable at these conditions are considered very robust, and become likely candidates for further evaluation in benchtop transport experiments.

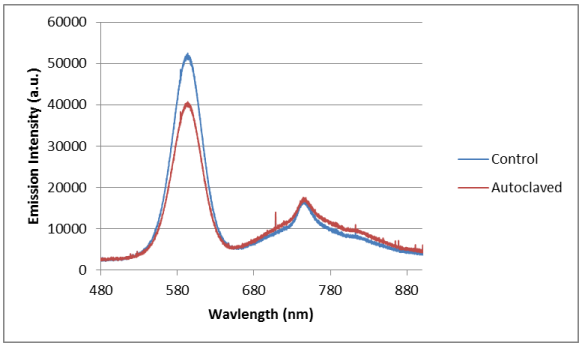

Figure 7- Stable quantum dot sample after being autoclaved for 4 hours at 150 □C. There is only a slight decrease in emission intensity and no shift in wavelength

QDs synthesized from earlier established methods showed extremely poor stability at the most elementary conditions, evidenced by visible agglomeration while only left at room temperature. In order to prevent nanocrystal precipitation, the QDs were first purified by forcing them out of solution using an excess of organic solvent (acetate, isopropanol, ethanol, etc), centrifuging the sample, and suspending the nanocrystal pellet in ultra-pure water. This process visibly reduced the broad emission peak caused by impurities and trap states that emit in the NIR, shown in figure 8, which resulted in fluorescence emitted primarily from the quantum dots of interest.

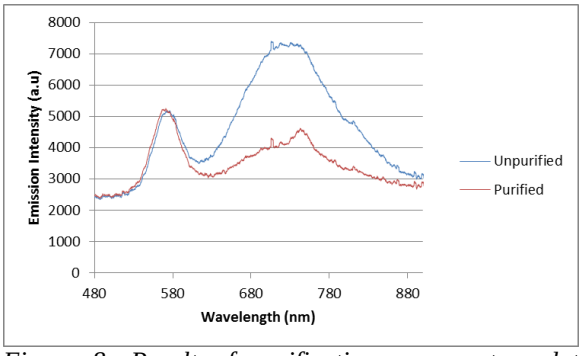

Figure 8- Result of purification on quantum dot sample emission.

The purification steps made the QDs less likely to change size at high temperatures due to the decreased amount of cadmium, selenium, and sulfur precursor monomers in solution. An excess of sodium citrate was added to the samples following the purification steps, which were then sonicated to ensure complete coverage of the nanocrystal surface with the ligand. Samples processed with excess ligand demonstrated long-term benchtop stability.

Long-term stability at high temperatures so far has not been achieved, with all samples autoclaved for 36 hours or more at 150 □C failing to remain suspended in solution and forming micrometer-sized agglomerates. This is a critical threshold that needs to be overcome for QDs to be further considered for tracer development. Current work has involved coating the CdSe/CdS QDs with a silica shell that would preserve the desired optical properties of the crystals while preventing QD agglomeration at high temperatures and long time scales. The silica barrier between the QDs and aqueous environment provides the added benefit of reducing the diffusion of oxygen to the crystal surface. Surface oxidation in unencapsulated QDs creates a shell that prevents the transmission of photogenerated charge carriers, forcing recombination of the electron-hole pairs and greatly enhancing luminescence. This phenomenon was observed in samples left exposed to ambient light over two to four weeks and resulted in a blue shift of the luminescence. The oxidative shell shrinks the crystal's core, reducing the region in which the charge carriers can exist and increasing the intensity of light emitted due to the higher probability of recombination, which can be seen in figures 9 and 10.

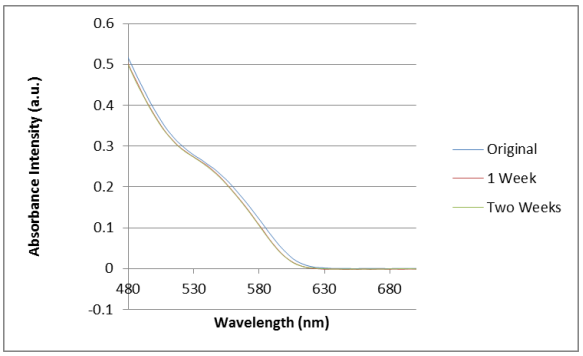

Figure 9- Absorbance intensity changes over a two week period.

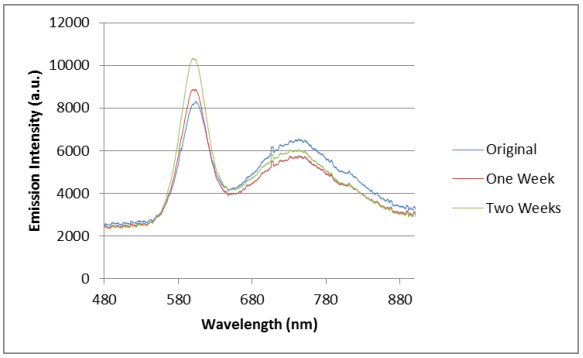

Figure 10- Emission intensity changes over a two week period. Note the visible increase in intensity, though the absorbance intensity is nearly unchanged

This also resulted in unstable samples that formed visible black clusters which could not be dispersed in the aqueous media. The QDs were reportedly much more stable when coated with a thick layer of silica due to the reduction of oxygen diffusion and interaction between reactive nanocrystal surfaces. Additional work on silica encapsulation by Riassetto *et. al* reported detectable (albeit blueshifted) luminescence following exposure of QDs to temperatures and pressures around 300 □C and 40 MPa; however, more experiments are needed to increase reproducibility over different sample conditions.

COLUMN EXPERIMENTS

The transport of colloids through porous media is an emerging topic of study with applications in virus and contaminant transport, and colloid-facilitated solute transport. For tracer application, any proposed particle must have transport properties at least similar to solute tracers, and cannot agglomerate because of the potential for filtering within the pore spaces of subsurface media. Here, our motivation was to demonstrate the feasibility of using QDs as geothermal tracers by providing qualitative examples of transport through a porous media.

Initial tests of QDs for use as geothermal tracers were conducted using a stainless steel chemical reactor packed with Ottawa sand media. The vessel medium was then equilibrated with 2-4 pore volumes of deionized water at room temperature in order to create the least complex solution environment within the vessel. QD solutions were synthesized following the above methods in 500 mL sample volumes and then used to dissolve 1,5-napthalene disulfonate to create a 100 ppm solution of conservative tracer. This allowed for the direct comparison of the novel QDs to a well-studied molecular tracer. The QDs were synthesized using the scaled-up volume in order to provide a large enough homogenous sample for a step injection input as opposed to the shorter, less solution-intensive pulse input. Tracers were detected in the column effluent with an in-line UV-Vis spectrometer and fluorescence spectrometer, using the absorption band of 1,5-NDS at 310 nm and the size-dependent characteristic emission bands of QDs. The injection of a homogenous solution of QDs with a conservative tracer provides a baseline to verify the successful passage of QDs through the porous media. Ideally, the injection scheme will be a short, highly concentrated tracer pulse, which is better suited to larger scale characterization and single-well injection backflow experiments. Without a full understanding of the retention mechanisms of QDs in porous media, a step injection was implemented in order to minimize obfuscations due to tracer dilution and filtering.

The leading QD breakthrough curve was retarded compared to the conservative tracer, while the trailing curve response mimicked the 1,5-NDS. The QD concentration reached equilibrium approximately 70 minutes after the conservative tracer equilibrium. Once both materials achieved a steady-state concentration, the column was flushed with deionized water and the effluent concentrations of 1,5-NDS and QDs were recorded. The tailing concentration of the QDs acted conservatively, as seen in figure 11 with the very close agreement of tracer concentration profiles.

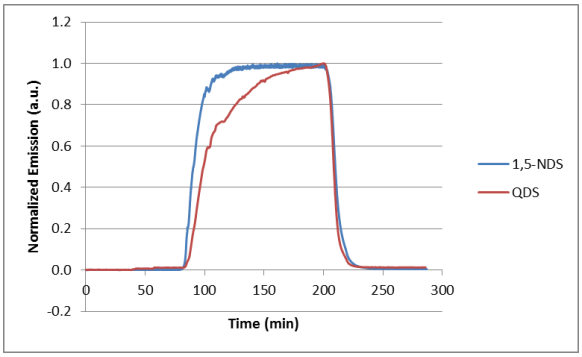

Figure 11-Breakthrough curves of conservative 1,5-NDS and quantum dots

This could be due to physical QD occupation of pore spaces within the sand grains, a phenomenon seen in colloid transport experiments. The conservative behavior of the tracer tail suggests that the entrapment of the nanoparticles is irreversible and the QDs are subsequently transported through the media past occupied sites. Over time, irreversible or very long time-scale adsorption kinetics would result in the occupation of available surface sites. Once these sites are fully occupied, the QDs would be transported via diffusive and convective phenomena, and would not be retarded due to adsorptive effects. The primary interaction mechanisms include physical filtration in narrow pore throats, physical and electrostatic interactions with the sand surfaces, or the entrapment of tracers in stagnant flow regions. Conservative tracer breakthrough occurred at 90 minutes and the QD concentration reached equilibrium at approximately 180 minutes.

The positive result of visible QD transport means we can move forward with quantitative tracer experiments. Also of interest would be to test QD transport under conditions that would more accurately represent geothermal conditions. These would include raised temperatures of the geothermal media and solution chemistries using field-studied ion concentrations. The latter of these has been identified as a potentially important factor in solute and colloid transport.

CONCLUSIONS

We have created fluorescent QD samples that demonstrated improved thermal stability by manipulating the synthetic reaction conditions. The QDs were found to be sensitive to initial molar concentrations and the amount of stabilizing ligand used to prevent agglomeration. The resulting samples represented significant advancement toward the chemistry required to create QDs with long-term thermal stability. Furthermore, the procedure has successfully been used in an order of magnitude scale-up of the reaction volume, creating larger amounts of high-quality QDs per synthesis.

The QD samples created in lab were used to demonstrate viability as tracer particles. A solution composed of QDs and a conservative tracer was pumped through a column of Ottawa sand with in-line detection of tracers in the effluent. QD breakthrough was retarded relative to the conservative tracer, but demonstrated conservative behavior when the column was flushed with deionized water.

ACKNOWLEDGEMENTS

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