QUANTUM DOTS AS TRACERS IN GEOTHERMAL AND EGS RESERVOIRS

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ABSTRACT

Colloidal nanocrystal quantum dots are small crystallites of semiconductors in the size range of 1 to about 20 nm and composed of a few hundred to several thousands of atoms. As a result of quantum size effects and strongly confined excitons, quantum dots display unique size and shape-related electronic and optical properties. In particular, they can be made to fluoresce over a wide range, including the visible and near infrared (NIR) regions of light – regions where geothermal and EGS reservoir waters possess very little interference. In this paper, we describe the excellent sensing/tracing ability of colloidal nanocrystals, which is rooted in their unique structure. While the inorganic semiconducting nanocrystal core delivers tunable emission colors (ranging from the visible to the NIR range), the surface chemistry of colloidal quantum dots can independently be adjusted by the choice of ligands to optimize their interaction with the sensing environment (e.g., hydrophilic/hydrophobic, chemically functional groups, positively/negatively charged surface, etc.). Thus, quantum dot tracers could be designed to possess all of the qualities of the conventional conservative tracers (i.e. the naphthalene sulfonates), or be converted to reactive tracers depending on the surface treatment. Quantum dot tracers would then be available for several new EGS-tracing applications that are currently unavailable using conventional geothermal tracers including the use of these novel tracers to characterize near-wellbore and interwell fracture-surface area resulting from hydraulic stimulation processes.

INTRODUCTION

Currently, no technologies exist for quantitatively measuring the surface area of fractures within a geothermal or EGS reservoir. Fracture surface area, however, is among the most crucial data required for estimating the long-term viability of a geothermal or EGS reservoir. The mapping of microseismicity during a hydraulic stimulation provides some indication of the extent and direction of fracture creation adjacent to the stimulated wellbore. But whereas a microseismic event may indicate fracture creation, microseismic activity is not, in itself, a clear indicator of an associated increase in permeability. The measurement of fracture surface area through the use of tracers that react in various ways with the reservoir will therefore allow for a technological innovation over the current state of the art, since it will provide direct evidence for increases in fracture permeabilities following a hydraulic stimulation.

One of the authors of this paper (Rose) developed a family of tracers (the naphthalene sulfonates) that are not only extremely thermally stable and detectable but are nontoxic and environmentally benign (Rose et al., 2001). And although they are used in essentially every geothermal field in the world where tracer testing is conducted, they possess one serious limitation. Since they fluoresce at ultraviolet wavelengths, they must be analyzed in a laboratory by High Performance Liquid Chromatography (HPLC). This is because many naturally occurring reservoir constituents also fluoresce in the ultraviolet, resulting in the need

for both spectral and chromatographic separation.

In contrast, colloidal nanocrystals ("quantum dots") can be made to fluoresce over a wide range, entirely covering the visible and near infrared (NIR) region of light – regions where geothermal and EGS reservoir waters possess very little interference. Colloidal nanocrystal quantum dots are small crystallites of semiconductors in the size range of 1 to about 20 nm composed of a few hundred to several thousands of atoms. Due to their reduced spatial dimensions, nanometer-sized semiconductors display unique size and shape-related electronic and optical properties as a result of quantum size effects and strongly confined excitons (Alivisatos, 1996; Efros et al, 2003).

These unique features make nanocrystal quantum dots ideally suited for emerging energy, information, and biological technologies as next-generation photon sources and detectors, sensors, tracers, and energy converters. Consequently, tremendous efforts have been made to fabricate single-crystalline semiconductors and control their shape. Typical bottom-up synthesis routes rely on the controlled, solution-based assembly of atoms or ions into defined nanoscale single-crystal materials (Murray et al, 1993; Peng and Peng, 2002; Rogach et al, 2007). Here, we will utilize the expertise of one of the PIs (Bartl) who recently developed a low-temperature route for the fabrication of high-quality semiconductor quantum dots as shown in Figure 5 (Bartl and Siy, 2009a; Bartl and Siy, 2009b).

In the proposed research we will use the excellent sensing/tracing ability of colloidal nanocrystals, which is rooted in their unique structure. While the inorganic semiconducting nanocrystal core delivers tunable emission colors (ranging from the visible to the NIR range), the surface chemistry of colloidal quantum dots can independly be adjusted by the choice of ligands to optimize their interaction with the sensing environment (e.g., hydrophilic/hydrophobic, chemically functional groups, positively/negatively charged surface etc.). Thus, quantum dot tracers could be designed to possess all of the qualities of the conventional conservative tracers (i.e. the naphthalene sulfonates), or be converted to reactive tracers depending on the surface treatment. Quantum dot tracers would then be available for several new EGS-tracing applications that are currently unavailable using conventional geothermal tracers.

QUANTUM DOT SYNTHESIS

Semiconductor colloidal quantum dots (or nanocrystals) can be synthesized by relatively simple organometallic chemistry. We have recently developed a low-temperature (50-130 °C) organometallic nucleation and crystallization-based synthesis route for the fabrication of high-quality colloidal nanocrystals with narrow size distribution and tunable (size-dependent) electronic and optical properties (Bartl and Siy, 2009a; Bartl and Siy, 2009b). Our low-temperature route is in sharp contrast to conventional synthesis methods that require temperatures between 230 °C and 350 °C (Murray et al, 1993; Peng and Peng, 2002; Rogach et al, 2007), enabling synthesis of quantum dots at lower costs and higher quantities as outlined below.

In our approach, nucleation of nanocrystals is induced at lower temperatures (via optimized ligand concentration) compared to conventional methods. Low-temperature growth of these nuclei is kinetically driven (via optimized reaction species concentrations). For example, in order to fabricate cadmium selenide (CdSe) colloidal quantum dots, readily available molecular precursors are reacted in an inert solvent in the presence of surface stabilizing ligands at a temperature of 50-130 °C.

We anticipate that our synthesis method at low temperatures will have several important advantages over conventional high-temperature routes for the proposed tracer-related applications and future commercialization that will require broad applicability and high sample-throughput:

1) Low-temperature synthesis methods can be much better controlled (product quality) and up-scaled.
2) Synthesis at low temperatures allows for use of conventional (inexpensive, readily available, industry-tested) solvents and co-solvents.
3) Low-temperature routes significantly lower engineering

requirements/restrictions and should facilitate high-throughput fabrication and integration into commercial fabrication facilities.

In analogy to established high-temperature synthesis routes, our method allows us to readily tune the synthesis conditions (temperature and length of crystallization) in order to fabricate size and shape-controlled monodisperse quantum dot samples with sizes ranging from about 1 to 20 nm. Since quantum-sized semiconductor nanocrystals display strongly confined exciton behavior, tuning their size results in tunable electronic and optical properties. For example, CdSe quantum dots can display photoluminescence emission colors from blue to green and red (and every color-shading in between) simply by varying their size. This is shown in Figure 1, which displays UV-vis absorption spectra as well as photoluminescence spectra and images of CdSe quantum dots fabricated in our lab. Moreover, by fabricating quantum dots with different compositions (CdTe, PbS, PbSe etc.), we are able to extend this range from the visible into the NIR region of the electromagnetic spectrum (see Figure 2), yielding a combined continuous range of tracers with available emission wavelengths from around 450 nm to more than 1500 nm.
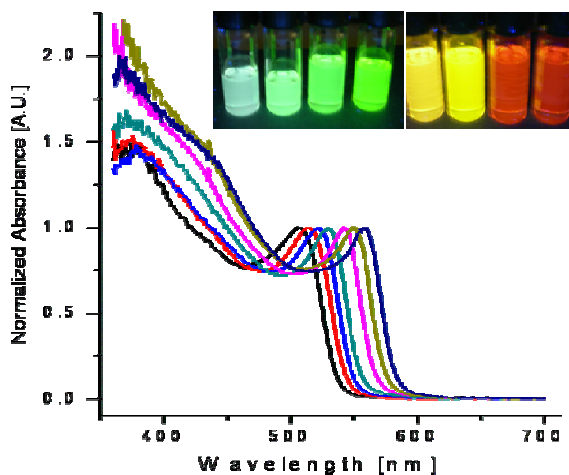

Figure 1. *Photoluminescence images and UV-vis absorption spectra of a range of CdSe quantum dot samples synthesized by our low-temperature method.*

Our strategy for protecting quantum dot tracers from potential harsh environmental conditions and protecting the environment from toxic

nanocrystal compounds in deep-well tracing is to cover their surface with a silica-based inert coating using simple alkoxysilane-chemistry. This is a similar approach that has been successfully applied in bio-imaging applications to ensure that cadmium and lead components cannot leak into the biological system (Bruchez et al, 1998; Rogach et al, 2000). Besides deep-well environmental protection, the glassy silica layer is also ideally suited to reversely protect the nanocrystals from the high temperatures and potentially corrosive conditions in EGS tracing. Furthermore, since the silica layer is completely transparent to visible and NIR light, the emission-based tracing ability by the nanocrystals will not be affected.
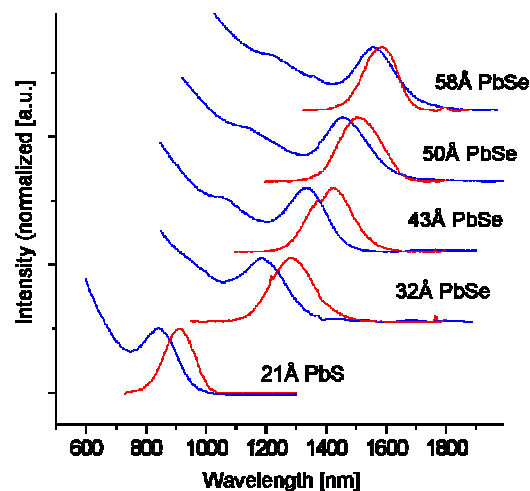

Figure 2. *NIR absorption (blue spectra) and photoluminescence emission (red spectra) of colloidal PbS and PbSe quantum dots with diameters ranging from 2.1 to 5.8 nm.*

This broad tunability of the electronic and optical properties of semiconductor quantum dots, combined with the ease of fabrication enabled by our low-temperature synthesis route should make quantum dots ideally suited for the proposed sensing and tracing applications. For this we will incorporate quantum dots into specific sensing/tracing hosts, by making use of the unique ability of decoupling the properties of the nanocrystalline semiconductor core and that of the surrounding organic ligand layer. While the composition, shape and size of the core determines the electronic and optical properties of quantum dots, the surrounding ligand layer can independently be modified to "adjust" the

chemical behavior (or surface chemistry) of the quantum dots. This is of particular importance for sensing and tracing applications, since it provides the ability to both render quantum dots stable to the sensing/tracing environment (temperature, pH, corrosion, etc.) and to optimize their interaction with the sensing environment.

One of the goals of our work is to reach synthesis batch levels high enough to produce quantum dots in sufficient quantity for field testing in an injection/backflow test in an EGS wellbore. Up-scaling is pursued in two steps: 1) Increasing the concentration of produced quantum dots per reaction volume and 2) increasing the reaction volume per run. We initially focused on step 1 and were able to increase the concentration of quantum dots by a factor of 1000. This was accomplished by optimizing the ratio of quantum precursor components to surface-stabilizing ligands.

Having increased the quantum dot yield, we focused on optimizing the optical properties of the quantum dots synthesized at such high yields. We were able to improve quantum dot quality in terms of optical and structural properties equal to those synthesized at low concentrations and/or high temperatures. This is evidenced in the narrow optical absorption and emission peak features (with full-width-at-half-maximum values as low as 30 nm) shown in Figure 3.

The second main aspect of our current research is aimed towards up-scaling the overall reaction volume. For this, we built a new quantum dot synthesis set-up that will allow increase of the per-batch reaction volume by a factor of up to 200 (from the current 20 mL to about 4 L). Figure 4 shows a photograph of the set-up and we are currently in the finishing stages of linking the various synthesis apparatus components and starting with quantum dot synthesis runs at these high reaction volumes.
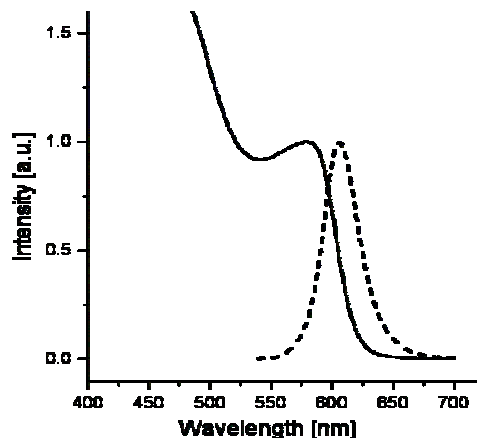

Figure 3. UV-vis absorption (full line) and photoluminescence emission (dotted line) spectra of CdSe nanocrystal quantum dots produced at low reaction temperatures (130 °C) and high yield (1000 fold increase).

Figure 4. Photograph of high-reaction-volume synthesis set-up for up-scaled quantum dot production.

QUANTUM DOTS AS REACTIVE TRACERS

One strong advantage in the use of quantum dot tracers is the potential for modifying their surface chemistries and/or their diameters in order to allow for surface sorption and/or contrasting diffusivities. These properties of sorptivity and contrasting diffusivity can subsequently be used as tools that interact variably with fracture surfaces and/or pores for characterizing fracture surface areas. A measurement of fracture surface area can be a very important parameter in the design and

creation of the fracture networks that constitute the heat exchanger in an EGS.

Positively charged alkali and alkaline-earth elements (first and second rows of the Periodic Chart, respectively) have been shown to sorb reversibly in groundwater studies to determine the fracture-surface areas of shallow granitic formations.This suggests that positively charged ligands attached to the surface of quantum dot tracers would allow for their reversible sorption. Likewise, scale inhibitors such as polycarboxylates, polyacrylates, and polymaleic anhydrides have been shown to sorb strongly but still reversibly within geothermal wellbores and formations. If these species are bonded to the quantum dots, they would render them reversibly sorptive on EGS formations, while retaining all of the fluorescence properties available from quantum dot tracers.

We will explore these features for use as color and size-discriminating colloidal tracers to provide information beyond well-to-well connectivity such as fracture surface area or fracture spacing. In particular, we will focus on three main areas:

1) Synthesis of water-soluble colloidal nanocrystals with single-wavelength excitable emission colors spanning the entire visible and NIR range.
2) Rendering these nanocrystal tracers temperature and corrosion-stable for deep-well applications by coating them with a thin layer of transparent silica.
3) Development of size-discriminating tracers by incorporating nanocrystals into nano to micrometer-sized glass spheres for use in fracture surface area and fracture spacing studies.

Rates of tracer diffusion out of fractures into secondary porosity (and back again) are dependent on tracer diffusivity, matrix porosity, and interfacial area between the fractures and matrix. By systematically varying tracer diffusivities, interfacial area can be estimated from differences in tracer responses, provided reasonable estimates of matrix porosity exist. The low and adjustable diffusivities of colloidal quantum dot tracers will significantly expand the range of tracer diffusivities that can be exploited, thus allowing better estimates of fracture surface area. Figure 5 shows a simulated example of breakthrough curves of a halide, a naphthalene sulfonate, and a hypothetical 10-nm-radius quantum dot tracer in a single-well test in a fractured reservoir with a low-porosity matrix. The responses of the halide and naphthalene sulfonate represent the current state of the art in differences in breakthrough curves that can be obtained due to different diffusivities of geothermal tracers.
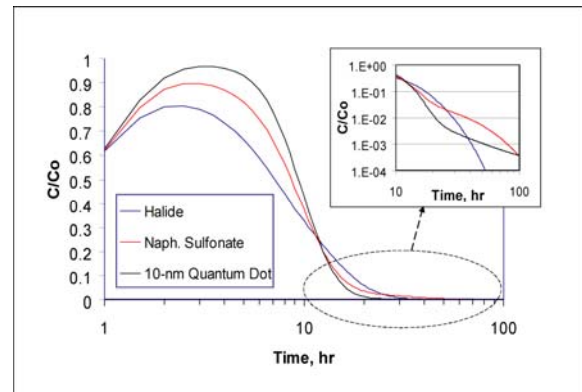

Figure 5. *Simulated breakthrough curves of a halide, a naphthalene sulfonate, and a 10-nm-radius quantum dot tracer in a single-well tracer test. Pumping started at zero hours, with injection occurring at -10 hours and lasting 9.9 hours. Inset shows log normalized concentrations in the tails. The differences between the curves will increase for greater surface area and decrease for less surface area.*

Quantum dot tracers would clearly extend the range of tracer responses that could be interrogated, leading to significant improvements in the ability to estimate surface area. Larger quantum dot tracers would extend this range even further – from a diffusivity contrast of about a factor of 4 or 5 with geothermal tracers in current use to as much as a factor of 50 to 100. Furthermore, the use of halides as tracers is generally limited to bromide and iodide, and because of their large diffusivities, the background concentrations of these tracers in EGS reservoirs will rapidly increase to the point where they can no longer serve as effective tracers (they could only be used once or twice). However, if quantum dot tracers with different optical signals were available, they could be used repeatedly without background interferences along with many existing non-interfering solute tracers that have larger diffusivities than halides (e.g., the

naphthalene sulfonates) to conduct repeated interrogations of surface area as an EGS reservoir is developed and stimulated.

Quantum dot tracers with controllable surface sorption characteristics also have the potential to provide surface area estimates in geothermal reservoirs. Such tracers could prove especially useful when the reservoir matrix porosity is so low that it is difficult to observe a contrast in breakthrough curves of tracers with different diffusivities. Figure 6 shows a hypothetical example of how sorbing tracers with well-characterized sorption properties (sorption and desorption rates and sorption capacities as a function of surface area) could be used to interrogate surface area in the absence of matrix diffusion. As this figure shows, conservative tracers with different diffusivities will have identical breakthrough curves when reservoir matrix porosity is negligible, but the responses of sorbing tracers relative to conservative tracers can still provide estimates of fracture surface area. The combined use of diffusing and sorbing tracers in reservoirs with finite matrix porosity would, in principle, allow the effects of diffusion and sorption to be deconvoluted, which would reduce uncertainties in surface area estimates below that which can be achieved using diffusing or sorbing tracers alone.
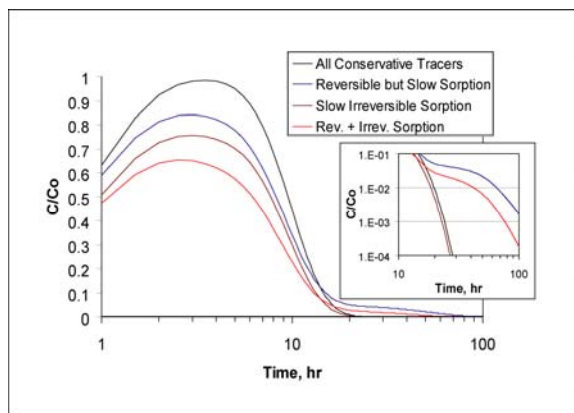

Figure 6. Simulated breakthrough curves of hypothetical sorbing tracers relative to a conservative tracer in a single-well tracer test in a reservoir with negligible matrix porosity. Pumping started at zero hours, with injection occurring at 10 hours and lasting 9.9 hours. Inset shows log normalized concentrations in the tails.

Figures 5 and 6 were generated using an existing numerical model that required simplifying assumptions to be made regarding tracer, fracture, and rock matrix properties. This existing model will serve as a starting point for development of a more sophisticated model that will allow many of these simplifying assumptions to be relaxed so that real-world complexities, such as spatial variability in fracture apertures and matrix properties, as well as nonideal tracer behavior (e.g., combinations of diffusion and sorption, thermal degradation), can be addressed. The combined use of such a model with single-well tracer testing methodologies and new low-diffusivity and sorbing quantum dot tracers should result in significant advances in the interrogation of surface area in enhanced geothermal reservoirs.

ACKNOWLEDGMENTS

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