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Nucleotide-Directed Growth of Semiconductor Nanocrystals

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Colloidal semiconductor quantum dots exhibit tunable optical properties arising from the quantum size effect, and provide a powerful tool for biological imaging.[1−3] The choice of ligands used in synthesis provides a powerful means of rationally controlling nanoparticle properties.[4−6] Biomolecules — built from naturally occurring repeat units that can be engineered into heteropolymeric structures with rational control — are a particularly attractive ligand system to direct nanoparticle growth.[7,8]

A recent report of DNA-directed semiconductor quantum dot syntheses described highly optically emissive PbS nanocrystals.[9] Infrared emitters, such as PbS quantum dots, are particularly promising candidates for biological imaging given the transparency of tissue in certain windows within this spectral regime.[4] The finding that nucleic acids can be used to facilitate nanocrystal synthesis indicates that rational bottom-up control over nanostructures could be achieved using DNA as a template and ligand. However, the salient chemical features of polynucleotides essential for semiconductor nanoparticle synthesis have yet to be identified. A number of moieties on nucleotides — including both backbone phosphate groups and base functionalities available — are candidates for promoting or terminating growth and serving as a capping layer.

Here we investigate systematically how nucleotide functionalities influence nanoparticle growth. We derive thereby a set of rules for using nucleic acids as ligands and programmable templates for nanoparticle synthesis. We proceed from the following model of nanoparticle growth: a ligand (i) binds the precursor metal cation during crystal growth, (ii) serves as a stabilizing cap for the nanoparticle once most of the reagents are consumed, helping to terminate growth, (iii) passivates defect states that would otherwise exist on the nanocrystal surface, and (iv) ensures that the nanoparticles remain stably dispersed in aqueous solution. The chemical functionalities present on a given ligand control the proficiency of the ligand in each of these roles.

In the present work, our PbS quantum dot synthesis begins with seeding a chosen ligand — a nucleotide — with Pb^{2+}. A S^{2-} source is subsequently added to the solution. Under suitable conditions (i.e. an excess of ligand), the ligand binds to Pb^{2+} and prevents formation of bulk semiconductor. Here, the nucleotide:Pb^{2+}:S^{2-} molar ratio was set to 3:1:1, corresponding to the stoichiometry used in our previously reported CT DNA PbS syntheses[9] and conditions where Pb^{2+} would be complexed with the nucleotide ligand.[10] Throughout this work, while individual functionalities on the bases were varied by choosing different nucleotides, the remaining synthetic parameters were fixed.[11]

We began by testing four nucleotide triphosphates, ATP, CTP, GTP, and UTP. We sought to determine whether these nucleotides, which display the base, sugar, and phosphate functionalities found in polynucleotides, could serve as useful ligands.

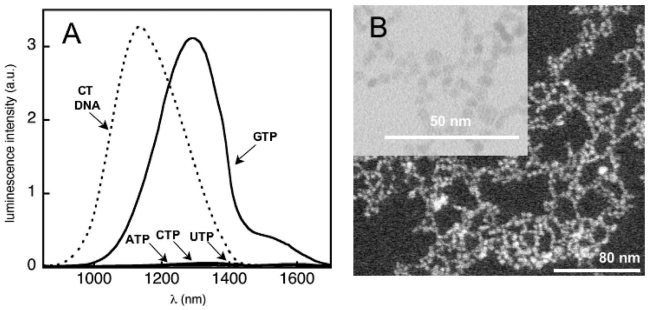

Figure 1. Effect of varying the nucleotide on the results of PbS nanocrystal synthesis. (A) Photoluminescence spectra under 633 nm, 3.3 mW excitation from a HeNe laser. The use of GTP ligand results in strongly luminescent, stably dispersed nanocrystals. In the presence of ATP, CTP, and UTP, syntheses produced mainly precipitate. CT DNA produces a strong luminescence spectrum that is narrower than and blue-shifted relative to GTP−NCs. (B) TEM of PbS quantum dots synthesized in the presence of GTP.

Syntheses using GTP produced PbS nanocrystals with IR luminescence (Figure 1A) corresponding to photoluminescence quantum efficiencies in the range 1−2%.[12] In the presence of ATP, CTP, and UTP, soluble nanocrystals were not the major product, and instead the syntheses produced mainly precipitate and nonemissive solutions. The results indicate that, under the synthetic conditions chosen here, only GTP served as a competent ligand for nucleation, growth, and capping of soluble PbS nanocrystals. Transmission electron microscopy (TEM) analysis[12] of the products of the GTP reaction, presented in Figure 1B, reveals ∼4 nm spherical nanoparticles. The emission of GTP−PbS is slightly red-shifted relative to materials synthesized in the presence of intact CT DNA under analogous conditions.[9,13]

The results obtained with the four naturally occurring nucleotides strongly suggest that the functionalities present on GTP are a prerequisite for the production of nucleotide-passivated PbS nanocrystals. We proceeded to investigate several of the different functional groups on the GTP to identify those that played a central role. Previous studies demonstrate that a macrochelate metal ion binding site exists at the N7 of G.[10] Another possible site for ligand−Pb^{2+} or ligand−PbS interactions is the exocyclic N2.[14]

The guanine N7 and N2 were probed by performing syntheses in the presence of 7-methyl GTP and inosine triphosphate (ITP). The alkylation of 7-methyl GTP would perturb binding interactions involving the N7. In ITP, the N2 has been deleted (see Figure 2).

Syntheses performed with 7-methyl GTP produced nanocrystals with luminescence similar to that seen with GTP (Figure 2A). From the spectra, it appears that the N7 influences nanoparticle size; however, it does not serve as a binary determinant of whether a successful, stable luminescent product is generated. In striking contrast to the results seen with 7-methyl GTP, syntheses employing ITP did not produce nanocrystals or luminescent material. The

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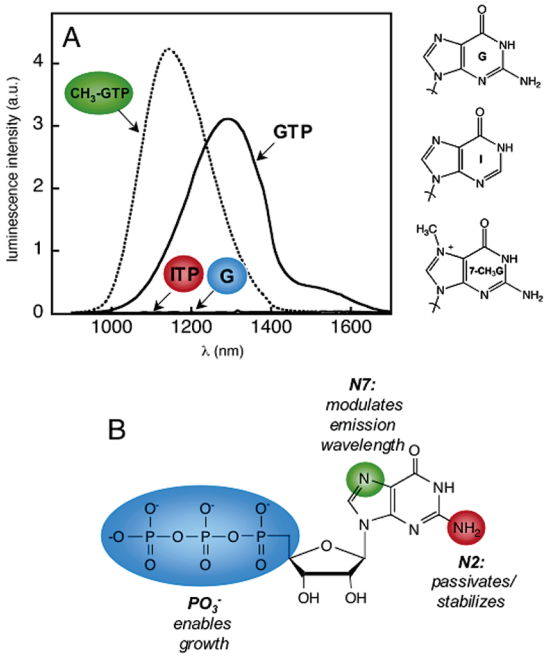

Figure 2. Effect of specific chemical functionalities present on GTP on PbS quantum dot synthesis. (A) Luminescence spectra obtained when GTP, G, ITP, and 7-CH_3-GTP were used for PbS synthesis. (B) Proposed roles of phosphate and base functionalities on GTP in nanoparticle nucleation, growth, termination, stabilization, and passivation.

exocyclic N2 of GTP appears crucial to nucleotide-mediated PbS nanocrystal synthesis. We used FTIR spectroscopy to directly determine the extent of interaction between the N2 and Pb^{2+} and PbS. We found that the addition of Pb^{2+} cations only minimally perturbed N2-correlated features, but that the synthesis of nanoparticles through the subsequent addition of S^{2-} yielded a change in N2-correlated features.[12] These findings indicate that the N2 does bind to the surface of PbS.

We also explored the role of the GTP phosphate moiety on PbS nanocrystal synthesis and luminescence. Given that ATP, UTP, or CTP did not support nanocrystal growth, it is clear that the phosphate group is not effective on its own. However, the possibility that this moiety worked in concert with the others on G merited investigation. We therefore investigated the G nucleoside, guanosine, which lacks phosphate (Figure 2A). Indeed, tests of guanosine as a ligand revealed that this compound did not produce soluble product, and no appreciable luminescence was detected in the solutions after PbS synthesis. We conclude that the charged group plays an essential role in the synthesis, by seeding and controlling nanoparticle growth.

To probe further the role of phosphates in PbS synthesis, FTIR was used to monitor this functional group through the course of the synthesis.[12] These experiments provided evidence that the phosphate group binds Pb^{2+} initially but reverts to the unbound state after the addition of S^{2-} (see Supporting Information) Therefore, it appears that phosphates participate in nanocrystal growth by binding Pb^{2+} from the solution, thereby altering (following sulfur source injection) the degree of supersaturation and thus the conditions for nucleation and the rate at which nanoparticles grow. In addition, given their charge and steric bulk, the phosphates also likely play a key role in solubilizing the nanoparticles in water.

On the basis of these results, we propose a general mechanistic framework describing how nucleotides promote and control nanocrystal growth (Figure 2B). At the concentrations, stoichiometries, and temperature employed herein, it appears that G-based nucleotides, through a combination of amine and phosphate functionalities, are effective at controlling PbS growth and capping the structures with a stable ligand system. Having at least two distinct classes of Pb^{2+} binding functionalities appears to be crucial to the growth of stable, luminescent nanoparticles. One class of functionalities (e.g. the phosphate and possibly the N7 binding site) appears to feed nanoparticle growth, while the other (e.g. the N2 on G) stabilizes the products. Differences in ATP vs GTP, for example, point to the importance of the binding affinities, and possibly even the geometries and relative placements, of these functionalities. It is also noteworthy that the N7 does play a role, as nanocrystals produced with 7-methyl GTP exhibit blue-shifted luminescence. This shift may reflect a change in the size of the nanocrystals.[13] Alternatively, changing the binding of the N7 through alkylation could change the binding mode of GTP and result in a shift in the spectra, indicating that cooperativity exists among the different functionalities in G. Cooperative and spatial effects like this may help explain why GTP is unique relative to the other nucleotides.

The results of these studies not only provide insight into the mechanism of nucleotide-mediated PbS nanocrystal growth but also lay the groundwork for programmable synthesis of nanoparticles. Coupling the natural biorecognition properties of DNA with its ability to template nanocrystal synthesis could prove to be a simple pathway to tunable, IR-emitting nanocrystals.

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Supporting Information Available: Synthetic protocols and details about photoluminescence, FTIR spectroscopy, and transmission electron microscopy. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) All syntheses were performed at 1:1 lead-to-sulfur precursor molar ratio in 2 mL Eppendorf tubes at room temperature with vortex agitation. In a typical synthesis, 100 μL of 10 mM lead precursor was added to 250 mL of 13.4 mM NT/NS and mixed, followed by 5-min incubation. Then 100 μL of 10 mM sodium sulfide was quickly injected to the reaction tube. The solution immediately turned from transparent to red-brown, indicating the formation of PbS nanocrystals. The supernatant was removed from precipitate after centrifuging at 4000 rpm for 5 min. These syntheses were reproducible and did not require postsynthesis manipulation or processing. See Supporting Information for more details.
(12) See Supporting Information for information about TEM, FTIR, and luminescence measurements.
(13) The observed 150 nm spectral shift would correspond to a 1 nm size difference not clearly resolved through the TEM images presented herein. Therefore, while the shift may reflect an altered nanoparticle size, the origin of this spectral feature cannot be specifically assigned.
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