Quantum dot arrays with controlled periodicity using DNA origami nanotubes

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Outline

- Background
- Motivation
- Statement of Work
- Experimental
- Results
- Analysis
- Conclusions
Background

- DNA oligonucleotides
  - Aggregate, crystallize, self-assemble into discrete assemblies and linear arrays
- DNA nanotechnology for nanoparticle arrays
  - DNA tiling with motifs
  - DNA origami


Ding et al., JACS, 2010, 132, 3248

AuNPs


AgNPs
Motivation

- Precise nanoparticle patterns
  ⇒ Nano-electronic, -optical, -plasmonic devices

- DNA origami as a template for self-assembly
  ⇒ Control nanoparticle patterning
  ⇒ “Nanobreadboard”

Cartoon of light emitting device utilizing gold and quantum dot nanoparticles
To fabricate nanoparticle arrays with controlled periodicity using 3D six-helix bundle DNA origami nanotubes
Experimental

- Quantum Dot Arrays using DNA Origami Nanotubes
  - Use the DNA Origami method to form a DNA nanotube from a 6-helix bundle.
  - Modify selected staple strands (DNA oligonucleotides) with a 5-Thymine tether and a biotin binding site.
  - Combine biotin labeled nanotubes with streptavidin conjugated quantum dots.
DNA Nanotube Design

Mathieu et al., Nano Lett., 2006, 5, 661

M13 scaffold

170 staple strands

6-helix bundle DNA origami nanotube resembles an parallel array of six double helices
Extended staple strand with an addition of 5 thymine nucleotides and a biotin
Four different arrays – Four different periodicities
Quantum Dots

- CdSe core, ZnS shell
- Streptavidin coated
- ~5-6 nm core

Invitrogen, Qdot 585

TEM, Qdot 585, average diameter = 5.3 nm

Quantum dot streptavidin conjugates’ core/shell met manufacture specification
Streptavidin has a strong affinity for biotin
Quantum Dot Attachment

- All data were characterized using atomic force microscopy – AC tapping mode (tapping in air)
- Successful attachment of semiconductor QDs to DNA nanotubes

Biotin-labeled DNA nanotubes with 9 binding sites
DNA Nanotube Characterization

- **Biotin**
  - AFM image
  - Height profile
  - Periodicity evaluation
  - 2.6 nm

- **Pure streptavidin**
  - AFM image
  - Height profile
  - Periodicity evaluation
  - 3.1 nm

- **Quantum dot**
  - AFM image
  - Height profile
  - Periodicity evaluation
  - 5.5 nm

Biotin-labeled DNA nanotubes with 9 binding sites
Quantum Dot Attachment

- AFM images of 4 different arrays with 4 different periodicities

# of sites:
- (a): 5
- (b): 9
- (c): 15
- (d): 29

# of QDs:
- (a): 5
- (b): 9
- (c): 10
- (d): 17

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Quantum Dot Binding Interference

Several factors that may limit QD attachment
Histogram data

- Histograms were compiled from AFM image analysis for over 225 separate nanotubes for each case.

- Average attachment probability, $p$, for each binding site:
  \[ p = \frac{\sum \text{attached QD}}{\sum \text{available sites}} \]

  The probability of a given site being occupied by a QD
Binomial Distribution

- Assume: binding events occur with an equal average attachment probability, \( p \), for each site.
- Compared calculated probability using a binomial distribution model with histogram

\[
P(m) = \frac{n!}{m!(n-m)!} \cdot p^m \cdot (1 - p)^{n-m}
\]

\( P(m) \) is the probability that \( m \) binding events will occur when \( n \) sites are available.
- If steric hindrance/bridging exists, we would expect a fewer attached particle.
For smaller period lengths, there is deviation from binomial distribution.

Supports steric hindrance and/or bridging.
Nearest-Neighbor Separation

- Nearest neighbor (N-N) separation should follow geometric distribution.
- $P(l)$ is the probability that the N-N distance is $l$ periods, with $l$ being an integer.

$$P(l) = p \cdot (1 - p)^{(l-1)}$$

- In the absence of steric hindrance/bridging, the probability would peak at the desired periodicity.
- N-N distance less than $\frac{1}{2}$ design period = 0.
71 nm and 43 nm designs had most probable N-N separation of 1 period.

29 nm and 14 nm were more likely to be separated by 2 and 3 periods, respectively.

Supports steric hindrance and/or bridging.
Center-to-Center Separation

- Center-to-center measurements yield minimum separation in solution.
- Lower limit observed to be 20 nm.
  \[ \Rightarrow 20 \text{ nm effective particle diameter.} \]

<table>
<thead>
<tr>
<th>Separation (nm)</th>
<th>Counts</th>
<th>N</th>
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<tbody>
<tr>
<td>71</td>
<td>25</td>
<td>392</td>
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<td>15</td>
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<tr>
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</table>

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Steric hindrance is expected for any array periodicity of 20 nm or less.
DNA origami nanotubes enable periodic quantum dot arrays

71 nm and 43 nm period designs have high attachment yields and periodicities that reflect design criteria

29 nm and 14 nm period designs have lower attachment yields and larger periodicities than designed

Strong evidence of steric hindrance and/or bridging exist for smaller periods

DNA origami nanotubes are possible candidates for the scaffold structure of nanoelectronic devices
Thank You
Questions?
Backup
Streptavidin Control

- Binomial distribution test repeated with streptavidin
- Number of attached streptavidin molecules was higher than for QDs
- Not considered statistically significant
- Poisoning is inconclusive

![Graphs showing probability distributions for Attached QD and Attached STV with N=233 and N=100 respectively.](image)
**Tapping soft vs. hard**

- AFM imaging of streptavidin on mica
  - Change the target amplitude (i.e. force)
  - Change the sample height

![AFM images](image)

- $H_{\text{avg}}$: 1.99 nm
- 2.0 V: 0.76 nm
- 0.5 V: 2.09 nm

*Scale bar is 300 nm*
$d_{C-C}$: center-to-center separation

$d_{N-N}$: projected separation