Multivariate Analysis of Peptide-Driven Nucleation and Growth of Au Nanoparticles

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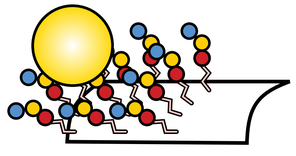
Abstract

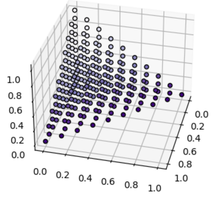
Sequence defined molecules such as peptides and peptoids gives researchers significant control over the formation of inorganic nano-structured materials. Bio-inspired synthesis and assembly approaches have been applied to noble metals, perovskites, quantum dots, titania, and other systems. Frequently, the use of sequenced defined molecules in inorganic nanoparticle synthesis is motivated by enabling the formation of complex structures at mild reaction conditions. However, predicting the effect of sequence defined molecules on inorganic material synthesis is an ongoing issue. Small changes to the identity or the order of a molecule's sequence can have a strong impact on how it interacts with the inorganic precursors or particles in a reaction (20n unique peptide sequences for peptide of length n). Moreover, molecular design rules also need to account for factors other than molecular sequence when comparing the effects of molecules on synthesis outcomes. To address this problem, we focus on the use of Au binding peptides in the synthesis of Au nanoparticles. We created 6 variants of a Au binding peptide (Z2) and studied how each peptide impacted the synthesis of Au nanoparticles in 64 reaction conditions per peptide by varying the concentration of precursor, reducing agent, and peptide. Each sample was characterized by UV-Vis spectroscopy which serves as a proxy for the structure of plasmonic nanoparticles. By applying functional data analysis to these measurements, we were able to make comparisons between the 6 peptide variants in a large experimental design space.

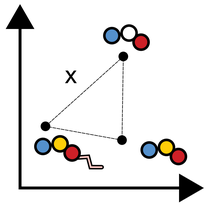
Motivation

- Sequence defined molecules enable the synthesis of complex nanoscale structures in mild conditions

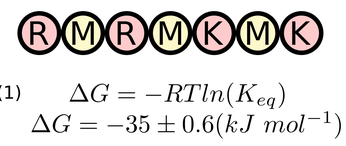


- The molecular and reaction design space are exceedingly large
- Need to develop methods to obtain quantitative structure-property relations



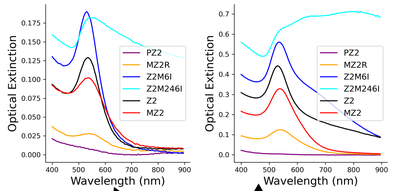


Au Binding Peptides as a Model System

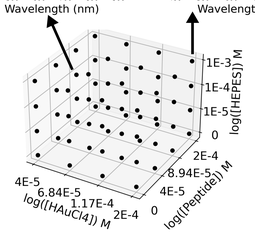


(1) $$\Delta G = -RTln(K_{eq})$$
$$\Delta G = -35 \pm 0.6(kJ\ mol^{-1})$$

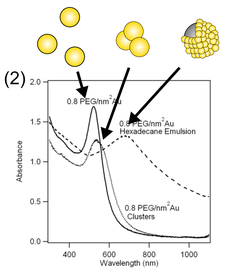
- Remove strong gold binding residues
- Conjugate alkyl tail to make peptide amphiphilic
- Reverse order of sequence in variant with alkyl tail



- Synthesize 64 combinations of reducing agent, peptide, and gold precursor for each of 6 peptide variants
- Characterize using UV-Vis spectroscopy



(2)



UV-Vis optical extinction is a proxy for plasmonic nanoparticle structure

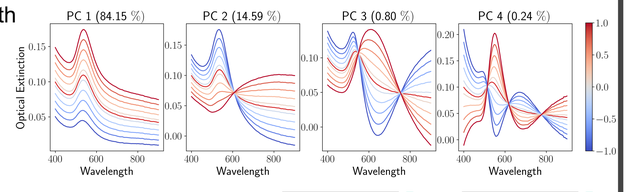
Functional Data Analysis

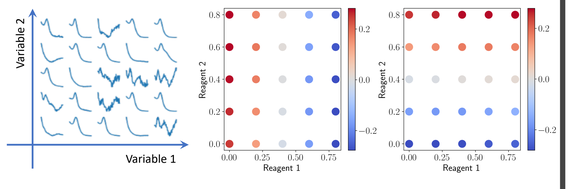
1 Represent each of n spectra of length i as 4 coefficients of 4 principal component functions.

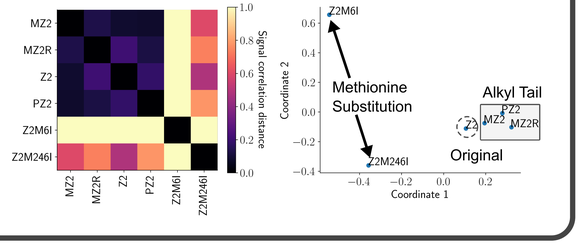
$$A_n(\lambda_i) = \sum(c_j \phi_j)$$

2 Each peptide reaction space is a graph consisting of 64 reactions and measurements, where each measurement is represented using coefficients from the summation above. Compress each reaction space using graph Fourier transform.

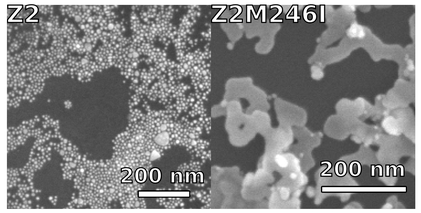
3 Calculate signal correlation distance between each peptide reaction space. Embed using multidimensional scaling for visualization







Structural Characterization



- Z2 primarily formed spherical nanoparticles
- Replacing all methionine residues with isoleucine led to formation of large structures with apparent preferential growth at the edge

Conclusions/Future Work

- Substituting methionine had a greater effect on nanoparticle synthesis than addition of alkyl tails (C14 and C16) or reversing the sequence
- Developed a quantitative method of comparing reaction spaces of peptide mediated gold nanoparticle synthesis
- Need to quantify structural variations in a reaction space using state diagrams
- Probe different states in reaction space using SAXS and TEM

References

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(2) Larson-Smith, K.; Pozzo, D. C. Pickering Emulsions Stabilized by Nanoparticle Surfactants. Langmuir 2012, 28 (32), 11725–11732.

Acknowledgements

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