



Graduate Student Seminar

Department of Chemistry

Sunday, June 11th, 2023

Time 14:30

Bldg. 43 Room 015

Mark Baranov

Under the supervision of Prof. Ira Weinstock

Polyoxometalate Ligands: From Fundamental Coordination Chemistry to Advanced Applications

The utilization of polyoxometalate (POM) ligands has emerged as a transformative approach in the field of coordination chemistry,¹⁻⁵ enabling diverse applications in the synthesis, stabilization, and functionalization of nanocrystals. This seminar explores the multifaceted role of POM ligands in three distinct topics, showcasing their impact on stabilizing metastable nanocrystals, elucidating non-classical crystallization pathways, and enhancing catalytic reactivity.

- Harnessing entirely inorganic POM cluster-anion ligands it was possible to entrap and impart heat resistance to metastable metal-oxide-based nanocrystals. A general method is proposed for stabilizing metastable phases, expanding the repertoire of accessible materials with enhanced phase stability in various solvents and temperatures.
- Advancements in understanding nanoparticle superlattices (SLs) have unveiled a wide range of pathways for their organization. Here, the addition of alkali-metal cations to negatively charged MnO₂ nanocrystals leads to the formation of body-centered cubic superlattices. Time-resolved cryo-TEM captures the complete process, revealing the role of dendrimeric chains as nonclassical nuclei and providing insights for the rational design of self-assembled functional materials.



- POM ligated CeO₂ nanocrystals exhibit remarkable dual oxidase-like catalytic activity. By harnessing oxygen vacancies and the self-renewing cycle of Ce³⁺/Ce⁴⁺, these nanocrystals scavenge reactive oxygen species. Notably, their modulation by protonation influences the catalytic activity, offering opportunities for the development of advanced enzyme-mimetic systems for catalytic processes.

References:

[1] Baranov, M.; Duan, Y.; Leffler, N.; Avineri, S.; Ezersky, V. & Weinstock, I. A. *Chem. Comm.*, 2023, 59, 4364-4367.

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[3] Baranov, M.; Polin, L.; Leffler, N.; Leitun, G.; Shames, A. I. & Weinstock, I. A. *Dalton trans.*, 2022, 51 (22), 8600-8600.

[4] Zhang, G.; Baranov, M.; Wang, F.; Poblet, J. M.; Kozuch, S.; Leffler, N.; Shames, A. I.; Clemente, J. M.; Neyman, A. & Weinstock, I. A. *J. Am. Chem. Soc.*, 2021, 143 (49), 20769-20778

[5] Baranov, M.; Tubul, T.; Azulai, Y. & Weinstock, I. A. *Inorg. Chem.*, 2019, 58 (13), 8877-8883.