Research in the Brock Group: (1) Transition Metal Pnictide Nanoparticles for Magnetic and Catalytic Applications; (2) 3-D Assemblies of Metal Chalcogenide Quantum Dots for Energy Conversion

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Transition Metal Pnictides (Pnicogen = P, As, Sb, Bi)

Metal Phosphides for HDS

- Hydrosulfurization (HDS): Removal of sulfur containing impurities from petroleum feedstock.
- Metal phosphides are stable, sulfur resistant, metallic compounds that have exceptional hydrodesulfurization catalytic activity.
- Among binary phases studied (Co, P; Ni, P; Fe, P), NiP has shown the highest catalytic activity.

Goals for Model Catalyst Development and Evaluation

- Develop a set of synthetic Lewis acids enabling control of the size and shape of the NiP nanoparticles using solution phase methods.
- Develop methods for transition metal substitution on the catalytic sites (P).
- Establish structure-activity relationships for NiP HDS as a function of site size, surface composition/structure/active site reactivity.
- Evaluate the effect of transition metal dopants on activity/selecivity normalized for size.
- Probe the role of more active supports on HDS.

Basic Synthetic Route to Make NiP Nanoparticles

Manganese Phosphides for OER

- Water splitting is a clean and renewable source of energy.
- Oxygen evolution reaction (OER): 2H₂O + 4e⁻ + 4H⁺ = O₂ + 4H₂O
- OER is a rate-limiting step of water oxidation.
- Novel efficient OER catalysts with low overpotential.
- Metal phosphide (NiP, CoP, Cu2P) and Mn-based materials (oxide and phosphates) are promising OER catalysts, motivating a study of Mn-based phosphides.

Synthetic Route to Make CoMnP Nanoparticles

Covariant assembly of QDs by cross-linking with metal cations

- Surface ligands – control nucleation, growth and chemical and cristallinity of QDs but impede electrical transport.
- Replace bulk organic ligands with chalcogenide and metal chalcogenide complexes – reduces interparticle spacing and enhances electronic coupling between QDs (Takács & co).
- Oxidative sol-gel assembly – leads to 3-D connected networks, but these break up upon chemical reduction (0²⁺ → 2⁻).
- Can we use metal cation cross-linkers to form covariant linkages with geometrically interconnected QDs?

Strategy

1. Exchange surface chalcogen ligands (e.g., H₂S) with Na₂S
2. Add a cation co-linker via self-assembly

Compositional analysis of 0⁻/2⁻ covariant assemblies cross-linked with metal cation (S²⁻).

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Luragen Instrument Center

Table 1.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Metal fraction (M/(M+Ni)) M= Co or Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>Ni1.9Fe0.1P</td>
</tr>
<tr>
<td>300</td>
<td>Ni1.9Fe0.1P</td>
</tr>
<tr>
<td>400</td>
<td>Ni1.9Fe0.1P</td>
</tr>
<tr>
<td>500</td>
<td>Ni1.9Fe0.1P</td>
</tr>
<tr>
<td>600</td>
<td>Ni1.9Fe0.1P</td>
</tr>
<tr>
<td>700</td>
<td>Ni1.9Fe0.1P</td>
</tr>
</tbody>
</table>

Magnetic refrigeration (MR)

- Temperature dependence: (T) → 0K
- Magnetic ordering: (T) → 0K
- Temperature dependence: (T) → 0K
- Magnetic ordering: (T) → 0K

Oxidative Gelation Process

Towards Multi-component Gels with Controlled Heterogeneity

Monitoring the Kinetics of Gelation by light scattering

Stokes-Einstein-Relationship: \( \eta \approx \eta_0 \frac{m}{M} \)

4. Add volume: 3 mL
5. Gelation by
6. Heat-up methodology to
7. Monitor the kinetics of gelation by light scattering

Table 2.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Dibenzothiophene Conversion (%)</th>
</tr>
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<tbody>
<tr>
<td>200</td>
<td>9.1 wt% Ni2P@mSiO2 (5.9 nm)</td>
</tr>
<tr>
<td>300</td>
<td>9.4 wt% Ni2P@mSiO2 (11.2 nm)</td>
</tr>
<tr>
<td>400</td>
<td>9.7 wt% Ni2P@mSiO2 (17.1 nm)</td>
</tr>
</tbody>
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Eﬀective temperature-dependent transition in which a first-order magnetic transition occurs at 315 K upon warming.
- The first-order phase transition takes place at 400K.
- The first-order phase transition temperature is a sensitive function of Mn-H and Mn-P distances.

Magnetic Refrigeration Project Goals

- Develop a solution phase route to make phase pure, discrete MnAs and doped MnAs nanoparticles (MnAs$_{1-x}$Mn$_x$P$_2$) as narrow size distributions.
- Evaluate the magnetostuctural phase transition, magnetic/catalytic activity, and thermal hysteresis in nanoparticles, as a function of size and dopant concentration.

Temporal Shape Evolution of MnP$_{As_x}$ Nanoparticles

- The size of the nanoparticles increases with increasing temperature.
- The size distribution of the nanoparticles increases with increasing temperature.
- The size distribution of the nanoparticles decreases with increasing temperature.

Covalent assembly of QDs by cross-linking with metal cations

- Surface ligands – control nucleation, growth and chemical and cristallinity of QDs but impede electrical transport.
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Figure 1.

- The resulting MnSb nanoparticles are ca 14 nm in diameter and exhibit low polydispersity.