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Synthesis of Novel Precursors to Complex Nanoparticles

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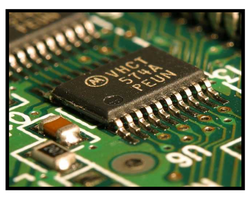
Introduction

In extreme environments, materials need to be able to adapt to changes in a moments notice. Responsive nanocomposites offer a unique solution to this problem by providing materials that will react to variables in an environment. The nanocomposites for this program will focus on the use of reactive polymers imbedded with complex nanoparticles.

Fillers have been widely used to control the properties of the polymer – generating a composite material. Typically these require high load levels (40 -50 %) to achieve the desired change. However, since the property changes are due to the interface, nanomaterials which are surface dominated species, can be added at levels as low as 1 - 5 % and still achieve the necessary changes.

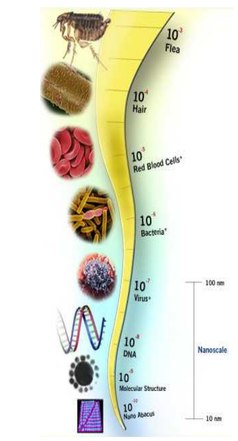
Industry is interested in these Responsive Nanocomposites for a variety of possible programs.





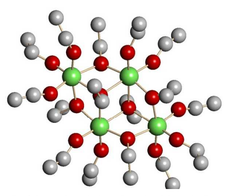
The need for high quality nanomaterials is necessary to synthesize these Responsive Nanocomposite materials. My goal is to investigate novel precursors for the production of complex nanoparticles.

Complex Ceramic Nanoparticles (CCNP)



- CCNPs are multi-cation metal oxide materials that are 100 nm in size or smaller
  - simple nanoparticles have only one cation

- In addition to the above uses, these CCNP particles can serve multiple uses such as:
  - Photovoltaic Components
  - Semi Conductors
  - Electronic Device Components
  - Scintillators
  - Detectors



$[Ti(\mu_3\text{-}OEt)(\mu\text{-}OEt)_2(OEt)_5]_2$

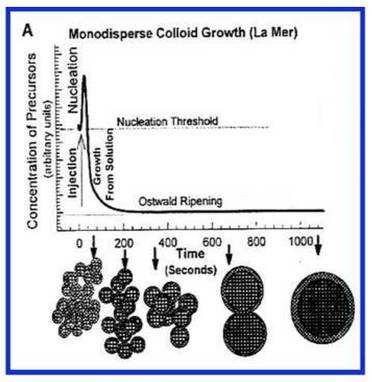
Metal Alkoxides Precursors to Nanomaterials

Metal alkoxides are excellent precursors to nanoparticles due to their low decomposition temperatures, high solubility, high volatility, and commercial availability. Metal alkoxides are alcohols that have had the H atom replaced by a metal ($Ti(OEt)_4$ shown to left). However, these compounds are air-sensitive and require inert atmosphere handling (i.e., gloveboxes: left).


Synthesis of nanomaterials using solution routes

Following La Mer growth principles, a superstaturated solution must be genreated and then overcome. This will initiate a nucleation shower and following Ostwald ripening particles will grow larger. Supersaturation is the state of a solution being more concentrated than normally possible.

−Time, temperature, and the use of surfactants can all help to control the growth of nanoparticles.



Solvothermal and Solution Precipitation routes

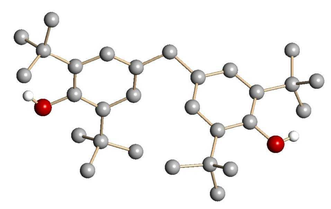
Solvothermal

In solvothermal synthesis the precursor materials are placed in solution inside a Parr bomb, then sealed and placed in a furnace for a period of time (usually 12-24 hrs). From the pressure and heat build up, nanoparticles form.

Solution Precipitation

For solution precipitation routes, a cold solution of the precursor is injected into a hot solution to initiate the formation of nanoparticles through the process described above.

Novel Precursors to CCNPs will be attempted using the 4DBP ligand

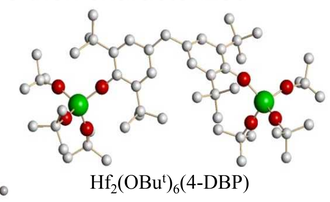


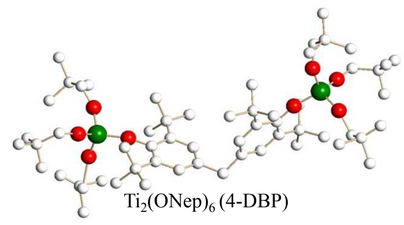
4,4′-Methylenebis(2, 6-di-*tert*-butylphenol)
($H_2$4-DBP)

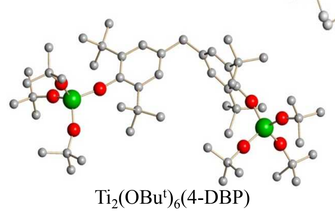
H_2-4DBP:
- The 4DBP ligand shown at the left has several unique properties that make it ideal for the synthesis of novel precursors to CCNPs. Having two bonding sites at opposite sides of the ligand allows for the attachment of multiple cations. Additionally the ligand retains enough steric bulk to keep from chelation upon a single metal center.

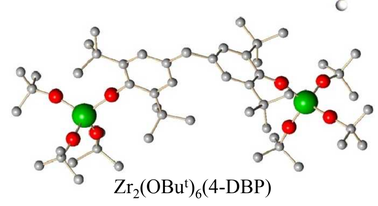
$$2M(OR)_x + H_2\text{4DBP} \xrightarrow{Solv} M_2(OR)_y(\text{4DBP})$$

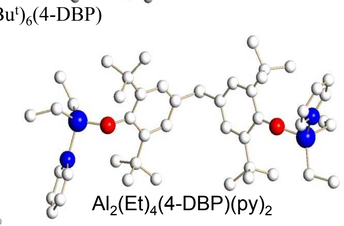
- The various metal alkoxides were reacted on a 2:1 molar ratio in an argon filled glovebox
- Once the metal alkoxides and ligand were combined the reaction was stirred for 12 hours
- The reactions were then characterized

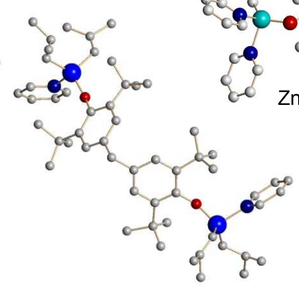

$Hf_2(OBu^t)_6$(4-DBP)

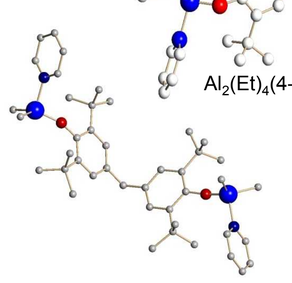

$Ti_2(ONep)_6$(4-DBP)


$Ti_2(OBu^t)_6$(4-DBP)

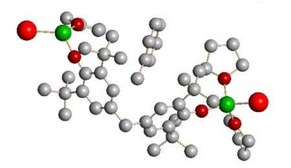

$Zr_2(OBu^t)_6$(4-DBP)


$Al_2(Et)_4$(4-DBP)$(py)_2$

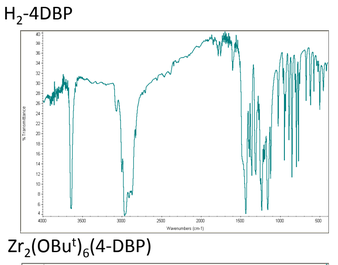

$Zn_2(Et)_2$(4-DBP)$(py)_4$


$Al_2(Me)_4$(4-DBP)$(py)_2$

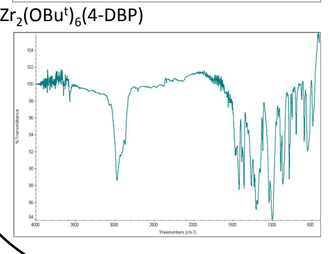
$Al_4OBu^i{}_4py_2$4-DBP


$Mg_2Br_2$4-DBP$(THF)_3$•tol THF

H_2-4DBP

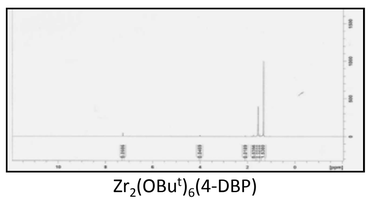


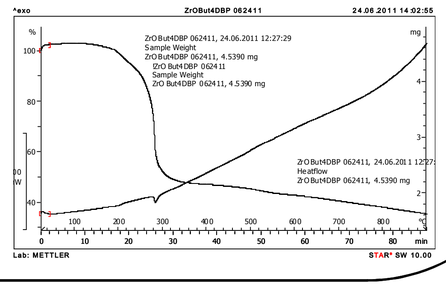
$Zr_2(OBu^t)_6$(4-DBP)



Compound	Melting Point in Degrees Celsius
1. $H_2$4DBP	155
2. TiOBu^{t}4DBP	185-210
3. TiONep4DBP	185-190
4. ZrOBu^{t}4DBP	110-115
5. HfOBu^{t}4DBP	120-185
6. AlMe4DBP	220-240
7. AlEt4DBP	220-?
8. AlOBu^{i}4DBP	120-140
9. ZnEt4DBP	Did not melt
10. MgBr4DBP	Did not melt

Elemental Analysis (EA) of the 4DBP compounds did not agree with our experimental data


$Zr_2(OBu^t)_6$(4-DBP)



Summary and Conclusion

- Numerous 4DBP compounds have been synthesized outlining the potential for a single source precursor.
- Low decomposition temperatures observed with the 4DBP compounds are excellent indicators that the 4DBP ligand will act as a good precursor to our complex nanoparticles.
- Dinuclear species have been found not to react with the 4DBP ligand due to steric hindrance.

Future

- Nanoparticle synthesis of the homo-ionic compounds will occur to compare to current nanoparticle synthesis routes.
- Mixed metal precursors will be synthesized, characterized and used for nanocomposite synthesis as well.

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