Synthesis of Plain and Labeled TiO_2 Nanoparticles for Study of Fate and Transport in the Environment

Chad Thomsen, Dr. Jeffrey Nason – OSU Chemical, Biological, and Environmental Engineering

Importance of Nanoparticle Research

One of the fastest growing and most exciting new technologies of today is nanotechnology. Business in the nanotechnology field is booming and it has been predicted to break $1 trillion by 2015.[1] Nanoparticles can be used in drug delivery and diagnosis for the medical field, energy production, electronic devices, and environmental remediation. The dynamic properties of nanoparticles are due to the very small size, large surface area, and other physicochemical properties. Since the production of engineered nanoparticles is increasing, the potential for environmental release and the following ecological effects is growing into a real concern that needs to be reviewed and analyzed. Before this can be properly done it is necessary that the fate and transport behavior in the environment of said engineered nanoparticles is completely understood.[2]

Project Description

The fate and transport of nanoparticles is difficult to track in the environment due to the small size and concentrations. Detection of the nanoparticles is further complicated by the presence of bulk form compounds (chemically identical to the nanoparticles, only larger in size) already existing in the environment. This project proposes using a dopant material found less commonly in the environment to "label" the particles for tracking.

Objectives

- Synthesize discrete anatase titanium dioxide nanoparticles using a unique "low-temperature synthesis method"[3]
- Characterize with the following methods
  - Dynamic Light Scattering, X-Ray Diffraction, Scanning Electron Microscopy, and Energy Dispersive X-Ray Spectroscopy
- Adapt synthesis procedure to include dopant material
  - Chose dopant physicochemically similar to TiO_2 (Hafnium dioxide)
- Characterize doped nanoparticles with above methods
- Form conclusions about ability of labeled particles to simulate how the non-labeled (plain) particles would act in the environment

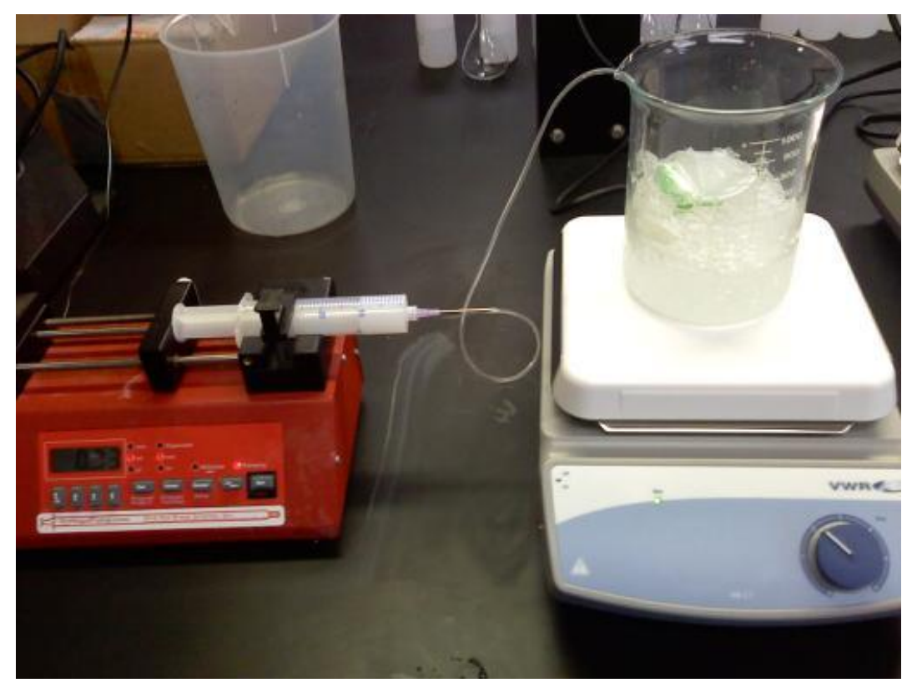
Choosing Titanium Dioxide

Metal oxide nanoparticles represent a significant percentage of the wide range of nanomaterials currently in use for environmental remediation and other commercial applications. Featured prominently for normal consumer use of the metal oxides is titanium dioxide. TiO_2 particles are valued most often for their photo-catalytic properties and dyeing potential and are commonly found in paint, cosmetics, sunscreen, toothpaste, food colorants among other various items.[4]

Titanium based nanoparticles were originally believed to be biologically harmless because the compound itself is chemically inert in the body. However, recent studies have shown that the high surface area ratios of the nanoparticles can cause oxidative stress which raises many potential health hazards, including cancer, with increased exposure.[4]

In the environment TiO_2 nanoparticles have been shown to compromise microbial membranes causing damage to various organisms.[5] Despite this negative effect, titanium dioxide nanoparticles are being widely studied because of the particles' ability to use UV light to degrade various environmental contaminants.

Materials and Methods



Chemicals Used (All from Sigma-Aldrich)

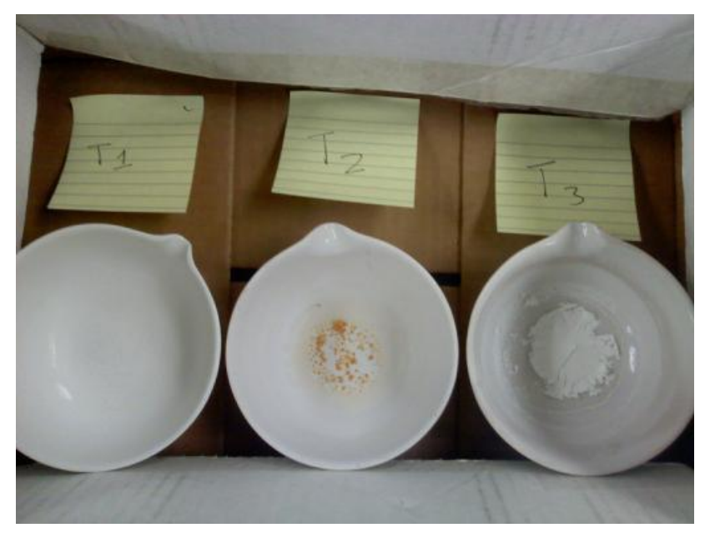
- Ethylene Glycol (EG)
- Titanium(IV) Butoxide (TnBt)
- Hafnium(IV) n-Butoxide (HfBt)

Prepared Solutions

- First Solution: 5mL TnBt in 35mL EG
- Second Solution: 3mL DDI in 27mL EG

Mixing Procedure

- First Solution added drop wise to second in Ice Bath via syringe pump at a rate of 0.45mL/min



Centrifugation/Washing Procedure

- 9000 rpm for 45 min
- Decanted, rinsed with DDI and repeated four times

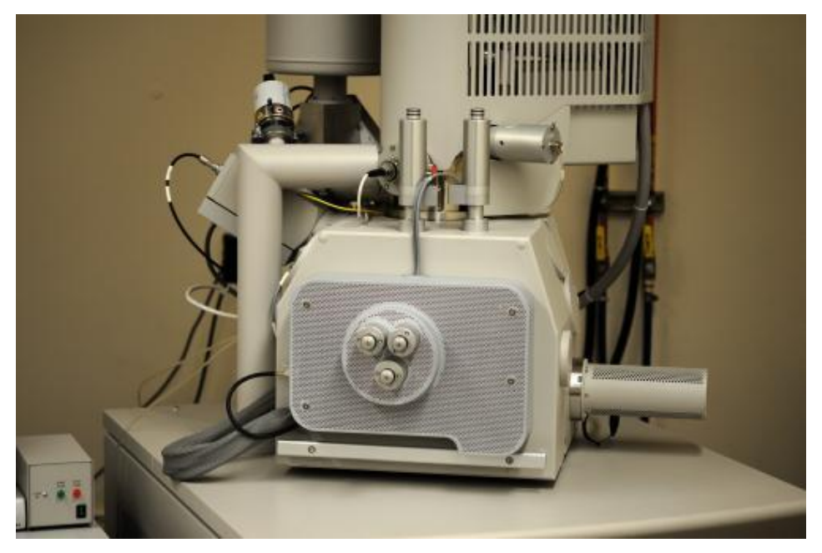
Drying/Calcining Procedure

- Dried particles in vented oven at 200°C for two hours
- Calcined in tube furnace at 550°C for six hours

Analytical Methods

- Dynamic Light Scattering
- X-Ray Diffraction
- Scanning Electron Microscopy
- Energy Dispersive X-Ray Spectroscopy

ZetaPALS

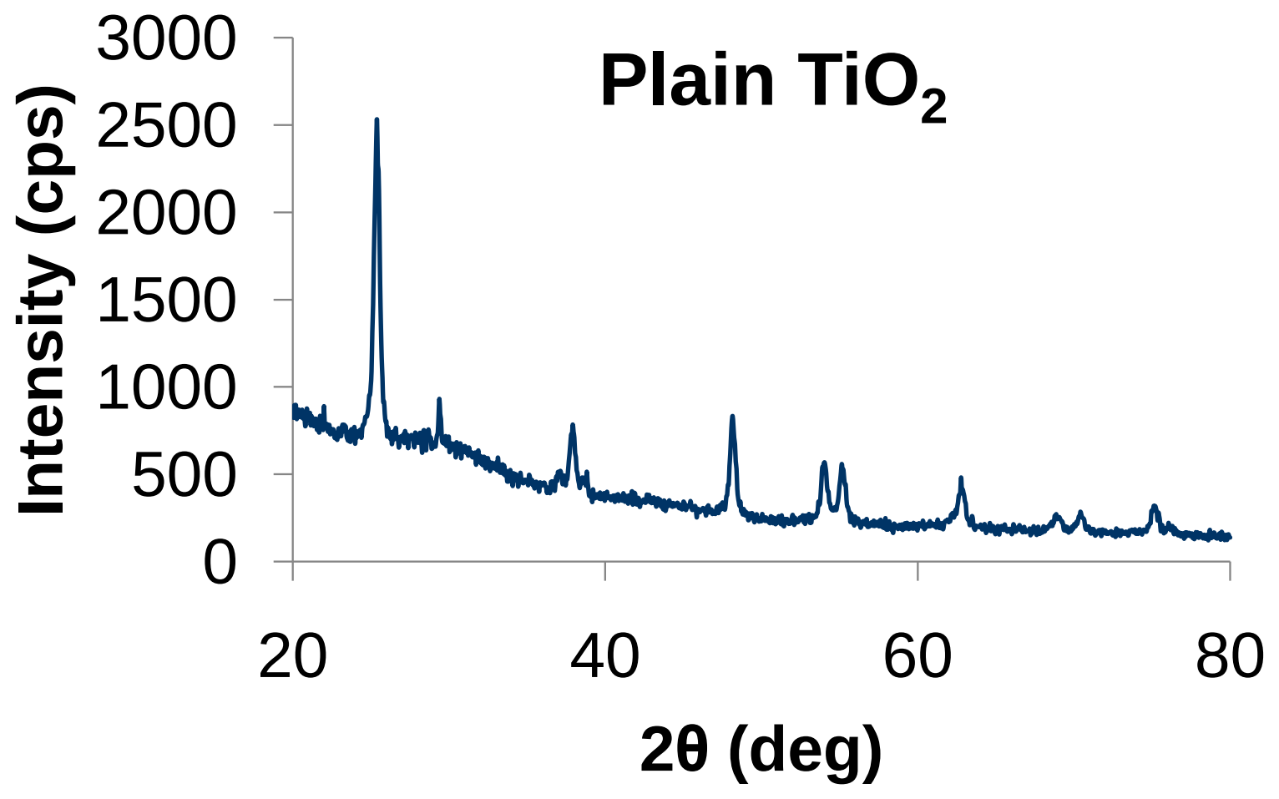


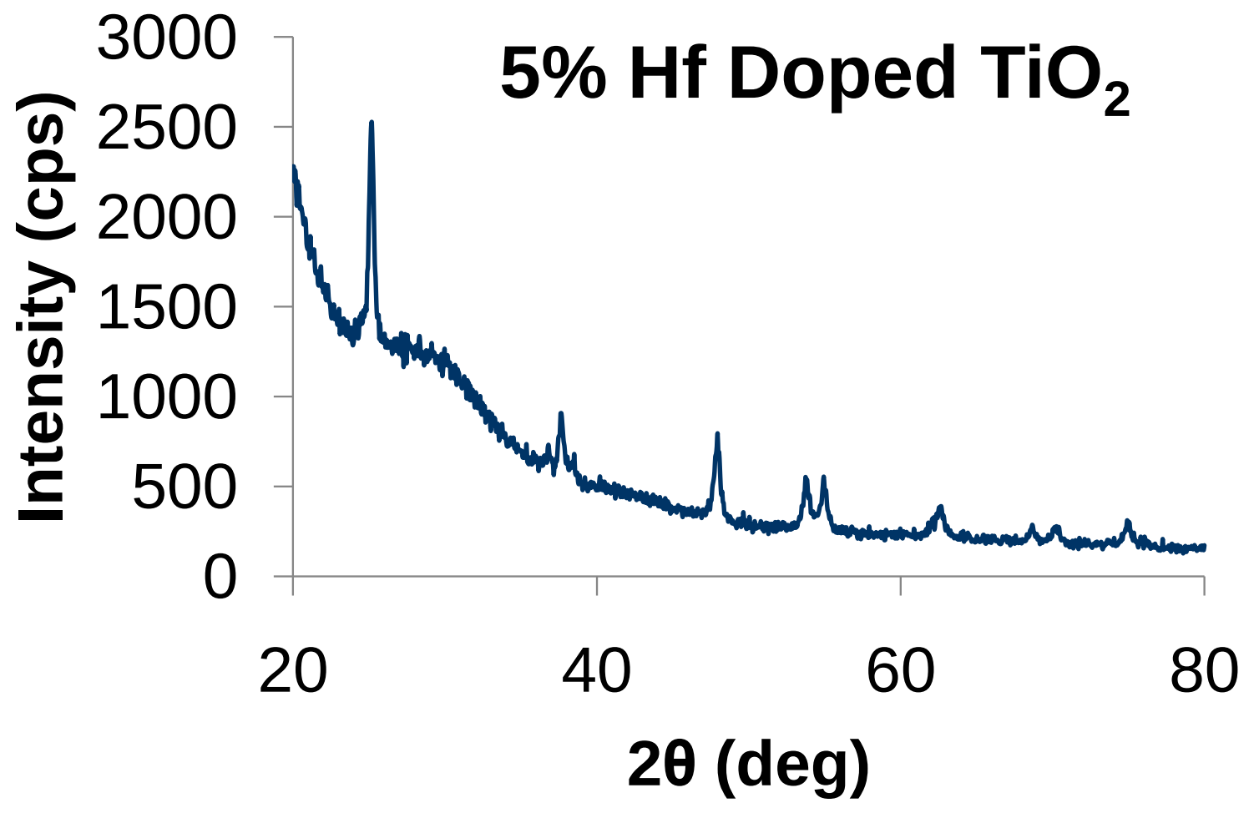
FEI Quanta 600 FEG SEM

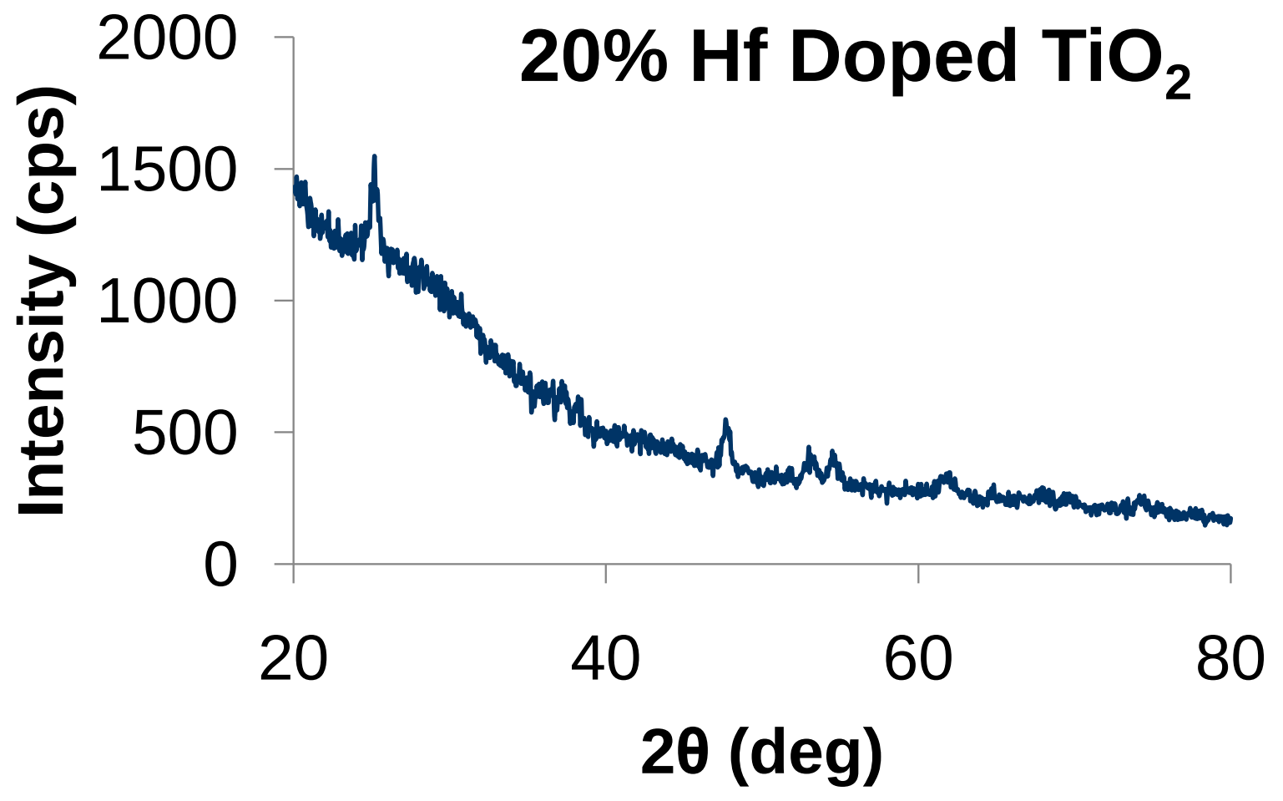
X-Ray Diffractometer

XRD Data

One method of characterizing is to analyze a sample in powder form using X-Ray Diffraction. TiO_2 is known for a distinctive peak at around 25°. Though no new peaks showed for the doped particles the primary TiO_2 peak shifted from 25.34° to 25.19° which could indicate the presence of a dopant. Doped particles also appeared to be more amorphous than the plain TiO_2.

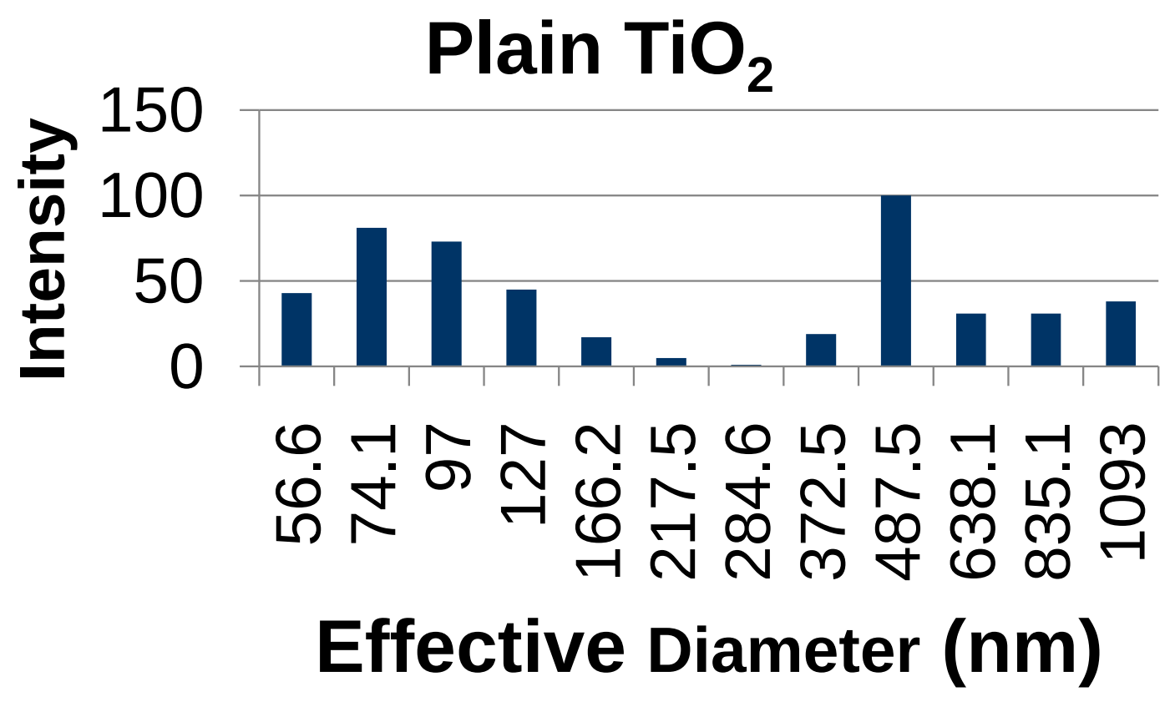


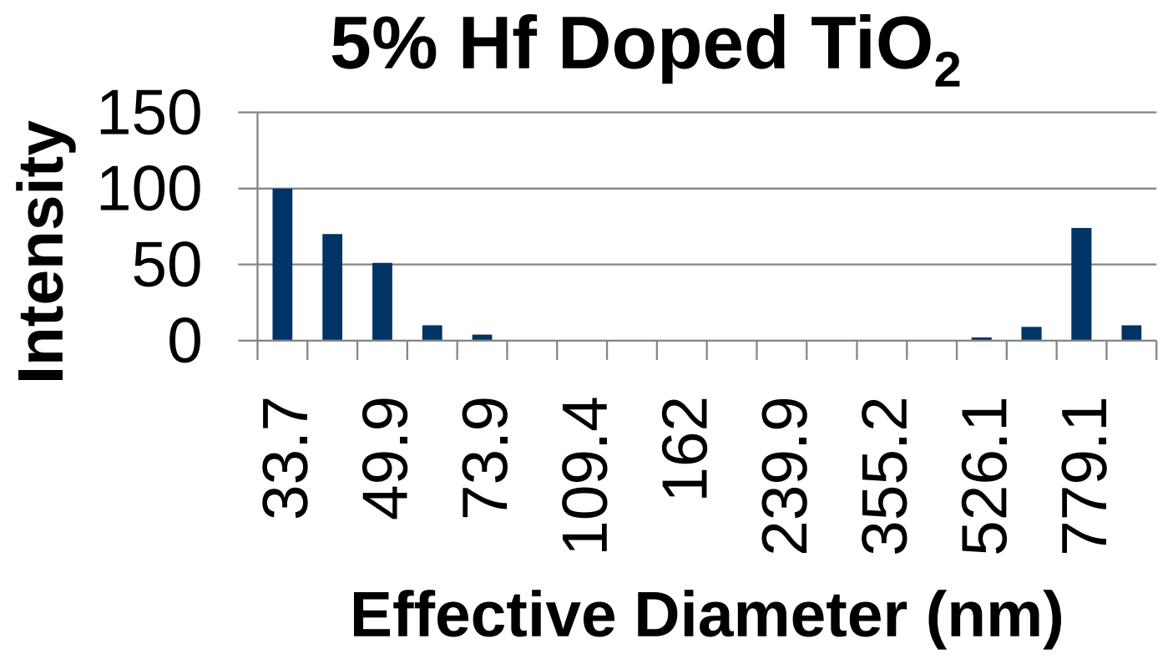


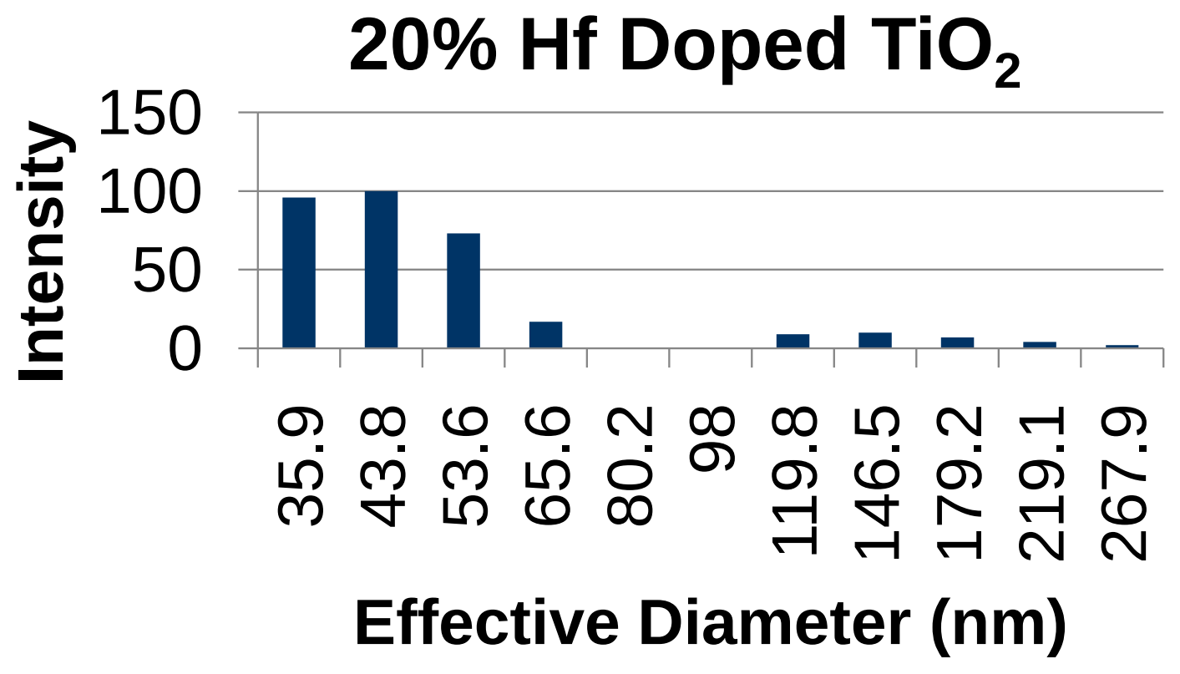


Particle Size and Distributions

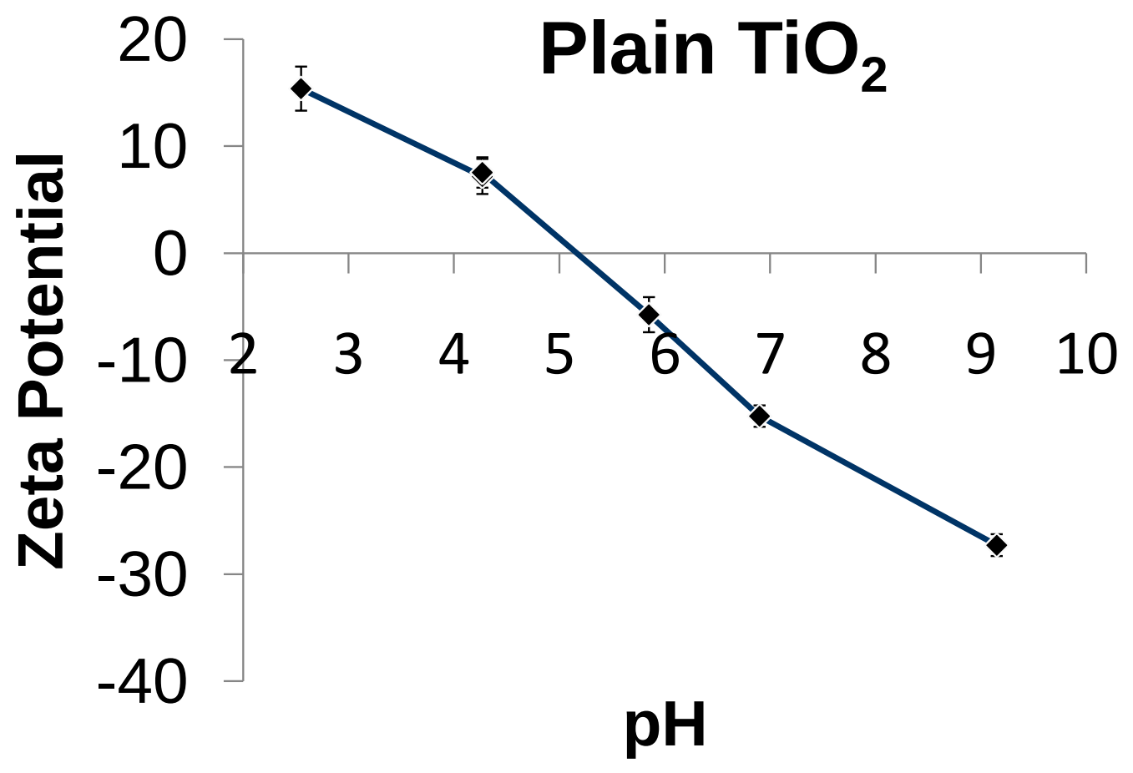
The synthesized nanoparticles were first characterized using DLS while still dispersed in EG. The results from the plain and 20% Hf samples were comparable in combined size and polydispersity but those from the 5% Hf sample were larger and more polydispersed. All samples showed possible particles in the <100nm range.







Conclusions and Continuing Work



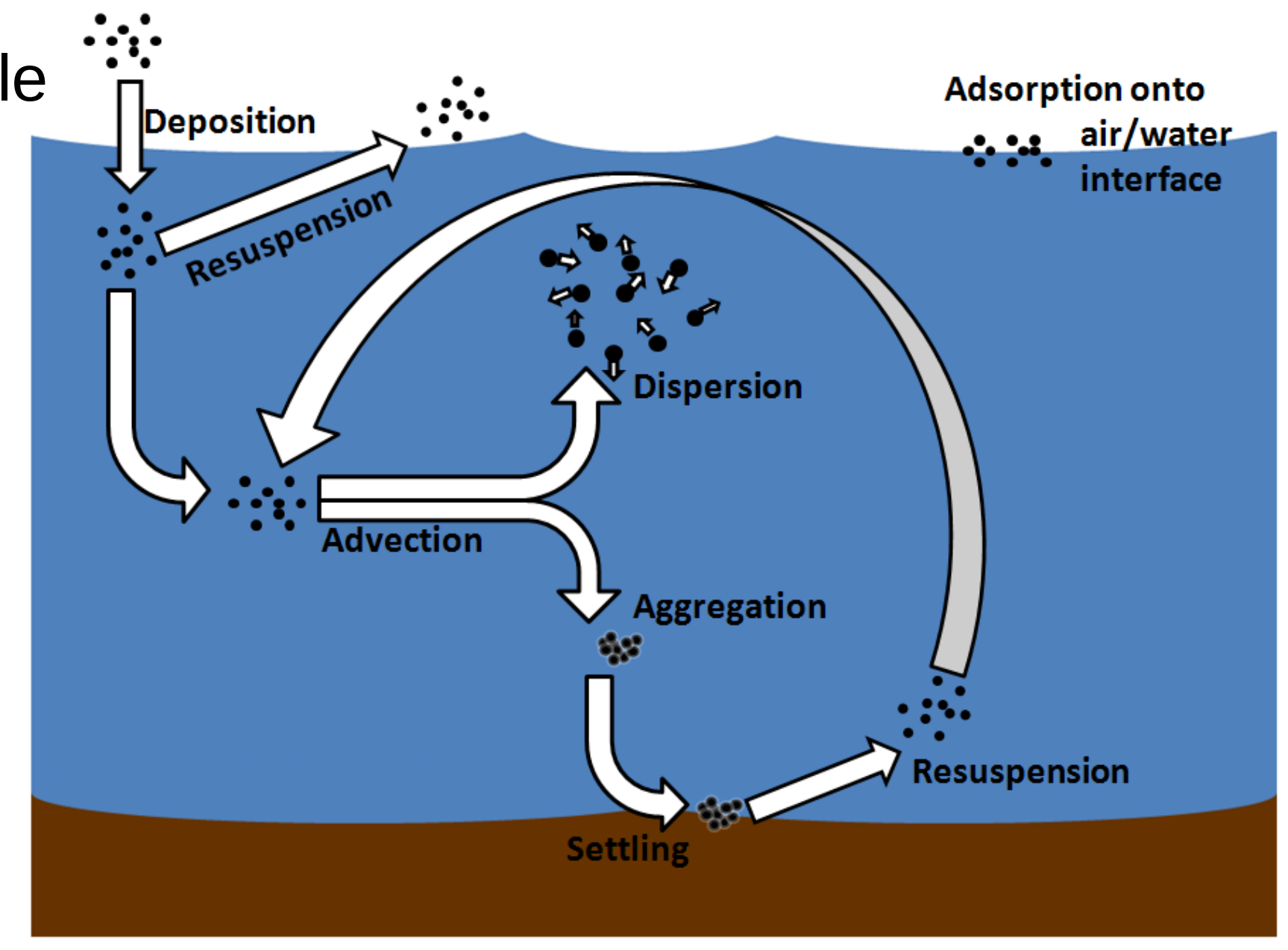
Preliminary tests have been run on the ZetaPALS using the Zeta Potential function in order to determine the isoelectric point (IEP) of the particles. Once this data has been collected the 5% and 25% Hf doped samples will also be tested to see if the IEP changes with the introduction of the hafnium dioxide to the titania particle structure. The IEP testing is very important because the suface charge of the particles strongly influences how the particles behave in different environments. If the labeled and plain particles are significantly different then a new dopant will need to be found.

Additional Characterization

- Finish sample composition analysis
  - EDS and INAA (instrumental neutron activation analysis)
- DLS aggregation studies over time
  - Shows how quickly particles settle out of solution

Future Experiments

- Examination of nanoparticle fate during drinking water and waste water treatment
  - Jar testing to simulate coagulation, flocculation and settling
  - Adsorption onto waste-water sludge
- Transport experiments in packed bed systems to simulate water filtration through porous media



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Acknowledgements

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