Synthesis and Characterization of Titania-Graphene Nanocomposites

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Abstract

Titania-graphene-oxide composites have been prepared utilizing the hydrolysis of titanium tetrafluoride to form the ceramic at low temperature in the presence of aqueous suspensions of graphene oxide (GO). In most cases, the resulting composite is isolated by a simple filtration and washing protocol.

Titania-reduced-graphene-oxide composites were prepared by reducing a suspension of a pre-made ceramic-GO composite chemically with hydrazine hydrate, or by thermal treatment of TiO_2-GO composites at 800 °C.

These composites have been characterized by SEM, TEM, XRD, BET, Raman, SAED and EDS. The synthesis and materials characterization efforts to date are presented.

Goals

- **Synthesize TiO_2-Graphene composites**
- **Fully characterize these composite materials**
- **Examine possible applications of these composites**

Introduction

Graphene nanosheets are of considerable scientific and technological interest due their potential applications in structural, thermal, electronic and various other nanotechnologies.[1-4] Graphene, is a two dimensional macromolecule comprised of a carbon layers with one atomic thickness. Theoretically it has a surface area of ~ 2630 m^2/g.[5] Chemical exfoliation of graphite, to form graphene oxide, followed by chemical reduction (i.e. hydrazine) is the dominant route to graphene like materials in the literature.[6] The marriage of inorganic ceramic materials with graphene could allow for the preparation of a new class of nano-hybrid materials with interesting properties. We have recently gained interest in preparing ceramic-graphene nanocomposites for a number of applications, including the mechanical reinforcement of elastomers, electrical energy storage materials, and as catalysts in UV wastewater treatment.

Here we present our synthesis of TiO_2-GO from the hydrolysis of TiF_4 and its subsequent chemical and thermal reduction to give TiO_2-RGO. We also investigate the physiochemical properties of our ceramic-graphene composites.

References

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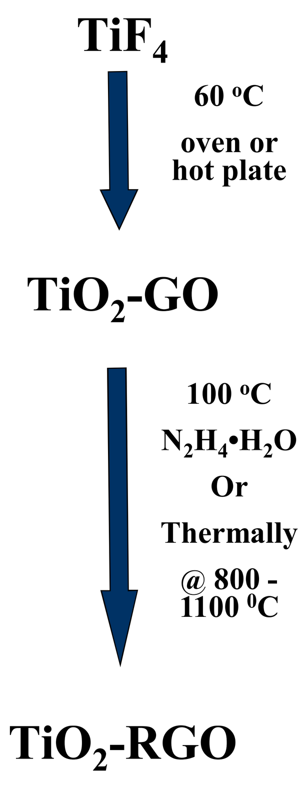
Titania-Graphene Hybrid Composites

Our Approach

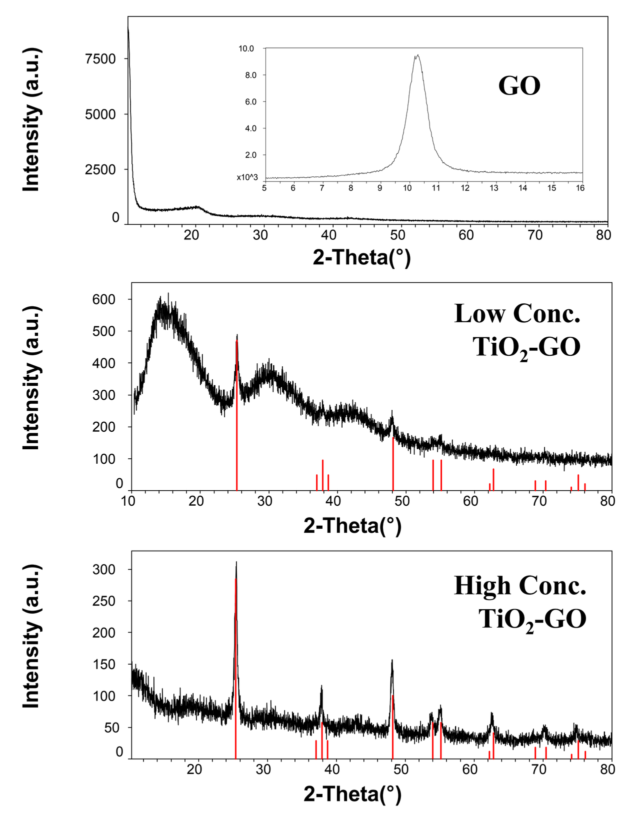
Synthesis Plan

Our approach utilizes the hydrolysis of titanium(IV) fluoride[7] in the presence of aqueous graphene oxide (GO) dispersions to form TiO_2-GO composites.[8,9,10]

TiO_2-GO composites were then chemically reduced with hydrazine hydrate[11] (N_2H_4• H_2O) or thermally to form the reduced graphene oxide composites, termed TiO_2-CRGO or TiO_2-TRGO

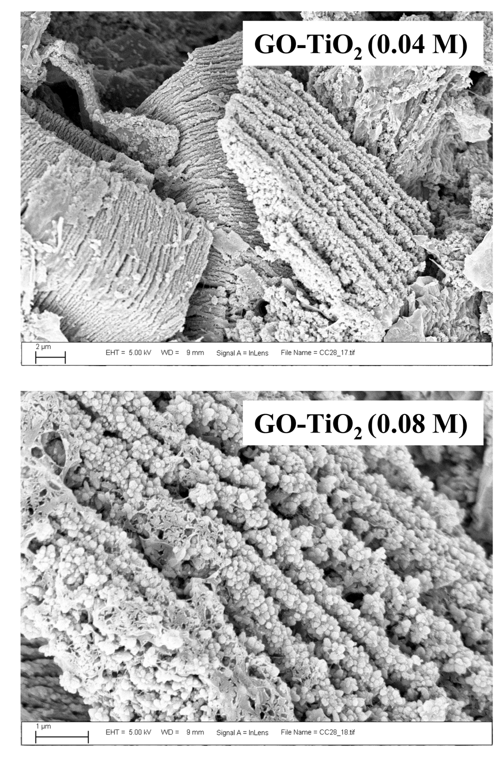


Powder X-ray Diffraction (PXRD)



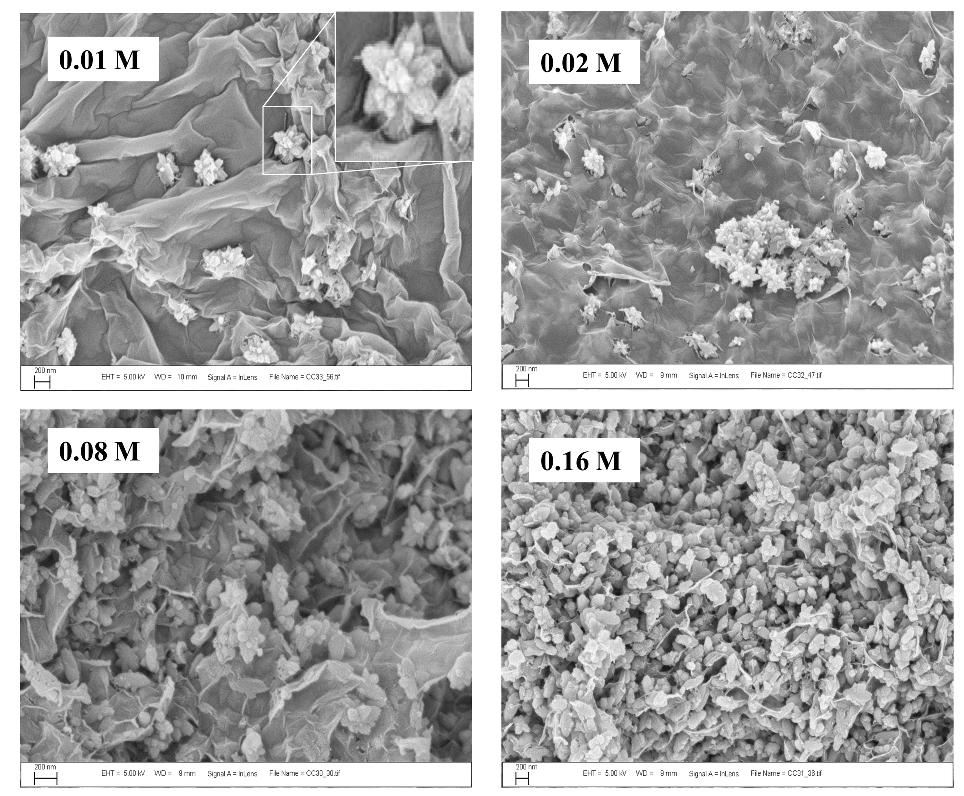
TiO_2 Anatase (JCPDS file no. 21-1272)

Scanning Electron Microscopy (SEM)



Non-stirred reactions result in self-assembly of TiO_2-GO sheets

Stirred reactions results in the intercalation of TiO_2 between GO sheets

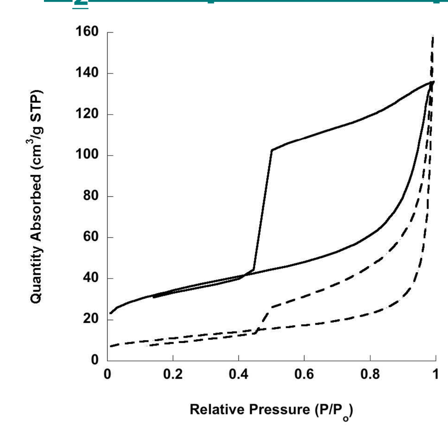


TiO_2 particle morphology is concentration dependant

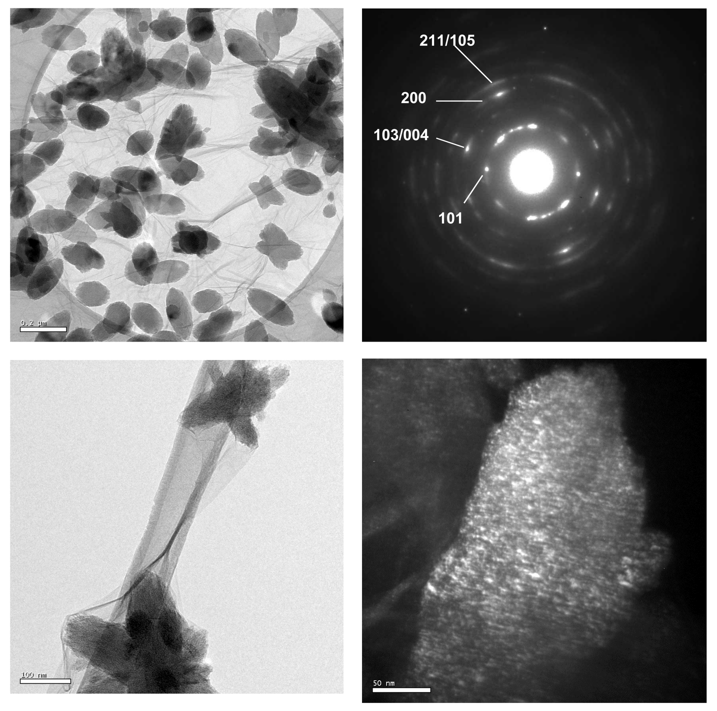
BET Surface Area

GO: 39 m^2/g
GO-TiO_2 (0.04 M): 71 m^2/g
GO-TiO_2 (0.08 M): 121 m^2/g
GO-TiO_2 (0.08 M): 81 m^2/g
RGO: 459 m^2/g

N_2 Adsorption/Desorption

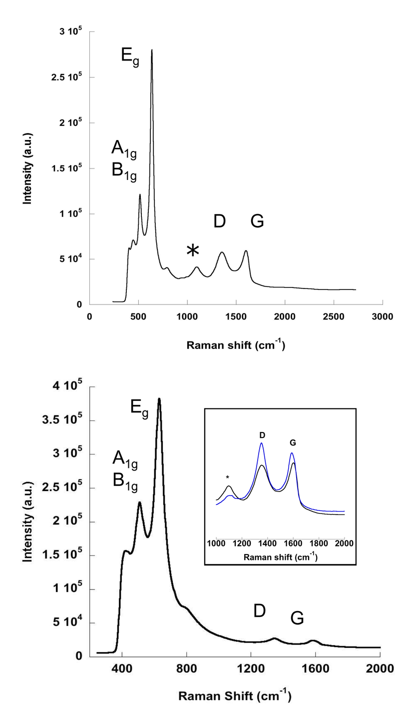


Transmission Electron Microscopy (TEM)



The particles are crystalline in nature. Bright-field TEM: Seed-like shapes and faceted structures are observed. Dark-field TEM: the composites are composed of smaller nanoparticles that are crystallographically aligned. Selected Area Electron Diffraction (SAED): is consistent with Anatase phase as determined by XRD

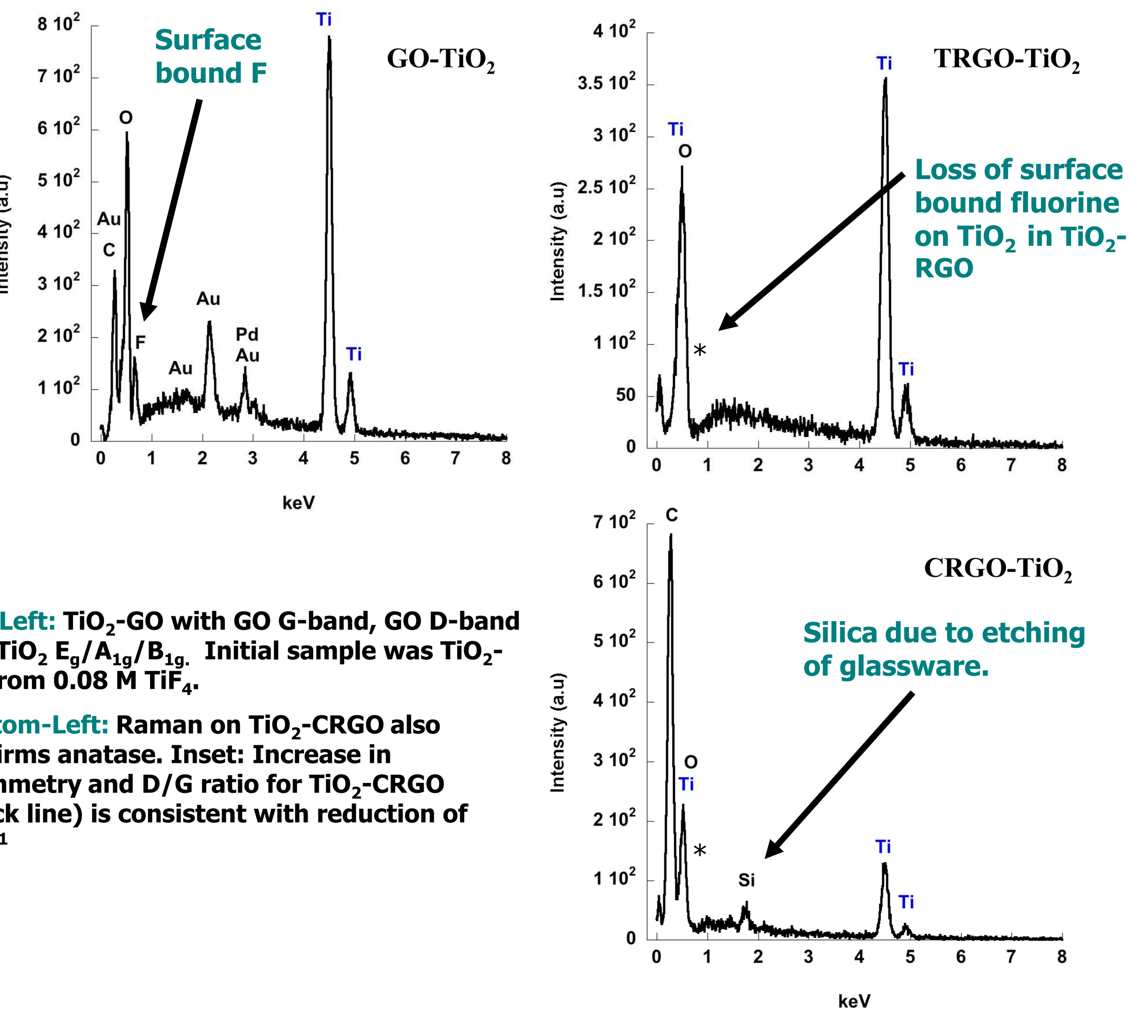
Raman Spectroscopy



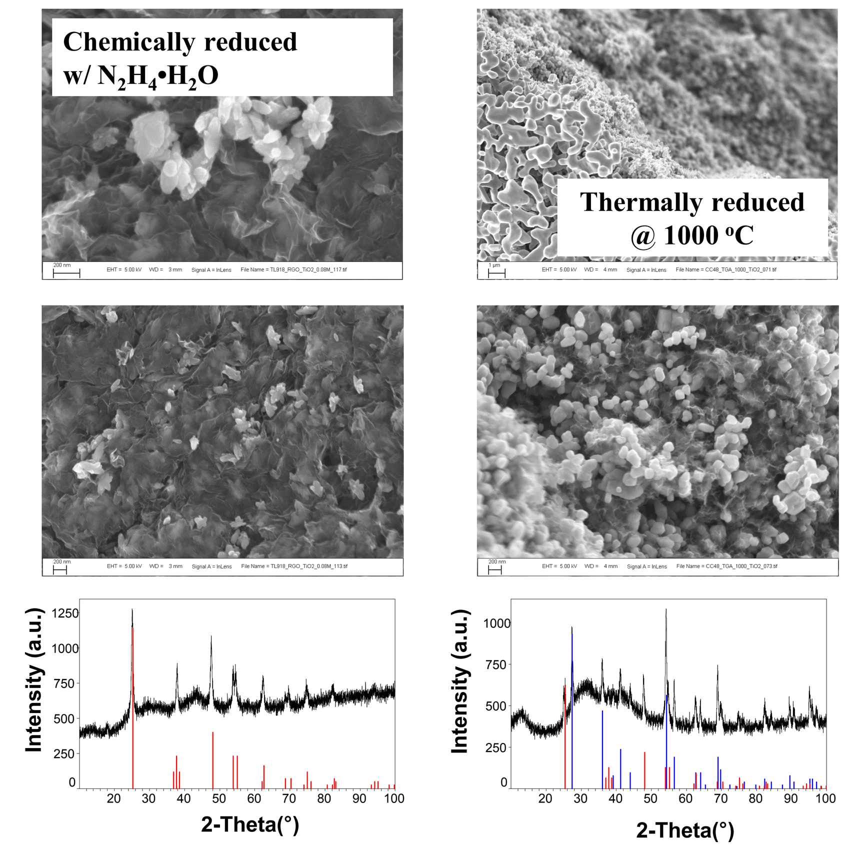
Top-Left: TiO_2-GO with GO G-band, GO D-band and TiO_2 $E_g/A_{1g}/B_{1g}$. Initial sample was TiO_2-GO from 0.08 M TiF_4.

Bottom-Left: Raman on TiO_2-CRGO also confirms anatase. Inset: Increase in asymmetry and D/G ratio for TiO_2-CRGO (black line) is consistent with reduction of GO.[11]

Energy Dispersive X-Ray Spectroscopy (EDS)



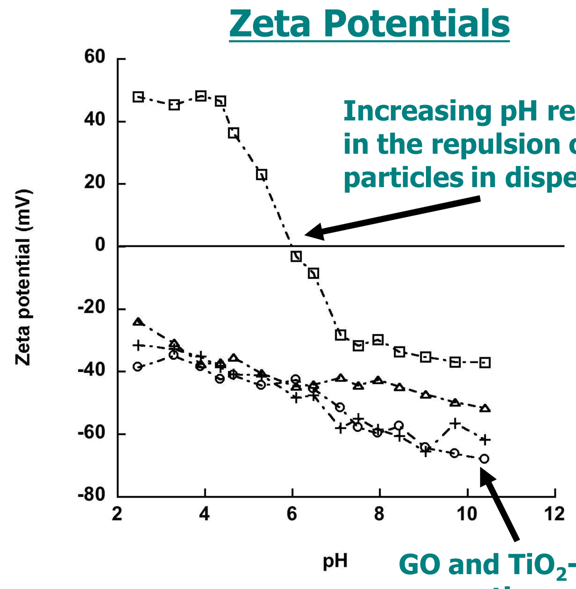
TiO_2-RGO



Left: Chemically reduced composites (TiO_2-CRGO) retain anatase phase. Right: Thermally reduced (TiO_2-TRGO) partially transforms into rutile phase.

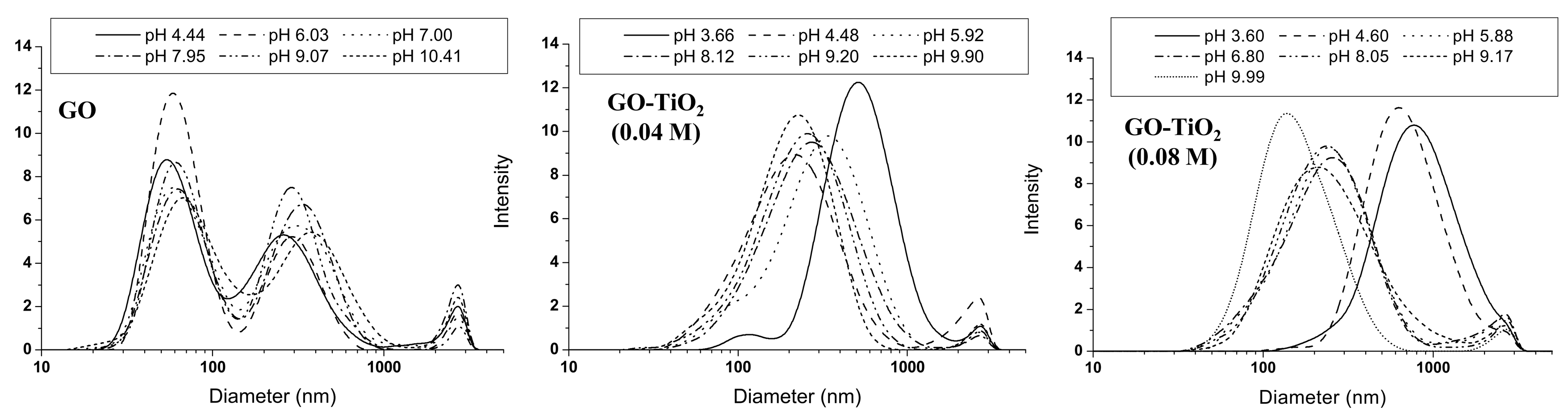
Colloidal Properties

Zeta Potentials



Zeta potentials of (○) GO, (+) TiO_2-GO from 0.04 M TiF_4, (△) TiO_2-GO from 0.08 M TiF_4, (□) commercial anatase TiO_2 nanopowder.

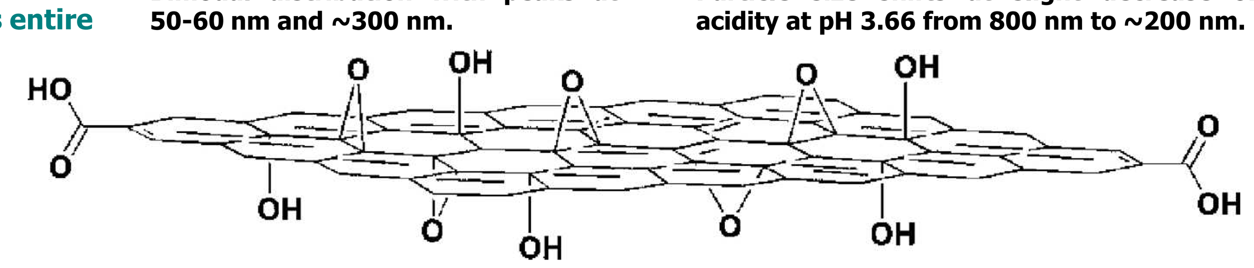
Dynamic Light Scattering



Graphene-oxide shows similar particle size across entire pH range. Bimodal distribution with peaks at 50-60 nm and ~300 nm.

GO-TiO_2 exhibits a pH dependence due to aggregation of titania and graphene sheets. Particle size shifts at slight decrease of acidity at pH 3.66 from 800 nm to ~200 nm.

Higher loaded sample of GO-TiO_2 shows even more drastic dependence of pH. At lower pH values there is a broad peak at 900 nm, which begins to shift to a lower value as the pH is raised. This shift is complete even as low as pH 5.9.



*Zeta potentials and Dynamic Light Scattering measurements by Nelson Bell (SNL)

Conclusions

We have demonstrated the ability to prepare TiO_2-GO composites via the hydrolysis of TiF_4 at 60 °C in the presence of an aqueous dispersion (~ 0.75 mg/mL) of GO. This approach yielded highly faceted anatase nanocrystals, with petal-like morphologies on and embedded between the graphene sheets. At higher GO concentrations (ex. 1.5 mg/mL) with no stirring of the reaction media, long-range ordered assembly for TiO_2-GO sheets was observed due to self-assembly. GO-TiO_2 composites formed colloidal dispersions (~ 0.75 mg/mL) at low concentrations in water with zeta potentials and dynamic light scattering data explaining these results.

Future Work

- Adsorption studies with methyl orange dye and UV photocatalysis of RGO-TiO_2 is planned.
- Mechanical testing will examine physical strength of TiO_2-GO nanocomposites.