

Crumpled Graphene Oxide Nanostructures for Advanced Water Treatment Technologies

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Abstract:

The global water crisis calls for water treatment technological advancements, which, based on the state of the art, will be increasingly underpinned by engineering/application of nanoscale materials. Our project aimed to develop an efficient aerosol-based technique to synthesize crumpled graphene oxide (CGO) nanocomposites for enhanced water purification applications. Specifically, we aimed to synthesize and characterize two types of CGO nanocomposites: CGO-TiO₂ (as a high-performance photocatalyst for pollutant degradation) and CGO-magnetite (as a monomeric self-assembling component of a robust and magnetically manipulatable thin-film membrane). We also intended to examine CGO nanocomposites' water-stability under different water chemistries (such as pH). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were utilized for size and morphology measurement while electrophoretic light scattering (ELS) and dynamic light scattering (DLS) were used to test zeta potential and nanoparticle size, respectively. Our results indicate an inverse relationship between pH and mean nanoparticle size, and solutions with pH > 3.0 enable CGO stability (zeta potential < -30 mV).

Introduction:

Currently, there are over three million deaths annually, resulting from water-, sanitation-, and hygiene-related diseases [1]. According to the World Water Council, 3.9 billion people are predicted to live with deficient and unsanitary water supply by 2030 [2].

Thus, our project aimed to construct a water treatment membrane using a thin film of CGO-based nanocomposites consisting of both encapsulated photocatalytic materials like TiO₂, which enables enhanced photo-reactive (UVA irradiation) activity for organic pollutant degradation, and adequate amounts of monomeric, nanoscale magnetite components, allowing for magnetic manipulation of nanocomposites in water. CGO provides the membrane with sufficient accessible surface area for water permeability and increased pollutant adsorption.

Two-dimensional graphene oxide has been extensively researched previously because of its unique nanosheet morph-

ology, extreme specific surface area (~ 2650 m²/g) and broad chemical functionalization possibilities. However, restacking issues caused by van der Waals attraction between the sheets significantly reduces its surface area, thereby limiting its applications. Fortunately, a new field has opened up with the discovery of three-dimensional CGO [3]. Its properties, which include a crumpled ball-like morphology, high free volume, and aqueous stability, make it an ideal candidate for various applications, including water treatment.

Experimental Procedure:

Graphene oxide was synthesized using a modified Hummers method [4]; TiO₂ (Degussa Aerodisp 740X) and magnetite (Fe₃O₄, Sigma Aldrich) were used. A furnace aerosol reactor was used to synthesize CGO through an aerosolization process. First, a Collision nebulizer atomized a GO-TiO₂ precursor into fine droplets; and the droplets were delivered by N₂ into the furnace. Crumpling of GO and encapsulation of TiO₂ was induced by capillary compression caused by rapid evaporation of the aerosol droplets in the furnace (400°C). Finally, CGO nanocomposites were collected at the downstream of the reactor. SEM (NOVA NanoSEM 230) and TEM (Tecnai TM Spirit) were used to determine the size and morphology of the CGO. Zeta potential and aqueous nanoparticle size distribution were measured by ELS and DLS, respectively (Malvern Zetasizer Nano ZS).

Results and Discussion:

GO crumpled and TiO₂ successfully became encapsulated, as evidenced from the SEM (Figure 1) and TEM (Figure 2) images. The SEM images illustrated the nanocomposites' crumpled ball-like morphology, while the TEM images confirm TiO₂ encapsulation and nanoparticles with a size range of 250-350 nm. The CGO nanocomposites had a quasi-spherical morphology resembling a crumpled piece of notebook paper, considerably smooth surfaces, and black color. The color results from GO reduction.

Figure 3 displays ELS results showing the relationship between pH and zeta potential of the aqueous GO-TiO₂ solution. Zeta

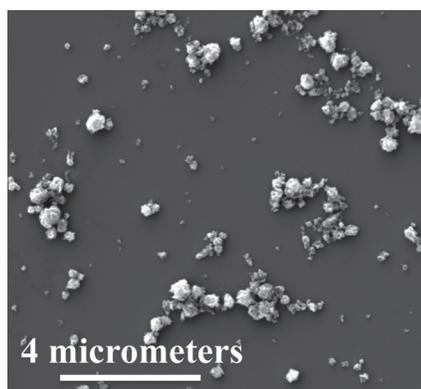


Figure 1: The SEM image demonstrates CGO's crumpled ball morphology.

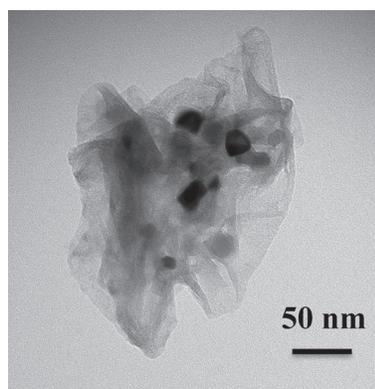


Figure 2: The TEM image denotes TiO_2 encapsulation.

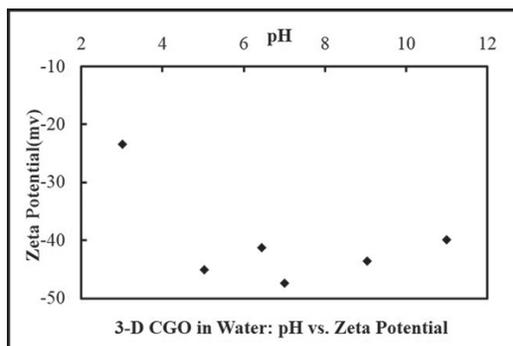


Figure 3: The relationship between pH and zeta-potential of GO- TiO_2 solution.

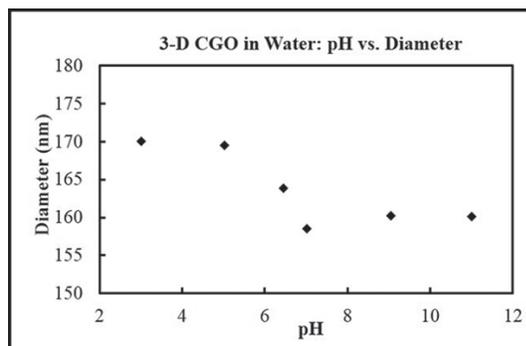


Figure 4: The relationship between pH and nanoparticle size of GO- TiO_2 solution. As pH increases, NP size decreases.

potential, reflecting a nanoparticle's surface charge, indicates the degree of its tendency to resist aggregation and therefore its stability in solution. The data suggested that solutions with $\text{pH} > 3$ yield stable CGO (< -30 mV).

A general inverse relationship was also observed between pH and nanoparticle size (Figure 4). Higher pH values (more basic) imply large OH⁻ concentrations, which enable more negative CGO surface charges. The repulsive electrostatic forces increased between nanoparticles, leading to less aggregation and smaller nanoparticles.

Understanding the interrelationship between pH, nanoparticle size, and zeta potential will facilitate tailoring of CGO behavior according to the acidic conditions of aqueous suspensions for optimized water purification.

Future Work:

Doping TiO_2 has attracted research interest because it narrows TiO_2 's band gap, allowing it to activate under sunlight exposure, hence minimizing energy costs. Doping is when impurities are added to semiconductor crystals to tune their conductivity and other characteristics. We will experiment with various dopants/dopant combinations to measure their efficacy in further enhancing TiO_2 's photocatalytic properties. A porous, reactive,

thin-film membrane will be assembled using the fabricated CGO and a polyvinylidene difluoride support membrane.

Membrane performance will be tested using ultraviolet-visible light spectroscopy and methyl orange will be employed as a model pollutant.

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