

SPECTROSCOPIC TECHNIQUES TO CHARACTERIZE AND DEVELOP
SENSING METHODS FOR TITANIUM DIOXIDE
NANOPARTICLES IN WATER

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Dedication

To my parents, my son, my wife and our future children. You make it all worthwhile.

PREVIEW

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SPECTROSCOPIC TECHNIQUES TO CHARACTERIZE AND DEVELOP
SENSING METHODS FOR TITANIUM DIOXIDE
NANOPARTICLES IN WATER

by

REAGAN SCOTT TURLEY

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Abstract

Titanium dioxide nanoparticles are being used in ever increasing amounts and applications in many consumer products and industrial processes including water treatment. These nanoparticles have not been shown to be toxic to humans via ingestion, but it is worthwhile to develop a portable and rapid detection method to quantify the concentration of nanoparticles in treated drinking water. A preliminary study on how chelating ligands influence the dispersion and ζ -potential of TiO_2 nanoparticles was performed. An additional study was designed to find ligands that would fluoresce when bound to TiO_2 by measuring the level of adsorption but was ultimately unsuccessful. These two studies did, however, show which ligands best improve the suspension of TiO_2 in water.

Photocatalytic nanomaterials are widely utilized in a variety of products including self-cleaning coatings and some water treatment technologies. To support the safe use of photocatalytic nanomaterials, it is essential to have low cost methods to rapidly, preferably in the field, detect residual photocatalysts in water. Current technologies with low detection limits are largely based upon mass quantification rather than functional behavior that is intrinsic to the nanomaterial (e.g., photocatalysis). Current mass-based detection techniques require expensive analytical equipment (e.g., inductively coupled plasma mass spectroscopy, ICP-MS) and often complex sample preparation (e.g., filtration, acidification, microwave digestion). Therefore, we developed a simple and portable method that exploits the photocatalytic reactivity of titanium dioxide (TiO_2) nanoparticles to detect and quantify these materials in various aqueous matrices including synthetic soft and hard waters. Three TiO_2 nanomaterials are used in this study

with various crystalline structure and sizes from 18 nm up to 30 nm. The method quantifies TiO_2 nanomaterials in water at levels comparable to background titanium concentrations in surface waters. Within a 15-minute run time, the detection limit for a NIST reference TiO_2 in distilled water is 0.6 ppb with a quantitation limit of 1.9 ppb. However, these limits increased for soft and hard water due to artifacts associated with dissolved inorganic solids. Detection and quantitation limits were also higher for less photocatalytic materials such as pure anatase and rutile nanoparticles.

Lastly, TiO_2 nanoparticles were studied using single particle ICP-MS in a two-week aging study in synthetic water matrices including distilled, soft, and hard drinking water. This study was designed to quantify the effect of how increasing concentrations of dissolved inorganic solids affect the size distribution and particle number of nanoparticles over an extended period. However, the nanoparticles used in the study were slowly removed from suspension by adhering to the inner walls of the test tubes used to contain each sample solution. Some insights are made on the changes over time in nanoparticle sizes, the influence of dissolved inorganics on these particles, and the influence of particle size and type.

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Chapter 1 : Introduction

Nanoparticles are a current hot and attractive topic in science and research, and have led to myriads of applications and inventions in many fields.¹ Nanoparticles, or nanomaterials, are defined as a structure or material, either naturally occurring, incidental, or engineered, typically with two lengths or dimensions between 1 and 100 nanometers but sometimes only one dimension as in the case of nanosheets.²⁻⁴ These nanoparticles may contain metals, metal oxides, or carbon compounds and can be functionalized or coated in many different ways including inorganic and organic coatings or functional groups.⁵ Furthermore, their activity and reactivity may be controlled via their crystalline structure, size, and shape, which includes spherical, cylindrical, cubic, octahedral, or planar nanoparticles.^{6,7}

One reason nanoparticles are of great scientific interest is their nano-scale size-dependent properties such as plasmon resonance and superparamagnetism.⁸⁻¹⁰ These novel properties arise, in part, from the high surface area to volume ratio found in nanomaterials and the large proportion of exposed atoms at the surface of these particles. These surface exposed atoms have more energy than that of the internal atoms in other, larger materials (called bulk materials) due to the high-energy bonds found in insufficiently coordinated atoms at the surface.^{7,11,12} These uncoordinated atoms are called surface defects and contribute to the high reactivity and catalytic activity of some nanoparticles.¹³ Bulk materials, on the other hand, often exhibit the same chemical and physical properties at any size.

As the proportion of surface atoms increases with decreasing particle size, materials that would otherwise be inert become highly reactive catalysts. Some size

dependent properties that can alter chemical properties include reactivity and catalysis (resulting in changes in toxicity to live organisms)^{14–16}, changes in thermal properties such as a reduced melting point for many metal nanomaterials^{17–19}, changes in mechanical properties including adhesion and capillary forces^{20,21}, changes in optical properties such as absorption and scattering of light^{22,23}, changes in electronic properties such as tunneling current, conductivity and quantum confinement^{24,25}, and magnetic properties such as superparamagnetism.

The growing number of applications for engineered nanomaterials has led to an increase in demand in the production of nanomaterials. In 2013, it was estimated that global production of engineered nanomaterials would be between 260,000 to 309,000 metric tons for a variety of nanomaterials including titanium dioxide, silver, iron and iron oxides, zinc oxide, copper and copper oxides, alumina, cerium oxide, nanoclays, carbon nanotubes, and silica.²⁶ In 2018, via an industrial survey, it was estimated that production of engineered nanomaterials would increase by an average of 5% annually.²⁷ However, these numbers are highly speculative since most companies do not freely publish data on production, products, or formulations for materials. Furthermore, advancements in various products may increase production of certain materials such as quantum dots for electronics or silver nanoparticles in medical devices and packaging when compared to others.²⁸

Suffice it to say that nanomaterials will be produced in growing amounts and incorporated into new or existing products at increasing rates. It is, therefore, vital to develop the science surrounding nanomaterials, their aging in various media, and methods of detection wherein engineered nanomaterials can be properly quantified in

soils, water, air, and waste. Specifically, however, is the incorporation of nanomaterials in products that may be used to treat water or alter the characteristics of food that is to be ingested. Nanotechnology-enabled water treatment is a growing sector of nanomaterial products and is intended to exploit the novel properties of nanomaterials increase the efficiency, efficacy, and selectivity of water treatment processes.^{29–31}

Of the many varied nanomaterials and composites, nano-titanium dioxide has been used extensively in consumer products and is one of the most produced engineered nanomaterials.²⁶ This dissertation will focus on the chemistry of titanium dioxide interactions with organic molecules and inorganic ions in water. In particular, the interaction of various organic ligands with titanium dioxide nanoparticles, the process and rates of degradation or oxidation of organic compounds that can be used for sensing titanium dioxide, and how various water formulations with varying levels of dissolved organic and inorganic compounds affect the aging, agglomeration, and size of the nanoparticles.

Chapter 2 : Literature Review

2.1. Titanium Dioxide Nanoparticles

Titanium dioxide (TiO_2) powders and materials have been widely used and researched recently due to their usefulness as a light scattering compound³², reactive oxygen species (ROS) generator^{33,34}, food and cosmetic additive³⁵, and photocatalyst among many applications.³⁶ TiO_2 particles with sizes less than 100 nm, classified as nanoparticles, have also increased in production and use.³⁷ Indeed, the applications of titanium dioxide nanoparticles have been increasing year by year at an accelerated pace.^{38–40} TiO_2 is now used in numerous solutions, coatings, food products, materials, and catalytic processes. The list extends to reflective paints, self-cleaning coatings, coloring for powdered food products, anti-caking agents, photocatalysis, and water treatment.⁴¹ Furthermore, these particles have high catalytic properties per a given mass and display interesting electronic properties that can be used in water treatment including organic material oxidation and nitrate reduction.^{42,43}

It was estimated in 2011 that TiO_2 nanoparticles were among the top five nanoparticles used in paints and consumer products.⁴⁴ Nanoparticles used in these applications have a wide range of crystallographic compositions, size, shape, and surface coatings.⁴⁵ There are three common crystalline forms of titanium dioxide found in nature: anatase, rutile, and brookite. Brookite is not produced commercially or incorporated in many products and is relatively rare in nature.⁴⁶ Rutile has the highest commercial production and is the most common titanium dioxide bearing mineral found in nature. The next most stable and common form, anatase, is featured in most research on TiO_2

photocatalysts due to its photoactivity.⁴⁷ However, some compounds used commercially are a mixture of rutile and anatase phases (e.g. Aeroxide P25).⁴⁸

Titanium dioxide materials and nanoparticles have been used extensively in water treatment and much research has been performed in that sphere.^{10,41,49} Some examples include photocatalytic nitrate reduction⁴² and advanced oxidation technology (photocatalysis).⁵⁰ Advanced oxidation technologies employ the generation of reaction oxidation species to degrade organic pollutants as shown with bisphenol A⁵¹, trichlorophenol (TCP), 2,4-dichlorophenol (2,4-DCP), and sodium benzoate⁵², methylethylketone⁵³, rhodamine B as a representative dye pollutant⁵⁴, petroleum refinery wastewater⁵⁵, and other model pollutants.⁵⁶

Recently, greater interest has been expressed in the potential toxicity of TiO₂ to human, animal, and plant health.^{46,57,58} Indeed, the French Agency for Food, Environmental and Occupational Health and Safety (ANSES) recently published an article exploring the risks and hazards of titanium dioxide as a food additive.^{59,60} For this reason, there will likely be more research into characterization and detection methods for TiO₂ nanoparticles. Furthermore, an expansion of research into the interactions of TiO₂ and bacteria, plants, and animal cells is likely to occur. Developing a detection method for TiO₂ that provides a rapid and portable means of detecting particles in water is important and worthwhile.^{61–67}

2.2. Detection Methods for Nanoparticles in Water

The most commonly used and commercially produced titanium dioxide nanoparticles in water treatment are Aeroxide (Degussa) P25 and Hombikat UV100. As the utilization of nanomaterials increases, release and consequent exposure will be more

likely in the future. Water treatment vessels will be built to prevent the loss of nanoparticles for sustainability and safety reasons; however, no system is perfectly safe, and some release may occur. It logically follows that more nanoparticles will be released into environmental sinks such as water, landfills, soil, and, to a lesser extent, the air.⁶⁸ An increasing number of studies have shown risks to human health from nanoparticle exposure using animal and plant models but the possible hazards cannot be adequately measured at this moment.^{69–72} However, it is important to detect and quantify nanoparticles in materials that provide an easy path of exposure such as drinking water and especially drinking water that has been treated with nano-enabled water technologies.

The standard for the detection and quantification of most nanoparticles in solution (mainly metal oxides or metal materials) is the single particle-inductively coupled plasma mass spectrometer (spICP-MS). Whereas, scanning electron microscopy and transmission electron microscopy have a high degree of sample preparation and complexity, spICP-MS has very high throughput and extremely high sensitivity.⁷³ However, spICP-MS does not adequately measure the morphology or size of a nanoparticle but instead assumes a shape (selected by the user) to calculate primary particle size.⁷⁴ Dynamic light scattering (DLS) is also a useful technique for measuring the size or presence of nanoparticles in solution but suffers from interference by agglomerates or poly-disperse samples and primarily measures the hydrodynamic size and not the true particle size.⁷⁵ DLS was not designed as a detection technique but as a characterization technique for particles with known composition in suspension.

However, these methods require some level of sample preparation (albeit minimal for ICP-MS and DLS for water samples), are expensive, are not typically rapid and are not portable. Furthermore, except for DLS, the instruments require a high degree of facility support including vacuum pumps, refrigerants, high voltage sources, gas cylinders (such as argon for ICP-MS) and exhaust systems. There is a need for a simple, portable, rapid, and inexpensive technique for determining the concentration of nanoparticles in water samples that can be performed on site or at a lab with minimal facility support or training. The primary way to detect nanoparticles under these parameters are via UV-Vis absorption spectroscopy or fluorescence spectroscopy.

2.3. Nanoparticles Detection via Fluorescence

When comparing UV-Visible spectroscopy and fluorescence spectroscopy, fluorescence techniques have the capability to have a better detection limit due to the active nature of fluorescence vs the passive nature of UV-Vis absorption. Fluorescence measures the active emission of photons from a sample against a “dark” background whereas UV-Visible absorption measures the difference between a blank (typically the solvent) and the light absorbed by a sample. Therefore, it is likely that a highly sensitive technique that can measure nanoparticles in a part per billion (ppb) range would be a fluorescent technique. Indeed, recent publications have shown that UV-Vis absorption or fluorescence spectroscopy could use an indirect method by measuring the loss of a dye, loss of fluorescence, or increase in fluorescence due to oxidation catalyzed by a suspended nanoparticle.^{76,77}

To date, most research involving fluorescence particles or nanomaterials has taken place in the biomedical sphere. Titanium dioxide nanoparticles have been used in

medical imaging and in cancer treatments. These fluorescent nanomaterials are typically functionalized with fluorescein isothiocyanate.⁷⁸ Some questions remain on the stability of the fluorescent labels when attached to nanoparticles that are used in photocatalytic processes. TiO_2 is mainly used in photocatalytic processes that degrade organic matter and molecules in water. To prevent the possibility of a fluorescent tag being degraded, TiO_2 could instead be used to create a fluorescent molecule using its photocatalytic activity. Studies have shown that terephthalic acid can be used as a hydroxyl scavenging molecule which fluoresces upon its reaction with a hydroxyl radical and the formation of 2-hydroxyterephthalate (2-hTPA).⁷⁷

2.4. Dynamic and Electrophoretic Light Scattering

Fluorescent and UV-Vis detection studies cannot, however, be easily performed for materials that tend to agglomerate in solution and fall out of suspension. For example, TiO_2 nanoparticles have a significant tendency to agglomerate in solution, especially aqueous solutions, and settle out. The hydrophobic neutral charge on the surface of TiO_2 is the primary cause for the reversible agglomeration and resulting sedimentation. Removing the neutral charge through surface modification may result in improved aqueous suspensions with lower rates of aggregation and sedimentation.

Dynamic light scattering (DLS) and electrophoretic light scattering (ELS) are both powerful methods that can be used to explore not only the size of particles but the electrical double layer that plays an influential role on the suspension and dispersal of the nanoparticles in aqueous solutions. ELS is a technique used to measure the surface charge of a particle in a suspension as shown in Figure 2.1. By applying a potential to

the solution within a folded capillary disposal cell and observing the movement of particles within that capillary, the surface charge of the particle can be measured.

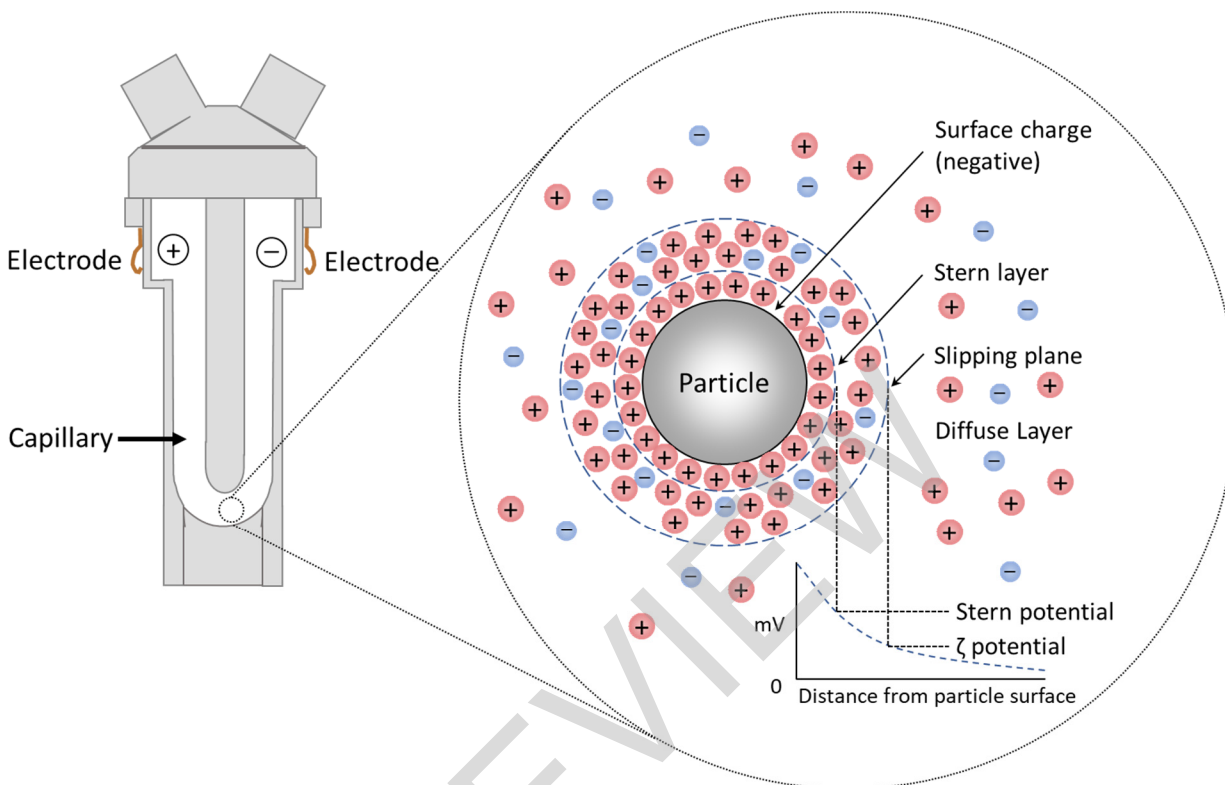


Figure 2.1. Diagram displaying a folded capillary cuvette used for ζ -potential measurements and the collection of ions around a negatively charged particle suspended in a dispersion medium and the potential difference as a function of distance from the particle surface

Using this method, the adsorbed layers of charge can be understood and manipulated to improve suspension and dispersal. These charged layers are responsible for generating repulsive forces within a suspension and are therefore essential for preventing aggregation. DLS and ELS have been used in many studies to investigate the interactions between titanium dioxide nanoparticles and various organic molecules including citric acid, natural organic molecules, dimercaptosuccinic acid, and polyacrylic acid.^{79–81} Simple surface modification by pH variation and ligand coating may provide increased suspension and decreased aggregation thus preserving particle size and surface-dependent properties. Furthermore, green approaches, such as using benign or