



# Effects of water chemistry on the destabilization and sedimentation of commercial TiO<sub>2</sub> nanoparticles: Role of double-layer compression and charge neutralization



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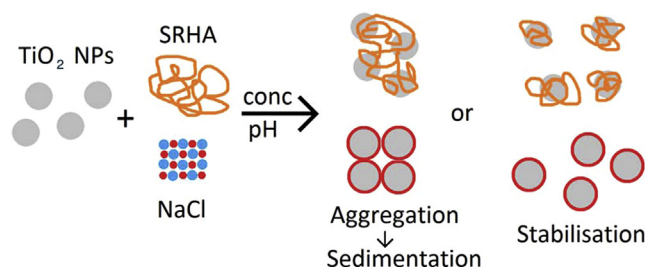
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## HIGHLIGHTS

- Stability of commercial stabilized TiO<sub>2</sub> nanoparticles (NPs) in water was analyzed.
- TiO<sub>2</sub> NPs rapidly settled down near its pH<sub>zpc</sub> once NPs aggregated >1 μm.
- In the presence of electrolytes, TiO<sub>2</sub> NPs aggregated but not settled down instantly.
- The suspension of TiO<sub>2</sub> NP aggregates could increase the exposure risk of NPs.
- Humic acid more than 20 mg/L could also keep stabilized NPs from aggregating.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Nanomaterials are considered to be emerging contaminants because their release into the environment could cause a threat to our ecosystem and human health. This study aims to evaluate the effects of pH, ions, and humic acid on the destabilization and sedimentation of commercial stabilized TiO<sub>2</sub> nanoparticles (NPs) in aquatic environments. The average hydrodynamic size of TiO<sub>2</sub> NPs was determined to be 52 ± 19 nm by dynamic light scattering. The zero point charge (ZPC) of the commercial TiO<sub>2</sub> NPs was found to occur at pH 6. The stability of commercial TiO<sub>2</sub> NPs is independent of its concentration in the range of 50–200 mg/L. In the absence of NaCl, the commercial TiO<sub>2</sub> NPs rapidly settled down near pH<sub>zpc</sub> when the aggregated nanoparticle size surpassed 1 μm. However, when the commercial TiO<sub>2</sub> NPs aggregated with the increase of NaCl concentrations, the large aggregates (>1 μm) were found to remain suspended. For example, even at the critical aggregation concentration of NaCl (100 meq/L), TiO<sub>2</sub> NP aggregates suspended for 45 min and then slowly deposited. This implies an increase in the exposure risk of NPs. In the presence of Suwannee river humic acid (SRHA), the commercial TiO<sub>2</sub> NPs did not settle down until the SRHA concentration increased to 20 mg/L, and were seen to restabilize at SRHA concentrations of 50 mg/L. The uncommon behaviors of the commercial TiO<sub>2</sub> NPs we observed may be

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attributed to the different destabilization mechanisms caused by different species (i.e., NaCl and SRHA) in water.

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## 1. Introduction

Ongoing advancements in nanotechnology have led to a large-scale production of nanomaterials with a growing number of applications. Amongst these various nanomaterials, titanium dioxide nanoparticles (TiO<sub>2</sub> NPs) continue to be the most extensively synthesized, with a global production reaching 1000s of tons annually (Gottschalk et al., 2009). TiO<sub>2</sub> NPs have been widely employed as anti-scratch additives (Zurlini et al., 2009), color additives, sunscreens (Myllylä, 2005), and photocatalysts (Fernández-Ibáñez et al., 2003).

With an increasing amount of commercial nanoparticles (NPs) being released into the environment, their fate and effects on the ecosystem and human health are of rising concern, and is therefore a very important matter for environmental risk evaluation. Many sources of TiO<sub>2</sub> have already entered wastewater (Lee et al., 2001), sewage (Nowack and Bucheli, 2007) and runoff (Kaegi et al., 2008) around the globe and there is strong evidence that TiO<sub>2</sub> NPs pose toxicological risks to the environment (Boxall et al., 2007) and impact the bioavailability of other pollutants (Sun et al., 2009). For example, Zhu et al. (2011) evaluated that TiO<sub>2</sub> may have important indirect impacts on aquatic organisms by varying the toxicity of coexisting pollutants. The exposure of NPs to organisms is largely driven by the NP's dispersion and behavior in aqueous systems, while their potential hazard, although not always well understood, is often related to their properties (Labille and Brant, 2010). Upon environmental release, NPs could be harmful to organisms, as evidenced by laboratory studies. Wu et al. (2009) reported that TiO<sub>2</sub> NPs might pose a health risk to humans after dermal exposure over a relative long time period. More recently, Giovanni et al. (2014) reported that the current levels of TiO<sub>2</sub> NPs amongst others found in water systems pose little cytotoxic threat to certain human organ systems. Of course, the demand for nanomaterials is growing year on year and these conclusions may be liable to change. Similar studies have also been documented (Aruoja et al., 2009; Kasemets et al., 2009; Li et al., 2011). The antibacterial activity of nanoparticles was inversely proportional to the size of the nanoparticles (Raghupathi et al., 2011). Furthermore, Horst et al. (2010) presented that the *Pseudomonas aeruginosa* could disperse TiO<sub>2</sub> agglomerates by preferential biosorption of nanoparticles onto cell surfaces.

The stability of NPs in aqueous environments plays an important role in determining their environmental implication and potential risk to human health. Many studies investigated the behavior of TiO<sub>2</sub> NPs under different pH, ionic strengths (IS), ion valence, and surface charge conditions (e.g., Loosli et al., 2013). TiO<sub>2</sub> NP aggregation starts to occur as the pH approaches the point of zero charge, while the NPs stabilize at both higher and lower pH conditions (French et al., 2009). Higher IS is reported to facilitate NP aggregation and electrolytes can quickly enhance the aggregation of NPs in aquatic environments (Guzman et al., 2006). The pH, IS, and ion valence were discovered to alter the TiO<sub>2</sub> NP morphology. Chowdhury et al. (2013) reported a linear relationship between the surface area of NPs and fractal dimension, indicating that larger size NPs form less compact aggregates. The fate of metal oxide NPs in natural water bodies would be determined by the type and concentration of cations and organic matters (Zhang et al., 2009; Tso et al., 2010; Shih et al., 2012b). Zhang et al. (2009) also studied

the impact of natural organic matter (NOM) and divalent cations (Ca<sup>2+</sup>) on the stability of engineered metal oxide NPs (e.g. ZnO, NiO, TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>). Furthermore, the stability of TiO<sub>2</sub> nanoparticles in soil suspensions and their transport behavior through soils has been studied (Fang et al., 2009).

After the aggregation of NPs, these aggregates could remain in the aqueous phase or settle down and then be removed from water. In general, aggregation is closely followed by sedimentation, but some NOM may stabilize the aggregates in solution for a longer period, owing to the steric hindrance of the NOM and other factors (French et al., 2009; Erhayem and Sohn, 2014). Although the sedimentation behavior of TiO<sub>2</sub> NPs in the presence of electrolytes as a function of pH (Gustafsson et al., 2003) and in eight different natural aqueous media (Keller et al., 2010) has been investigated, they generally used the powder form of nanoparticles. We also found the nanopowders readily aggregated once they were added to water (Tso et al., 2010). Previously, we studied the effect of electrolytes on the aggregation of stabilized TiO<sub>2</sub> NPs in water (Shih et al., 2012a). However, the sedimentation kinetics of the stabilized TiO<sub>2</sub> NPs in water is still unclear. To better understand the transport, fate, and behavior of NPs in aquatic systems, it is essential to understand their interactions with different components of waters including NOM over a broad range of physico-chemical conditions (Domingos et al., 2009). However, only a few studies have addressed the aggregation and sedimentation of commercially stabilized TiO<sub>2</sub> NPs in different water conditions.

In this study, we investigate the effect of pH, salt concentrations, and humic acids on the aggregation and sedimentation of commercial TiO<sub>2</sub> NPs in suspensions. The commercial TiO<sub>2</sub> NPs modified by patented capping agents are highly stable under ambient conditions. Our results would provide insight into better understanding of the commercial TiO<sub>2</sub> NPs behavior and their aggregation and sedimentation rates under different aqueous conditions.

## 2. Materials and methods

### 2.1. Characteristics of commercial TiO<sub>2</sub> NP suspensions

Commercial TiO<sub>2</sub> NP suspensions (anatase) were obtained from Conyuan Biochemical Technology Co., Ltd. (Taiwan). The as-received TiO<sub>2</sub> concentration was 30%. Sodium chloride was purchased from Acros Chemical. Suwannee River humic acid (SRHA) was obtained from International Humic Substance Society. The water used in this study was double distilled and deionized with a Milli-Q water purification system (Millipore). The commercial TiO<sub>2</sub> NPs were suspended in the solution with a patented stabilizer, which exhibits a good suspension effect. To minimize the effect of the stabilizer for each batch experiment, 0.1 mL of the TiO<sub>2</sub> suspended solution was taken and added into a 100 mL aqueous solution. Thus, the stabilizer concentration was diluted to at least 10,000 times. All NP suspension samples were used only once.

In aqueous systems, the average particle size (commonly referred to as “z-average diameter”), particle size distributions, and zeta potential of TiO<sub>2</sub> suspensions were determined by dynamic light scattering (DLS, Zetasizer Nano). The DLS instrument contains a 4 mW He–Ne laser operating at a wavelength of 633 nm and incorporates non-invasive backscatter optics. Particle size

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