



# A mechanistic study of stable dispersion of titanium oxide nanoparticles by humic acid

Yin Chen<sup>a</sup>, Qian Gao<sup>a</sup>, Weixiao Chen<sup>a</sup>, Fan Wu<sup>a</sup>, Yu Yang<sup>b</sup>, David Werner<sup>c</sup>, Shu Tao<sup>a</sup>, Xilong Wang<sup>a,\*</sup>

<sup>a</sup> Laboratory for Earth Surface Processes, College of Urban and Environmental Sciences, Peking University, Beijing 100871, China

<sup>b</sup> Department of Civil and Environmental Engineering, University of Nevada, Reno, NV 89557, USA

<sup>c</sup> School of Engineering, Newcastle University, Newcastle upon Tyne, UK

## ARTICLE INFO

### Article history:

Received 22 September 2017

Received in revised form

18 December 2017

Accepted 7 February 2018

Available online 7 February 2018

### Keywords:

Stable dispersion

Titanium oxide nanoparticles

Humic acid

Mechanism

Crystalline structure

## ABSTRACT

Stable dispersion of nanoparticles with environmentally-friendly materials is important for their various applications including environmental remediation. In this study, we systematically examined the mechanisms of stable dispersion of two types of TiO<sub>2</sub> nanoparticles (TNPs) with anatase and rutile crystalline structures by naturally occurring dissolved organic matter (humic acid) at different pHs, including at, below and above the Point of Zero Charge (PZC). The results showed that stable dispersion of TNPs by humic acid (HA) at all pHs tested can only be achieved with the assistance of ultra-sonication. The dispersion of TNPs by HA differed at the three pHs tested. Generally, HA greatly decreased the hydrodynamic diameters of TNPs at a very low concentration. The dispersion of TNPs became relatively stable when the HA concentration exceeded 5 mg/L, indicating that this HA concentration is required for stable dispersion of TNPs. The mechanisms involved in dispersion of TNPs by HA included electrostatic repulsion, steric hindrance and hydrophobic interaction. Electrostatic repulsion was identified to be the dominant mechanism. The dispersion of TNPs was enhanced when HA was added before ultra-sonication to avoid the partly irreversible re-aggregation of TNPs after sonication. The crystalline phases and concentrations of TNPs were also found to influence their stable dispersion. The findings from this work enhance understanding of the combined effects of HA, pH, ultra-sonication and crystalline structures of TNPs on their stable dispersion. The mechanisms identified can improve applications of TNPs in environmental water pollution control.

© 2018 Elsevier Ltd. All rights reserved.

## 1. Introduction

Nanoparticles are promising novel materials due to their unique physicochemical properties including small size, large surface area, special morphology, catalytic reactivity, and optical properties (Ju-Nam and Lead, 2008; Liu et al., 2011). Among all nanoparticles, titanium dioxide nanoparticles (TNPs) have large production volumes with extensive applications in photo catalysis, as UV protection agent, for sensing and energy storage (Chen and Mao, 2007). Although environmental risks of nanoparticles such as toxic effects on aquatic organisms have been widely reported (Hou et al., 2017a, 2017b), TNPs also have promising potential for environmental remediation because of their high photocatalytic activity

(Varshney et al., 2016). As low cost and effective sorbents, they have been applied in the removal of a variety of heavy metals including arsenic, lead and mercury (Qu et al., 2013). They also have a high sorption capacity for organic pollutants (Wang et al., 2008). However, the strong aggregation tendency of TNPs in the aqueous phase is an obstacle to their applications because aggregation may decrease their exposed surface area and alter their surface properties, resulting in decreased sorption capacity and catalytic efficiency (Ju-Nam and Lead, 2008). Modification of TNPs to prevent their agglomeration has been shown to be effective in improving their photocatalytic performance (Li et al., 2010). Enhanced sorption of sulfamethoxazole to carbon nanotubes suspended by HA was also reported (Pan et al., 2013). Thus, to utilize TNPs, it is imperative to improve their dispersion in the aqueous phase.

Ultra-sonication is more effective than other dispersing techniques in breaking up aggregated TNP clusters. It can refine the NPs structure by cavitation and erosion, thus dispersing them (Taurozzi

\* Corresponding author.

E-mail address: [xilong@pku.edu.cn](mailto:xilong@pku.edu.cn) (X. Wang).

et al., 2011). However, re-agglomeration after sonication is often observed, indicating that the nanoparticle suspension was not sufficiently stabilized (Nguyen et al., 2011; Zhang et al., 2009). As previously reported, the aggregate size of TNPs in tap water increased from 500 nm to 2000 nm within 8 h after sonication for 10 min (Zhang et al., 2008). To prepare stable nanoparticle suspensions, various methods were adopted in addition to sonication, including optimization of the aqueous chemistry (especially pH condition), surface modification of nanoparticles, and addition of dispersant including polymers and surfactants (He and Zhao, 2007; Singh et al., 2012). Although nanoparticle suspensions can be well-stabilized with some dispersants, it should be noted that introduction of these synthetic dispersants may bring new potential threats to the aquatic environment (Dickson et al., 2012). The surface properties of the nanoparticles would also be altered by these dispersants, thus affecting the interactions between nanoparticles and other pollutants (Phenrat et al., 2009). Therefore, one of the critical criteria for selecting dispersants is that they should be natural. Natural organic matter (NOM), which is ubiquitous in aquatic systems, can be an environmentally friendly dispersant option. Humic acid (HA), a major component of NOM and a typical representative of humic substances, may interact with TNPs via electrostatic attraction and ligand exchange (Yang et al., 2009). Its adsorption would increase the electrostatic repulsion and steric hindrance between individual nanoparticles, thereby enhancing their dispersion and stability (Chen et al., 2012). A few studies investigated the influence of humic acid on the stability of TNPs through studying variations of the hydrodynamic diameters of TNPs aggregates. It was observed that TNPs can be disaggregated into small clusters with sizes ranging from 50 to 250 nm by HA at a low concentration representative of environmental levels (Loosli et al., 2013; Zhang et al., 2009). However, these studies mainly focused on the aggregation behavior of TNPs instead of their dispersion. TNP aggregate size was generally adopted as an indicator of their stability at various HA concentrations. While aggregate size cannot fully characterize the dispersion of TNPs; the aggregated large clusters of TNPs would settle well after standing or centrifugation. The optimal HA concentration for stable TNPs dispersion merits further exploration, and the connection between aggregate size and dispersion of TNPs deserves careful investigation. Besides, the combined effects of sonication and HA on dispersion of TNPs has rarely been discussed, since TNPs were generally pre-dispersed and stabilized before use or were purchased as suspension in previous studies (Loosli et al., 2013; Zhang et al., 2009). The possible difference in stable dispersion of TNPs by HA added before and after sonication and the underlying mechanisms have not yet been investigated. Furthermore, impacts of the intrinsic properties of TNPs and HA such as the concentration and crystalline structure of TNPs, and the effects of extrinsic conditions including pH and ultra-sonication on the role of HA in dispersing TNPs have not yet been elucidated.

To help systematically understand the underlying mechanisms controlling stable dispersion of TNPs, the roles of naturally occurring dissolved organic matter (HA), pH, and ultra-sonication in the dispersion of TNPs with different crystalline structures (anatase and rutile) were tested and compared. The findings of the present work will facilitate the application of stably dispersed TNPs for sustainable water pollution control.

## 2. Materials and methods

### 2.1. TiO<sub>2</sub> nanoparticles

Both the pristine anatase and rutile TiO<sub>2</sub> nanoparticles (ATNPs and RTNPs) were used in this study. They were purchased from

Nanjing Guanye Chemical Industry Co., Ltd. XRD spectra of ATNPs and RTNPs are available in our previous publications (Wang et al., 2014). The TNP suspension at concentrations of 100 and 200 mg/L was prepared by adding TNP powder to the background solution containing 3 mM NaCl (prepared with Milli-Q water). The pH of the suspension was adjusted with 0.1 M HCl and NaOH. To study the dispersity of TNPs with or without the assistance of ultra-sonication, TNP suspensions were ultra-sonicated for 15 min (Branson 250 Digital Sonifier, USA, at 70% amplitude) or shaken for 2 d, respectively. The pH of the suspensions was measured and adjusted again after ultra-sonication and shaking to ensure it was maintained at the pH of interest ( $5.20 \pm 0.1$  and  $8.10 \pm 0.1$  for ATNP,  $4.30 \pm 0.1$  and  $7.60 \pm 0.1$  for RTNP). Aliquots of the suspensions were transferred to 40 mL vials for the following experiments.

### 2.2. Humic acid

The HA used was extracted from a peat soil collected from Amherst, Massachusetts with 0.1 M Na<sub>2</sub>P<sub>4</sub>O<sub>7</sub>. To remove minerals (mostly silicates), the extracted HA were treated with 0.1 M HCl/0.3 M HF, rinsed five times with deionized water, freeze-dried, and then ground to pass through a 250 μm sieve and stored. A stock solution of 200 mg/L HA was prepared and adjusted to neutral pH (Wang et al., 2011). To minimize bioactivity, NaN<sub>3</sub> (200 mg/L) was added to the stock solution. Details of the solution preparation are described in our previous publication (Zhou et al., 2012).

### 2.3. Dispersion of TNPs

The Z-average hydrodynamic diameters and percentage of stably dispersed TNPs after centrifugation were measured to examine the impacts of pH, HA and TNP concentrations on the dispersion of TNPs. A certain amount of HA stock solution was added to the vials containing TNP suspension that was prepared as mentioned above, to reach a final HA concentration of 0, 1, 5, 10, 20 mg/L, with a total mixture volume of 40 mL. The mixed suspension was immediately sampled for aggregate size measurement using a Nano-ZS90 ZetaSizer (Malvern Instruments Technical Ltd., UK). A ratio of  $A/A_0$  (here  $A_0$  and  $A$  are absorbance of the bulk TNP suspension and the supernatant before and after centrifugation at 1500 rpm for 10 min, respectively, obtained using a UV–Visible spectrometer at 500 nm) was measured to describe the percentage of the stably dispersed TNPs. Zeta potential values of TNPs in the suspension 120 min after HA addition were also collected with the same ZetaSizer. To study effects of ultra-sonication on the dispersion of TNPs, HA was added before instead of after ultra-sonication, and the subsequent sample treatments along with the measurements of Z-average hydrodynamic diameters and  $A/A_0$  values were the same as mentioned above. Details of the measurement of Z-average size, ζ potential and  $A/A_0$  value are provided as Supporting Information (SI).

### 2.4. HA sorption experiments

Sorption experiments of HA on TNPs were conducted to elucidate the impact of HA on their dispersion. After sampling for size and ζ potential measurements, the remaining TNP suspension was shaken for 2 d at room temperature. After mixing, the suspension was centrifuged at 20,000 rpm for 20 min. The total organic carbon (TOC) values of the supernatant were measured using a Shimadzu TOC5000a. The mass difference of HA before and after sorption was then calculated and converted to the sorbed amount of HA. A blank control was set up in which TNP suspension was prepared and centrifuged following the same procedure but in the absence of HA. The TOC value of the blank control was deducted to eliminate the

Download English Version:

<https://daneshyari.com/en/article/8874209>

Download Persian Version:

<https://daneshyari.com/article/8874209>

[Daneshyari.com](https://daneshyari.com)