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Surface speciation of *myo*-inositol hexakisphosphate adsorbed on TiO_2 nanoparticles and its impact on their colloidal stability in aqueous suspension: A comparative study with orthophosphate

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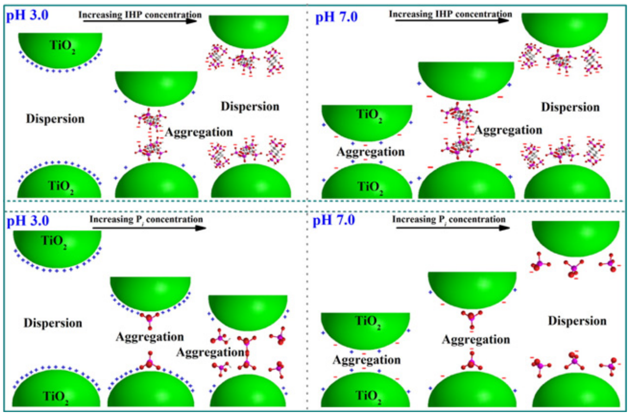
HIGHLIGHTS

- IHP/P_i plays a significant role in the colloidal stability of TiO_2 NPs.
- The effect of IHP is much greater than P_i.
- TiO_2 surface charge is modified by the formed inner-sphere P complexes.
- IHP binds on TiO_2 by 3 of its 6 P groups leaving the other 3 dissociated and ionized.
- Interaction between NPs depends on pH, surface P coverage, and surface P species.

GRAPHICAL ABSTRACT



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ABSTRACT

Despite extensive research demonstrating the influence of organic matter and inorganic phosphate on the stability of TiO_2 nanoparticles (NPs), far less research has assessed the impact of *myo*-inositol hexakisphosphate (IHP), a common organic phosphate widely present in the environment. In this study, the adsorption of IHP on TiO_2 NPs and its impact on their colloidal stability were investigated using batch experiments, dynamic light scattering (DLS) techniques, in situ attenuated total reflectance Fourier transform infrared (ATR-FTIR) and solid-state ^{31}P nuclear magnetic resonance (NMR) spectroscopy. Inorganic orthophosphate (P_i) adsorption was run for comparison. The ratio of the P_i/IHP adsorption density (1.528: 0.453) at pH 5.0 suggested that IHP may complex on the TiO_2 surface through three of its six phosphate groups. Zeta potential measurements, ATR-FTIR and NMR spectra indicated that IHP/P_i adsorbed onto TiO_2 NPs by forming inner-sphere complexes and modified the surface charge of these NPs, which exerted a great impact on their colloidal stability. Interactions between NPs measured by sedimentation and aggregation size highly depended on the pH, surface phosphorus coverage, and surface phosphorus species. The impact of IHP on the aggregation and dispersion of TiO_2 NPs was significantly larger than that of P_i, in agreement with the calculation from the DLVO theory. This study highlighted the impact of IHP relative to P_i on the colloidal stability of TiO_2 NPs in phosphorus-enriched environments.

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1. Introduction

TiO_2 nanoparticles (NPs) are the most produced engineered nanomaterial based on the global engineered nanomaterial production and application data (Keller and Lazareva, 2014). The increasing production and application will inevitably cause a rapid release of TiO_2 NPs into the natural environment (Chen and Mao, 2007; Lowry et al., 2012). TiO_2 NPs may enter the air, water and soil from anthropogenic sources such as wastewater treatment plant effluents (Keller and Lazareva, 2014; Mudunkotuwa and Grassian, 2010). Owing to the toxicity of TiO_2 NPs, their accumulation, transformation and transportation in the environment may cause risks to the ecosystem (Lowry et al., 2012; Sharma, 2009; Vevers and Jha, 2008; Xia et al., 2015). Therefore, great concerns are raised about the colloidal stability of TiO_2 NPs in aqueous suspension, which controls their mobility, bioavailability and toxicity in the environment (Mudunkotuwa and Grassian, 2010; Sharma, 2009; Zhu et al., 2014).

NP stability is influenced by their properties such as surface charge, particle size and shape, and media conditions (e.g., ionic strength, pH and ion composition) (Chen et al., 2012; Peng et al., 2015; Sharma, 2009; Solovitch et al., 2010; Thio et al., 2011; Zhu et al., 2014). Recently, it was reported that the colloidal stability of aqueous TiO_2 NP suspensions could be affected by the adsorption of divalent cations, inorganic phosphate, organic acids and organic matter (e.g., Ca^{2+}, orthophosphate, alginate, oxalic acid, citric acid, humic acid and fulvic acid) (Domingos et al., 2009, 2010; French et al., 2009; Loosli et al., 2013; Mudunkotuwa and Grassian, 2010; Pettibone et al., 2008; Philippe and Schaumann, 2014; Zhu et al., 2014).

The adsorption of phosphate caused an apparent change in the particle size of TiO_2 NPs due to alteration of the electrophoretic mobility (Domingos et al., 2010). The presence of oxalic acid at acidic pH levels led to aggregation of TiO_2 NPs, although the aggregation at pH 6.5 remained unaffected (Pettibone et al., 2008). However, the presence of citric acid at acidic and circumneutral pH levels reversed the stability of TiO_2 NP suspensions (Mudunkotuwa and Grassian, 2010). Additionally, the aggregation of NPs decreased in the presence of Suwannee River fulvic acid (SRFA) from highly acidic medium up to pH 6.0, which was possibly caused by the high steric repulsions exerting a high energy barrier for aggregation (Domingos et al., 2009). Therefore, the dispersion and mobility of TiO_2 NPs may be greatly dependent on their precise colloidal mixtures and ambient conditions.

Phosphorus (P) is essential for all living organisms and enriched in the natural environment. In different environments, the concentrations of P (Pi & IHP) can vary from μmol L^{-1} to mmol L^{-1} scale, ranging from 0.01 to 5000 ppm (Arai and Sparks, 2007; Lindsay, 1979). The various forms of P are expected to have great potential for interacting with metal oxide NPs and influencing NP transformation in the environment. Many researchers have examined the interaction between inorganic orthophosphate (P_i) and unstable NPs (e.g., ZnO) and assessed the associated impact on microstructural transformation of these NPs (Lv et al., 2012; Rathnayake et al., 2014). *Myo*-inositol hexakisphosphate (IHP) is the most common form of organic P with abundant stereoisomers and an important P pool in the environment (Turner et al., 2002, 2012). Similar to P_i, IHP can be adsorbed strongly on metal oxide particles via inner-sphere complexation (Celi et al., 2001; French et al., 2009; Wang et al., 2013; Yan et al., 2014b, 2014c; Wan et al., 2015). However, only a few studies have investigated the interaction between organic/inorganic phosphate (e.g., IHP/P_i) and stable NPs (e.g., TiO_2) (Domingos et al., 2010; Wan et al., 2015), making it difficult to evaluate the impact of P species on the colloidal stability of these NPs in aqueous suspension.

Our recent work suggested that the adsorption of IHP/P_i exerted a great effect on the aggregation of CeO_2 NPs in aqueous suspensions (Wan et al., 2015). Because spectroscopic references about P adsorption onto CeO_2 NPs are lacking, it remains difficult to reveal the coordination structure of P at the surface of these NPs (Wan et al., 2015). In addition, TiO_2 NPs are widely applied in practical areas and often used as typical stable NPs to investigate NP–NP interactions under various conditions (Domingos et al., 2009; Mudunkotuwa and Grassian, 2010; Pettibone et al., 2008; Zhu et al., 2014). Although adsorption of IHP on TiO_2 has not been reported, the structure of P_i surface complexes on TiO_2 was documented in the literature (Connor and McQuillan, 1999; Kang et al., 2011; Michelmore et al., 2000; Tejedor-Tejedor and Anderson, 1990). Thus, there is sufficient information to simultaneously elucidate the adsorption behavior of IHP/P_i on TiO_2 NPs and the associated impact on NP colloidal stability in aqueous suspension.

Therefore, the present study was designed: 1) to investigate the mechanism of IHP coordination on TiO_2 NP surfaces using batch experiments, zeta (ζ) potential analysis, in situ attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy and solid-state ^{31}P nuclear magnetic resonance (NMR) spectroscopy; and 2) to assess the colloidal stability of TiO_2 NP suspensions as a function of pH and surface IHP coverage using batch experiments and dynamic light scattering (DLS) techniques. Parallel experiments of P_i adsorption were conducted for comparison purposes. The results provide insights into the mechanisms of IHP/P_i adsorption on TiO_2 NPs, as well as the impact on TiO_2 NP sedimentation behavior in terms of aggregation and dispersion.

2. Materials and methods

2.1. Materials and characterization of TiO_2 NPs

Dipotassium *myo*-inositol hexaphosphate (IHP, purity > 95%) was purchased from Sigma-Aldrich (P5681-5G, Saint Louis, MO, USA). TiO_2 NPs were obtained from Emperor Nano Material Co., Ltd. (Nanjing, Jiangsu, China). The NPs contained no impurity phases or any surfactants and coatings, as detected by powder X-ray diffraction (XRD) and FTIR analyses. The specific surface area of TiO_2 solid was measured by the Brunauer–Emmett–Teller method. The morphology and diameter of the particles were determined by transmission electron microscopy. Detailed characteristic information is given in the Supplementary Data (SD).

2.2. Adsorption isotherms and adsorption pH edge experiments

Before IHP or P_i adsorption, a 2.0 g L^{-1} TiO_2 suspension was dispersed in 0.01 mol L^{-1} KCl and adjusted to a final pH of 5.0 ± 0.05 with 0.1 mol L^{-1} HCl. The suspension was purged overnight with N_2 to remove CO_2. Samples containing 10.0 mL of stock suspension (20 mg TiO_2) were then added to 10.0 mL of P-contained solutions at pH 5.0 in 0.01 mol L^{-1} KCl. The suspensions were equilibrated by shaking at 200 rpm and at 25 °C in the dark for 24 h. During equilibration, the pH of each batch sample was adjusted to pH 5.0 ± 0.05 at 1, 6, 12, and 24 h, respectively. The experiments of P adsorption isotherms, adsorption pH edge and measurement of sedimentation and DLS were conducted where the concentration of P_i was three times that of IHP, given that: 1) the concentrations of both IHP and P_i should be controlled to be higher than the maximum adsorption amount; and 2) the maximum adsorption density of P_i onto NPs or soil minerals is three or four times higher than that of IHP (Celi et al., 2001; Wan et al., 2015; Yan et al., 2014b, 2014c).

After 24 h of equilibration, the suspensions were centrifuged at 16,000 g for 15 min, and the supernatants were filtered through a 0.22-μm Millipore membrane to analyze the equilibrium IHP/P_i concentration and calculate the adsorbed density of IHP/P_i. The concentrations of TiO_2 NPs in the supernatants after being digested with HNO_3 and H_2SO_4 (Kiser et al., 2009) were below 7 ppb, as measured using an inductively coupled plasma mass spectrometer (NexION 350X, PerkinElmer, Shelton, CT, USA). Each experiment was performed in duplicate. Adsorption pH edge experiments of IHP/P_i onto TiO_2 were