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# Influences of anion concentration and valence on dispersion and aggregation of titanium dioxide nanoparticles in aqueous solutions

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## ABSTRACT

Dispersion and aggregation of nanoparticles in aqueous solutions are important factors for safe application of nanoparticles. In this study, dispersion and aggregation of nano-TiO<sub>2</sub> in aqueous solutions containing various anions were investigated. The influences of anion concentration and valence on the aggregation size, zeta potential and aggregation kinetics were individually investigated. Results showed that the zeta potential decreased from 19.8 to −41.4 mV when PO<sub>4</sub><sup>3−</sup> concentration was increased from 0 to 50 mg/L, while the corresponding average size of nano-TiO<sub>2</sub> particles decreased from 613.2 to 540.3 nm. Both SO<sub>4</sub><sup>2−</sup> and NO<sub>3</sub><sup>−</sup> enhanced aggregation of nano-TiO<sub>2</sub> in solution. As SO<sub>4</sub><sup>2−</sup> concentration was increased from 0 to 500 mg/L, the zeta potential decreased from 19.8 to 1.4 mV, and aggregate sizes increased from 613.2 to 961.3 nm. The trend for NO<sub>3</sub><sup>−</sup> fluctuation was similar to that for SO<sub>4</sub><sup>2−</sup> although the range of variation for NO<sub>3</sub><sup>−</sup> was relatively narrow. SO<sub>4</sub><sup>2−</sup> and NO<sub>3</sub><sup>−</sup> accelerated the aggregation rapidly, while PO<sub>4</sub><sup>3−</sup> did so slowly. These findings facilitate the understanding of aggregation and dispersion mechanisms of nano-TiO<sub>2</sub> in aqueous solutions in the presence of anions of interest.

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## Introduction

In the past decades, nanomaterials were globally applied. The societal impact of nanotechnology has been anticipated to be as drastic as that of the first industrial revolution (Keller et al., 2013). Materials including nano-Fe, nano-Au, nano-TiO<sub>2</sub>, and carbon nanoparticles could be prepared at nanoscale and have been widely applied in herbicides, cosmetics, electronics, wastewater treatment, air remediation, etc. (Yao et al., 2015; Lv et al., 2012; Puddu et al., 2010). However, production and application of nanomaterials have

led to the inevitable introduction of nanoparticles into the environment.

Nano-TiO<sub>2</sub>, one of the most utilized nanomaterials, is used in the production of cosmetics, catalysts and groundwater remediation (Robichaud et al., 2009; Yu et al., 2010; Zhang et al., 2015; Lalhriatpuia et al., 2015; Bet-moushoul et al., 2016). Nano-TiO<sub>2</sub> could be hazardous when released into the environment (Jin et al., 2008), causing toxicological risks to the ecosystem and human health due to its large specific surface area, nanoscale size, photocatalysis and chemical structure (Boxall et al., 2007; Chen et al., 2015). When lights were available, nano-TiO<sub>2</sub> would

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produce reactive oxygen species that could induce oxidative damage to microorganisms, crustaceans, and so on (Adams et al., 2006; Long et al., 2006). Delay of *Daphnia magna* growth and even death via bioaccumulation could also be observed in *Daphnia magna* (Zhu et al., 2010). Neurovirulent damage on mice hippocampal neurons could be caused by nano-TiO<sub>2</sub> via induction of cavitation (Wang et al., 2007). Furthermore it was found that the respiratory system was affected, resulting in sublethal effects when nano-TiO<sub>2</sub> coexisted with Na<sup>+</sup> and K<sup>+</sup> in rainbow trouts (Federici et al., 2007). The concentration of 2 mg/L of nano-TiO<sub>2</sub> exacerbated the toxicity of tributyltin to abalone embryos (Zhu et al., 2011). In summary, close attention should be paid to the impact of nanomaterials on human health and the ecosystem.

The stability, toxicity and ultimate fate of nanoparticles in the water environment are affected by the aggregate size and suspension time, which are related to ionic strength, valence of cations, pH, surfactants and natural organic matters (NOMs) (Zhang et al., 2012; Mukherjee and Weaver, 2010). Humic acid, which is one kind of NOMs, would be adsorbed onto nano-TiO<sub>2</sub> which could consequently become more stable and thus more toxic in water (Yang et al., 2013). In general, surfactants could improve the transport of nano-TiO<sub>2</sub> in aqueous solutions. Anionic surfactants led to a smaller aggregate size than non-ionic surfactants (Godinez and Darnault, 2011). Surface potential could be affected by pH, and the aggregate size increased when the zeta potential approach the point-of-zero-charge of the nanoparticles (Dunphy-Guzman et al., 2006). It was also observed that high ionic strength and low total organic carbon (TOC) led to larger aggregate size for nano-TiO<sub>2</sub>, while high TOC resulted in more stable nanoparticles in aqueous solutions (Keller et al., 2010). Divalent Ca<sup>2+</sup> and Mg<sup>2+</sup> ions led to larger nano-TiO<sub>2</sub> aggregate sizes than monovalent ions such as Na<sup>+</sup>, and the coexistence of Ca<sup>2+</sup> and NOMs increased the particle size due to the presence of specific Ca<sup>2+</sup>-NOM bridges (Romanello and Cortalezzi, 2013). The observed aggregation could be explained by the Darjaguin–Landau–Verwey–Overbeek (DLVO) theory, which states that the aggregation and stability of colloidal particles is determined by Van der Waals interactions and electrical repulsive forces (Elimelech et al., 1998). When the Van der Waals force is larger than the corresponding electrical repulsive force, aggregation prevails; otherwise, the particles tend to disperse.

Recently, the effects of cations on aggregation and dispersion of nanoparticles have been reported (Romanello and Cortalezzi, 2013; Chen et al., 2006, 2007). However, little information regarding the effects of anions on the aggregation of nano-TiO<sub>2</sub> is available. In this context, the objectives of this study are to investigate the effects of various anions on the aggregation size and zeta potential of nano-TiO<sub>2</sub> in aqueous solutions. Results and conclusions are supposed to lead to a better understanding of the performance and kinetics of nano-TiO<sub>2</sub> aggregation in aqueous solution.

## 1. Materials and methods

### 1.1. Preparation of nano-TiO<sub>2</sub> dispersions

TiO<sub>2</sub> (anatase) nanoparticles with an average particle size of 5–10 nm and over 99.8% purity employed were procured from Aladdin Chemistry Co. Ltd.

Stock solutions of anions were prepared with ACS grade reagents and ultrapure water. The three stock solutions prepared were 2500 mg/L NO<sub>3</sub><sup>-</sup>, 2500 mg/L SO<sub>4</sub><sup>2-</sup>, and 100 mg/L PO<sub>4</sub><sup>3-</sup>. Fifty milligrams per liter nano-TiO<sub>2</sub> particles were dispersed in different solutions containing NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, or PO<sub>4</sub><sup>3-</sup>. Of them, 50 mg/L nano-TiO<sub>2</sub> dispersions were mixed with 1.0, 3.0, 50, 200 and 500 mg/L NO<sub>3</sub><sup>-</sup>; 1.0, 3.0, 50, 200 and 500 mg/L SO<sub>4</sub><sup>2-</sup>; 0.5, 1.0, 3.0, and 50 mg/L PO<sub>4</sub><sup>3-</sup> by addition of stock solutions. Control experiments were also carried out in parallel.

To evaluate the dispersion characteristics of nano-TiO<sub>2</sub> particles, 50 mL of a dispersion was first filled in a tapered bottle (100 mL). Then, all dispersions were sonicated in a sonicator (Nishang Ultrasonics Company, Shanghai, China) to disperse the solutions. Sonication was performed at an ultrasonic power of 100 W at a frequency of 40 kHz, with a period of 30 min, and at 25°C. After sonication, the zeta potential and size of the dispersions were measured.

All samples were left without adjustment of pH except for experiments in which the pH value of point-of-zero-charge was examined.

### 1.2. Characterization of particles

Dynamic Light Scattering (DLS) for the measurement of the zeta potential and particle size was carried out using a Nano ZS90 Malvern Zetasizer (Malvern Instrument, Worcestershire, UK) (Li and Sun, 2011; Tkachenko et al., 2006; Badawy et al., 2010). The zeta potential values were calculated from electrophoretic mobility using the Smoluchowski model (Buttner et al., 2010), and particle sizes (average hydrodynamic diameter) was obtained from the diffusion coefficient using the Stokes–Einstein equation (Hsiao and Huang, 2011). The average of 30 measurements was taken to determine the zeta potential value. Particle size was measured once for every group. The Nano ZS90 Malvern Zetasizer was operated for 60 sec at 25°C to equilibrium. Disposable folded capillary cells and polystyrene cuvettes were employed to measure the zeta potential and size of particles, respectively.

When the effect of anion concentration on the aggregation of nano-TiO<sub>2</sub> was evaluated, measurements of the zeta potential and size of particles were performed within seconds after a dispersion was prepared.

When the effect of dispersion time was examined, the zeta potential and particle size was measured at a set time after a dispersion was completed.

When the aggregation kinetic of a dispersion was studied, particle size was measured immediately after a dispersion was carried out, and each sample was measured 30 times with an interval of 60 sec.

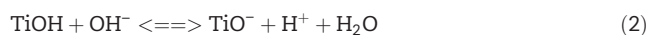
## 2. Results and discussion

### 2.1. Initial characterization of particles in suspension

Initial characterization of the particles in a suspension was studied at 50 mg/L of nano-TiO<sub>2</sub>. The values of pH of nano-TiO<sub>2</sub> suspensions were adjusted to be 1.0, 3.0, 5.0, 7.0, 9.0, and 11.0, respectively, using 1.0 mol/L NaOH and 1.0 mol/L HCl. Then, the zeta potential was measured immediately after the

suspensions were sonicated, and the data are presented in Fig. 1. From Fig. 1 it could be seen that the point-of-zero-charge of the nano-TiO<sub>2</sub> suspension was at pH of 6.2, which is in agreement with previous reports of pH at the point-of-zero-charge for anatase nano-TiO<sub>2</sub> (Zhu et al., 2014; Giammar et al., 2007).

There could possibly exist functional group of TiOH on the surface of nano-TiO<sub>2</sub> particles in a solution, consequently protonation or deprotonation could be resulted.

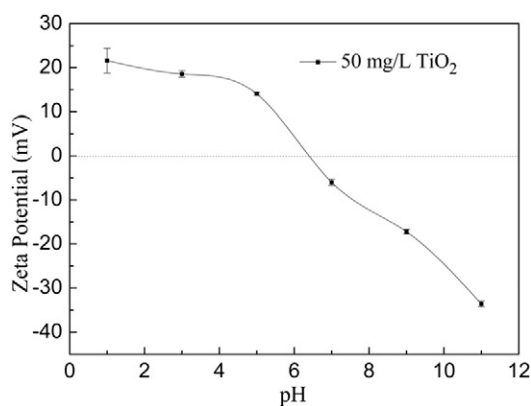


Therefore, Eq. (1) would prevail at a lower pH value, otherwise Eq. (2) would dominate.

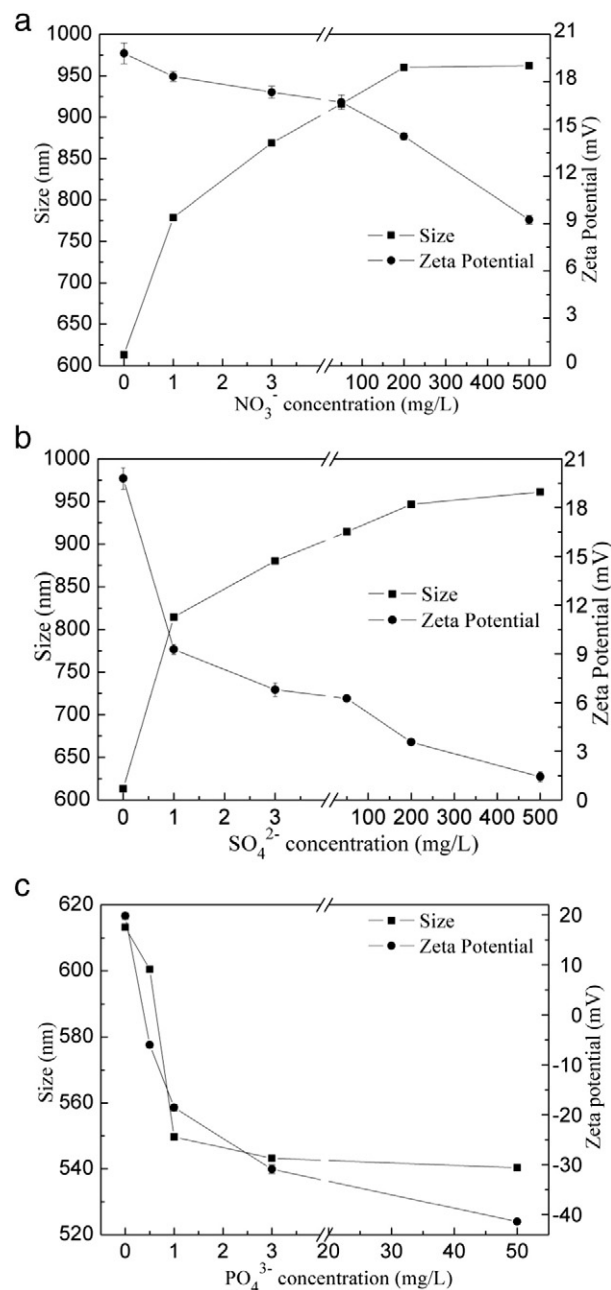
The control suspension in which only 50 mg/L of nano-TiO<sub>2</sub> was added in ultrapure water was sonicated at the condition mentioned above, and the particle size was measured to be 613.8 nm. The particle size in the suspension after sonication is much larger than the initial particle size which ranged 5–10 nm, which indicates that ultrasonic sonication was not powerful enough to overcome the strong Van der Waals attractive forces among nanoparticles in the suspension (Godinez and Darnault, 2011). The particle size in this study is larger than those reported by Godinez and Darnault (2011), Keller et al. (2010) and Thio et al. (2011) at similar conditions.

## 2.2. Effect of anion concentration

The effect of anion concentration on dispersion of nano-TiO<sub>2</sub> particles was evaluated selecting NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup> as the anions. For all experiments in this study, only Na<sup>+</sup> and H<sup>+</sup> existed in the suspensions as cations, because the Na<sup>+</sup> does not affect nano-TiO<sub>2</sub> appreciably within the experimental composition range (Chen et al., 2006; French et al., 2009). From Fig. 2 it can be seen that the zeta potential of nano-TiO<sub>2</sub> particles decreased with an increased concentration of each of the anions, while the variation range of the aggregate size differed significantly for the three anions.



**Fig. 1 – Relationship of Zeta potential of nano-TiO<sub>2</sub> and pH value in the suspension when no other chemical except NaOH and HCl was added.**



**Fig. 2 – Effect of anion concentration on size and zeta potential of 50 mg/L nano-TiO<sub>2</sub> particles in suspensions. (a) NO<sub>3</sub><sup>-</sup>; (b) SO<sub>4</sub><sup>2-</sup>; and (c) PO<sub>4</sub><sup>3-</sup>.**

For NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>, the zeta potential gradually decreased and approached zero when the concentration in the solution was increased, and the aggregate size increased consequently (Fig. 2a and b). From Fig. 2a it can be seen that the particle sizes increased gradually and zeta potential decreased consequently with the increasing NO<sub>3</sub><sup>-</sup> concentration in the experimental composition range. When the concentrations of NO<sub>3</sub><sup>-</sup> were 1.0, 3.0, 50, 200 and 500 mg/L, respectively, the corresponding zeta potential values were 18.3, 17.3, 16.7, 14.5 and 9.3 mV, and the aggregate sizes were 778.7, 868.8, 916.0, 960.1 and 962.3 nm. As for SO<sub>4</sub><sup>2-</sup>, the change speed of the zeta potential was more rapid than that for NO<sub>3</sub><sup>-</sup>. However, the size

of nanoparticle for  $\text{SO}_4^{2-}$  was similar to that for  $\text{NO}_3^-$ . Fig. 2a and b also showed that the aggregate size for nanoparticles at the presence of  $\text{NO}_3^-$  or  $\text{SO}_4^{2-}$  was much bigger than that for the control solution.

However, increase of  $\text{PO}_4^{3-}$  concentration led to a more rapid decrease of the zeta potential, which facilitated dispersion of particles. When the concentration of  $\text{PO}_4^{3-}$  was increased from 0.5 to 50 mg/L, the zeta potentials decreased from  $-5.9$  to  $-41.4$  mV, and the corresponding aggregate sizes decreased from 600.4 to 540.3 nm. Therefore,  $\text{PO}_4^{3-}$  led to less aggregation of nano- $\text{TiO}_2$  than both  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ .

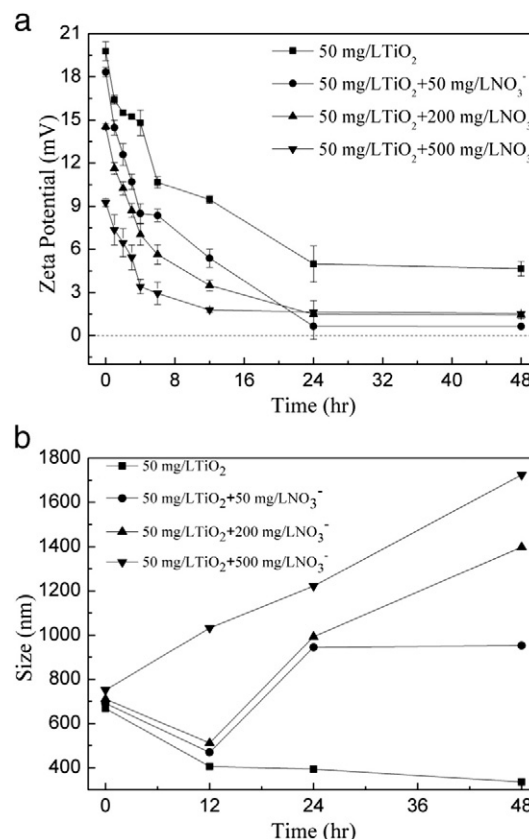
The aggregation of nano- $\text{TiO}_2$  could be explained by the DLVO theory (Ise and Sogami, 2005). The zeta potential of particles in the control experiment was 19.8 mV which is much higher than those when anions were present, which is possibly due to the adsorption of protons on the surface of nano- $\text{TiO}_2$ . The anions added could bond with  $\text{H}^+$  on the surface of nanoparticles, which resulted in the decrease of the zeta potential. So electric charge and consequent electrostatic repulsion forces were reduced, therefore the Van der Waals attractive forces between nanoparticles were strong enough to resist dispersion, thus the particles rapidly aggregated (Thio et al., 2011; Liu et al., 2013; Chen and Elimelech, 2007). When  $\text{Na}_3\text{PO}_4$  dissolves in water, this solution would be basic, the higher the  $\text{Na}_3\text{PO}_4$  concentration, the stronger the alkaline in solution. Therefore, the presence of  $\text{PO}_4^{3-}$  led to drop of the zeta potential from positive to negative, which resulted in an increased electrostatic repulsion forces among the particles, so the aggregation was prevented.

The aggregate size in  $\text{PO}_4^{3-}$  solution was much smaller than that in  $\text{NO}_3^-$  or  $\text{SO}_4^{2-}$  solution, which may be due to the different valences of anions (French et al., 2009). The electrostatic repulsion increased when the negative valence increased, which resulted in small aggregation size, so anion valence affected the aggregation of nano- $\text{TiO}_2$  much more heavily than anion concentration in a suspension.

### 2.3. Effect of dispersion time

The effect of dispersion time on the zeta potential and particle size of nano- $\text{TiO}_2$  was evaluated at various ionic concentrations. In a control suspension in which only nano- $\text{TiO}_2$  was added, the aggregate size decreased from 613.8 to 335.6 nm when the dispersion time increased from 0 to 48 hr (Fig. 3). With the extension of dispersion time, the zeta potential gradually approached zero, and the aggregate size gradually increased in the presence of  $\text{NO}_3^-$ . At  $\text{NO}_3^-$  concentration of 50 mg/L, the aggregate size increased from 691.2 nm at 0 hr to 952.9 nm at 48 hr. With the increase of  $\text{NO}_3^-$  concentration, the zeta potential decreased, consequently the aggregate size increased.

These results could be possibly due to the adsorption of  $\text{NO}_3^-$  on nano- $\text{TiO}_2$  which made the zeta potential approach zero (Zhu et al., 2014; Liu et al., 2011). Near the point-of-zero-charge, steric repulsive forces among nanoparticles decreased dramatically, and large size nanoaggregates formed. Thus, larger particles settled down over time, and smaller particles suspended in the suspension. Similar change trend was observed when  $\text{SO}_4^{2-}$  was present in the suspension (Fig. 4). With the extension of dispersion time, the zeta potential



**Fig. 3 – Effect of time on the zeta potential and size of nano- $\text{TiO}_2$  at different concentrations of  $\text{NO}_3^-$  in solutions. (a) Zeta potential; and (b) particle size.**

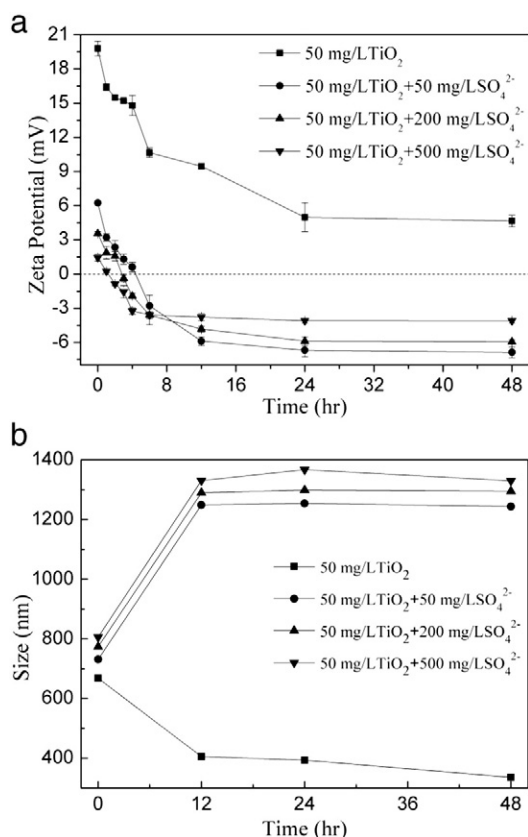
dropped below zero while still near the point-of-zero-charge, so the aggregate size gradually increased within 48 hr in the presence of  $\text{SO}_4^{2-}$ .

While  $\text{PO}_4^{3-}$  was added in a suspension, the zeta potential was negative, and decreased considerably with dispersion time (Fig. 5). The aggregate size decreased with dispersion time within 48 hr except for the lowest  $\text{PO}_4^{3-}$  concentration of 0.5 mg/L when the aggregate size increased within the first 24 hr. The dynamic change trend for  $\text{PO}_4^{3-}$  showed a similar one as that for  $\text{NO}_3^-$  or  $\text{SO}_4^{2-}$  only when  $\text{PO}_4^{3-}$  concentration was at the lowest one in the experiment, which is possibly due to decreased electrostatic repulsive forces among the particles when the zeta potential was around the point-of-zero-charge. When the zeta potential was far from the point-of-zero-charge, the particles dispersed easily, and small aggregates formed.

### 2.4. Aggregation kinetics of nano- $\text{TiO}_2$

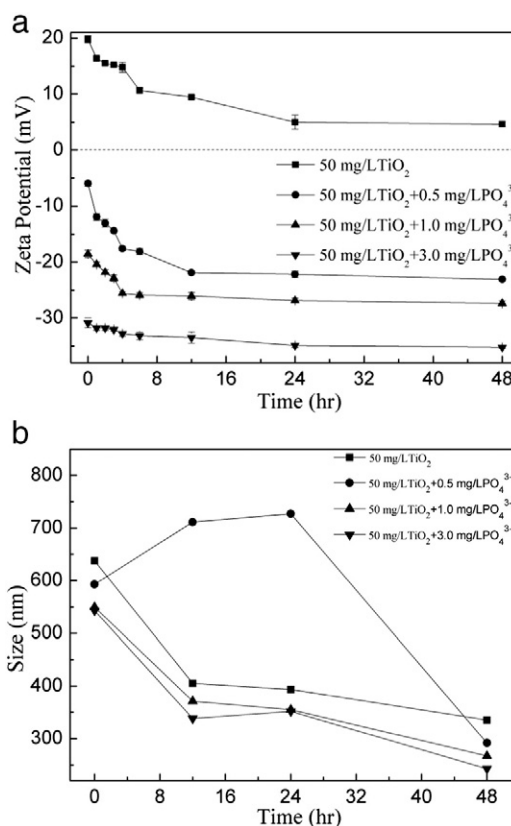
Aggregation kinetics of nano- $\text{TiO}_2$  were investigated under various concentrations of the three anions at 50 mg/L of nano- $\text{TiO}_2$  in suspensions. Data for the kinetic study collected within the first 30 min are presented in Fig. 6. It could be seen from Fig. 6 that the aggregation kinetics of nano- $\text{TiO}_2$  were related to both the type and concentration of the anions. For the control suspension in which only nano- $\text{TiO}_2$  was added, the aggregate sizes did not change considerably (Fig. 6a). With the addition of  $\text{NO}_3^-$  or  $\text{SO}_4^{2-}$ , both the size and size distribution





**Fig. 4 – Effect of time on the zeta potential and size of nano-TiO<sub>2</sub> at different concentrations of SO<sub>4</sub><sup>2-</sup> in solutions. (a) Zeta potential; and (b) particle size.**

of aggregates increased much more quickly than that in the control suspension, which means aggregation occurred (Fig. 6b and c). Fig. 6b and c also showed that both the aggregation speed and size of the aggregate increased with an increased concentration of NO<sub>3</sub><sup>-</sup> or SO<sub>4</sub><sup>2-</sup>. At the various PO<sub>4</sub><sup>3-</sup> concentrations, the aggregation sizes were less than that of either the control suspension or the suspensions with NO<sub>3</sub><sup>-</sup> or SO<sub>4</sub><sup>2-</sup>. The aggregation speeds for the PO<sub>4</sub><sup>3-</sup> suspensions were relative slow, and aggregate size maximized within 30 min, which is similar to the case of the control suspension (Fig. 6d). These phenomena could also be explained by the DLVO theory (Ise and Sogami, 2005). The anions added would bond with H<sup>+</sup> on the surface of the particles, resulting in decrease of the zeta potential. When the anion concentration was not high enough to bond with all or part of protons, the zeta potential was around the point-of-zero-charge, and repulsive electrostatic interactions among particles were decreased, therefore aggregation among particles was enhanced (Fig. 6b and c). When the anion concentration was high enough, there were redundant anions in a suspension besides those bonding with protons, so repulsive electrostatic increased, and consequently particle size was reduced. Meanwhile, a highly negative valence led to strong electrostatic repulsion and a consequent small aggregate size, so a low aggregation speed was resulted in. Therefore, the effect of anion valence on the aggregation of nano-TiO<sub>2</sub> was much stronger than that of concentration of the anion.



**Fig. 5 – Effect of time on the zeta potential and size of nano-TiO<sub>2</sub> at different concentrations of PO<sub>4</sub><sup>3-</sup> in solutions. (a) Zeta potential; and (b) particle size.**

### 3. Conclusions

The valence of anions affected the aggregation of nano-TiO<sub>2</sub> heavily. The higher the valence, the heavier the effect shows. Monovalent anion of NO<sub>3</sub><sup>-</sup> or divalent anion of SO<sub>4</sub><sup>2-</sup> in nano-TiO<sub>2</sub> solutions could decrease the zeta potential to around the point-of-zero-charge, while trivalent anion of PO<sub>4</sub><sup>3-</sup> could decrease the zeta potential from positive to negative. Consequently, PO<sub>4</sub><sup>3-</sup> led to smaller aggregate size of nanoparticles than NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>. When PO<sub>4</sub><sup>3-</sup> concentration was increased from 0 to 50 mg/L, the zeta potential decreased from +19.8 to -41.4 mV, and the corresponding particle size of nano-TiO<sub>2</sub> decreased from 613.2 to 540.3 nm. As SO<sub>4</sub><sup>2-</sup> concentration was increased from 0 to 500 mg/L, the zeta potential decreased from 19.8 to 1.4 mV, and the aggregate sizes increased from 613.2 to 961.3 nm. The change trend of nanoparticles for NO<sub>3</sub><sup>-</sup> was similar to that of SO<sub>4</sub><sup>2-</sup> although the range of variation for NO<sub>3</sub><sup>-</sup> was narrower.

With the extending of time, the presence of PO<sub>4</sub><sup>3-</sup> led to decreased aggregate size of nanoparticles, while the presence of NO<sub>3</sub><sup>-</sup> or SO<sub>4</sub><sup>2-</sup> resulted in increased ones. When PO<sub>4</sub><sup>3-</sup> concentration was 1.0 mg/L, aggregate size decreased from 549.7 nm at 0 hr to 267.3 nm at 48 hr. In the experimental concentration range, aggregate size decreased with the increase of anion concentration. However, at PO<sub>4</sub><sup>3-</sup> concentration of 0.5 mg/L, aggregate size increased from 0 hr to 24 hr.

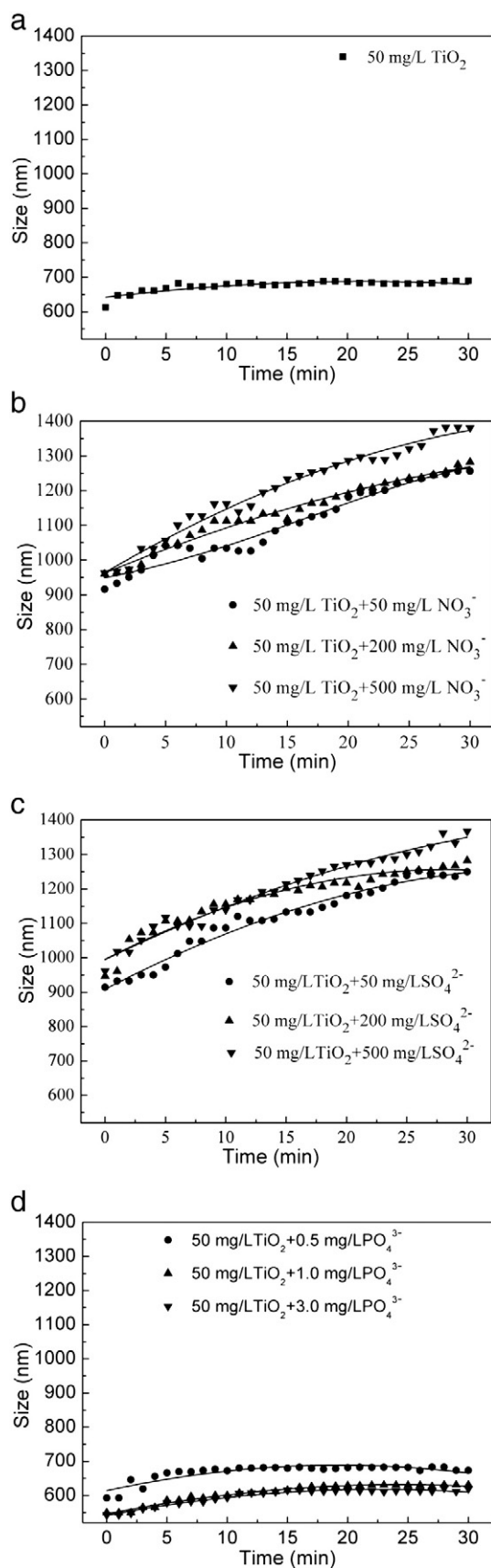


Fig. 6 – Aggregation kinetics of 50 mg/L nano-TiO<sub>2</sub> suspensions with different concentrations of anion concentrations. (a) control suspension; (b) NO<sub>3</sub><sup>-</sup>; (c) SO<sub>4</sub><sup>2-</sup>; and (d) PO<sub>4</sub><sup>3-</sup>.

At NO<sub>3</sub><sup>-</sup> concentration of 50 mg/L, aggregate size increased from 691.2 nm at 0 hr to 952.9 nm at 48 hr. An increased concentration of NO<sub>3</sub><sup>-</sup> led to a decreased zeta potential and a consequent increased aggregate size. The change trend of nanoparticles for SO<sub>4</sub><sup>2-</sup> was similar to that for NO<sub>3</sub><sup>-</sup>.

Kinetic study showed that aggregate sizes of nanoparticles decreased with the extension of time when PO<sub>4</sub><sup>3-</sup> existed, and increased when NO<sub>3</sub><sup>-</sup> or SO<sub>4</sub><sup>2-</sup> existed. The presence of NO<sub>3</sub><sup>-</sup> or SO<sub>4</sub><sup>2-</sup> facilitated aggregation rapidly, and the higher the concentration of NO<sub>3</sub><sup>-</sup> or SO<sub>4</sub><sup>2-</sup>, the more rapid the aggregation speed. In comparison, the presence of PO<sub>4</sub><sup>3-</sup> led to aggregation much slowly.

The stability, toxicity and ultimate fate of nano-TiO<sub>2</sub> are more closely associated with the components in aqueous solutions. Our results may provide an insight into the potential fate of nano-TiO<sub>2</sub> in natural aqueous and engineered environments. In addition, there are many other nanomaterials that existed in the environment except nano-TiO<sub>2</sub>, such as silver nanomaterials, iron nanomaterials, carbon nanomaterials. These results can also lead to a better understanding of the dispersion and aggregation of these nanomaterials in aqueous solutions.

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