

# The effect of electrolytes on the aggregation kinetics of titanium dioxide nanoparticle aggregates

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**Abstract** Metal oxide nanoparticles (NPs) are receiving increasing attention due to their increased industrial production and potential hazardous effect. The process of aggregation plays a key role in the fate of NPs in the environment and the resultant health risk. The aggregation of commercial titanium dioxide NP powder (25 nm) was investigated with various environmentally relevant solution chemistries containing different concentrations of monovalent ( $\text{Na}^+$ ,  $\text{K}^+$ ) and divalent ( $\text{Ca}^{2+}$ ) electrolytes. Titanium dioxide particle size increased with the increase in ion concentration. The stability of titanium dioxide also depended on the ionic composition. Titanium dioxide aggregated to a higher degree in the presence of divalent cations than monovalent ones. The attachment efficiency of NPs was constructed through aggregation kinetics data, from which the critical coagulation concentrations for the various electrolytes are determined (80, 19, and 1 meq/L for  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Ca}^{2+}$ , respectively). Our results suggest that titanium dioxide NP powders are relatively unstable in water and could easily be removed by adding multivalent cations so hazardous potentials decrease in aquatic environment.

**Keywords** Nanoparticle · Titanium dioxide · Cation · Attachment efficiency · Ionic strength

## Introduction

Nanoparticles (NPs) have been used in many commercial applications, including cosmetics and health care products that are present in our daily life. Lux research (2008) estimated that the value of nano-intermediates and nano-enabled products will be more than US\$2.5 trillion by 2014. This rapid increase in the production and use of engineered NPs will likely result in a release of these materials to the natural environment (Mueller and Nowack 2008). Without a firm understanding of NP transport and transformation following release to the environment, we will not be able to estimate biological exposure to NPs or gauge ecological or human health risk.

Titanium dioxide NPs are one of the most prevalent manufactured nanomaterials and widely used in several personal care products (e.g., sunscreens). Recently, more research has focused on the release of NPs into the environment and the resulting property changes of NPs (Domingos et al. 2009; Nowack and Bucheli 2007). Of particular interest is the NP size change that occurs under various environmental conditions. For example, aggregates of NPs (formed after NP release) may not partition into cell membrane and transport through human or animal tissue to cause the nanotoxicity indicated by (Oberdörster

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2004). Gao et al. (2009) also indicated that the toxicity of NPs varies significantly with water chemistry. The ionic strength and ionic composition are likely to have a significant effect on the stability of several types of NPs in water (Sano et al. 2001; Chen and Elimelech 2006; Zhang et al. 2008b; Saleh et al. 2008a). French et al. (2009) had researched that the particle size of their synthesized nano-TiO<sub>2</sub> would be strongly influenced by ionic strength. However, they did not present the critical coagulation concentrations (CCC) for different electrolytes and their NPs are not widely used. Commercial NPs are often sold in dry powder form due to the easy shipping. Although Zhang et al. (2008b) evaluated several disaggregation approaches and indicated that it is difficult to disperse dry commercial NPs in water, one ultrasonic method that can disaggregate large NP aggregates has been proposed in our previous study (Tso et al. 2010). Due to the limited study regarding the stability of commercial TiO<sub>2</sub> NP powders in water, the aggregation behaviors of TiO<sub>2</sub> NPs and the effect of common electrolytes on aggregation kinetics need to be studied.

Therefore, the aim of this study is to investigate the aggregation kinetics of TiO<sub>2</sub> NPs in aqueous solutions containing various concentrations of three common sodium, potassium, and calcium cations by a photon correlation spectroscopy (PCS). TiO<sub>2</sub> NP stability, i.e., the attachment efficiency of TiO<sub>2</sub> NPs versus the electrolyte concentration, was constructed using the aggregation kinetics. The CCC values of TiO<sub>2</sub> NPs for various electrolytes were determined. The zeta-potentials and other physico-chemical properties were measured to elucidate the aggregation process and used in the theoretical calculations. These findings allow us to understand the aggregation behaviors of TiO<sub>2</sub> NP powders in water and to facilitate the control of NPs in different ionic compositions and strengths in the aqueous environment.

## Materials and methods

### Characteristic of titanium dioxide nanomaterials

Titanium dioxide NPs (25 nm; 3.9 g/mL) were purchased from Aldrich. The particle size and morphology of TiO<sub>2</sub> NP powder were determined by field emission scanning electron microscopy (FE-SEM, JEOL JEM-2010) after attaching it to the sample stub with the

carbon tap. Three electrolytes, including sodium chloride, potassium chloride, and calcium chloride were all obtained from Acros Chemical. All solutions were prepared from pure water. Pure water was double-distilled and deionized with a Milli-Q water purification system (Millipore). According to Marion–Babcock equation (Marion and Babcock 1976) and the resistivity of pure water (18.2 MΩ cm), the ionic strength of pure water could be around  $7.55 \times 10^{-4}$  meq/L. In aqueous systems, particle size was determined by a PCS (N5, Beckman coulter, UK). The PCS measurement indicated that NPs suspended in water presented as aggregates, so further treatments were needed (Tso et al. 2010). The PCS measurements were conducted by positioning the detector at 90°. And we also used transmission electron microscopy (TEM, JEOL JEM-200CX) to measure the particle size of NPs in aqueous solutions with each of these three electrolytes. The sample solution was dropped onto a carbon-coated copper grid and dried for TEM measurement.

NP stock suspensions were prepared by adding the appropriate amount of TiO<sub>2</sub> NP powder to 1 L of pure water followed by treatment, at ambient temperature, with a sonicator (Misonix Sonicator 3000) (Tso et al. 2010). All suspension samples were used only once. Particle size measurements were conducted on the nanomaterial suspension at room temperature ( $25 \pm 1$  °C). Both the average particle size and particle size distributions of TiO<sub>2</sub> nanomaterial were measured by PCS with time.

The experiments of particle size change with monovalent and divalent electrolytes

The aggregation experiments of titanium dioxide NPs were conducted over a wide concentration range of monovalent (NaCl and KCl) and divalent (CaCl<sub>2</sub>) electrolytes, respectively. To prepare the test solutions, deionized water with different cations (Na<sup>+</sup>, K<sup>+</sup>, and Ca<sup>2+</sup>) were adjusted to the desired concentration ranges (from 0.2 to 100 mg/L). At that time, a 20 mg/L sample of titanium dioxide NP underwent 30 W of sonication. The final preparation method involved diluting the nanomaterial suspensions to around 10 mg/L and testing that the particle size of these suspensions neared the nanoscale range. The particle size change with time for the different concentrations of these three cations in titanium dioxide nanomaterial suspensions was measured using PCS.

### NP aggregation kinetics and CCC

Based on the aggregation kinetic experiments from the determination of average particle size with time, the aggregation rate constants were estimated by the pseudo-first-order kinetic model. The aggregation rate constants ( $k$ ) at different cation strengths were obtained. With the increase of cation concentrations,  $k$  values do not change a lot and then the fastest aggregation rate constant ( $k_{fast}$ ) was observed. The attachment efficiency,  $\alpha$ , can be described in the following equation (Chen and Elimelech 2006).

$$\alpha = \frac{k}{k_{fast}} \tag{1}$$

The attachment efficiencies,  $\alpha$ , for titanium dioxide NP aggregates at different cation strengths were estimated from the obtained aggregation rates. The attachment efficiency ranging from 0–1 serves an aggregation process of the NPs in different electrolyte concentrations. Based on two distinct aggregation kinetics regimes in the plot of the attachment efficiencies versus salt concentrations, the crossover of the slope of attachment efficiencies dependent on cation concentrations ( $\alpha < 1$ ) and the plateau independent on cation concentrations ( $\alpha = 1$ ) was taken to account for the CCC.

### Net NP interaction energy

In colloid chemistry, the attractive forces and electrostatic interactions between particles can be described by Derjaguin–Landau–Verwey–Overbeek (DLVO) theory. NP interaction energies can be also calculated by using classical DLVO theory (Dunphy Guzman et al. 2006). The van der Waals interaction ( $V_{VDW}$ ) was calculated using Eq. 2 (Elimelech et al. 1998; Hiemenz and Rajagopalan 1997).

$$V_{VDW} = \frac{-A}{6} \left[ \frac{2a^2}{s(4a + s)} + \frac{2a^2}{(2a + s)^2} + \ln s \frac{(4a + s)}{(2a + s)^2} \right] \tag{2}$$

Repulsive electrostatic interaction ( $V_{ES}$ ) was calculated using Eq. 3 (Elimelech et al. 1998; Hiemenz and Rajagopalan 1997).

$$V_{ES} = 2\pi\epsilon_r\epsilon_0a^2\zeta^2\ln(1 + e^{-ks}) \tag{3}$$

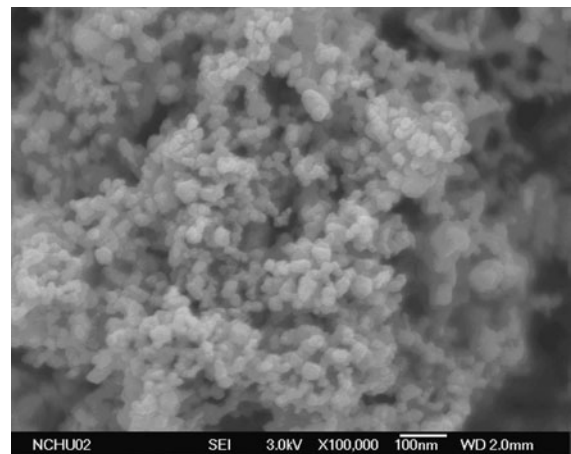
where  $a$  is the particle radius,  $A$  is the Hamaker constant,  $\epsilon_r$  is the relative dielectric constant of the

liquid,  $\epsilon_0$  is the permittivity of vacuum,  $\zeta$  is the zeta potential,  $s$  is distance between the surface of two interacting NPs, and  $k$  is the inverse Debye length.

## Results

### Characteristics of NPs

The SEM image of the dry titanium dioxide nanopowder showed agglomerates of spherical NPs (Fig. 1). In theory, the aggregation coefficients can be determined by a ratio of van der Waals attractive energy to the sum of the kinetic energy of Brownian motion and the change in potential energy (Yaremko et al. 2006). Because the calculated aggregation coefficients of NP powders stored under dry conditions are much larger than 1 (Zhang et al. 2008b), the TiO<sub>2</sub> NPs aggregated when they are stored as powders. Zhang et al. (2008b) also indicated that the titanium dioxide NP aggregates (around 500 nm) in water can be obtained after several dispersion treatments. In our previous study (Tso et al. 2010), the particle size of three metal oxide NP aggregates can be disaggregated down to around 200 nm after ultrasonication. The TiO<sub>2</sub> NPs are primarily anatase (Shih and Tso 2012), which is consistent with the anatase purity of 99.7 % reported by Aldrich. The zero point of charge (pH<sub>zpc</sub>) is around 5.9 (Shih and Tso 2012). It is consistent with the average reported value for the pH<sub>zpc</sub> of bulk titanium dioxide (Kosmulski 2002).



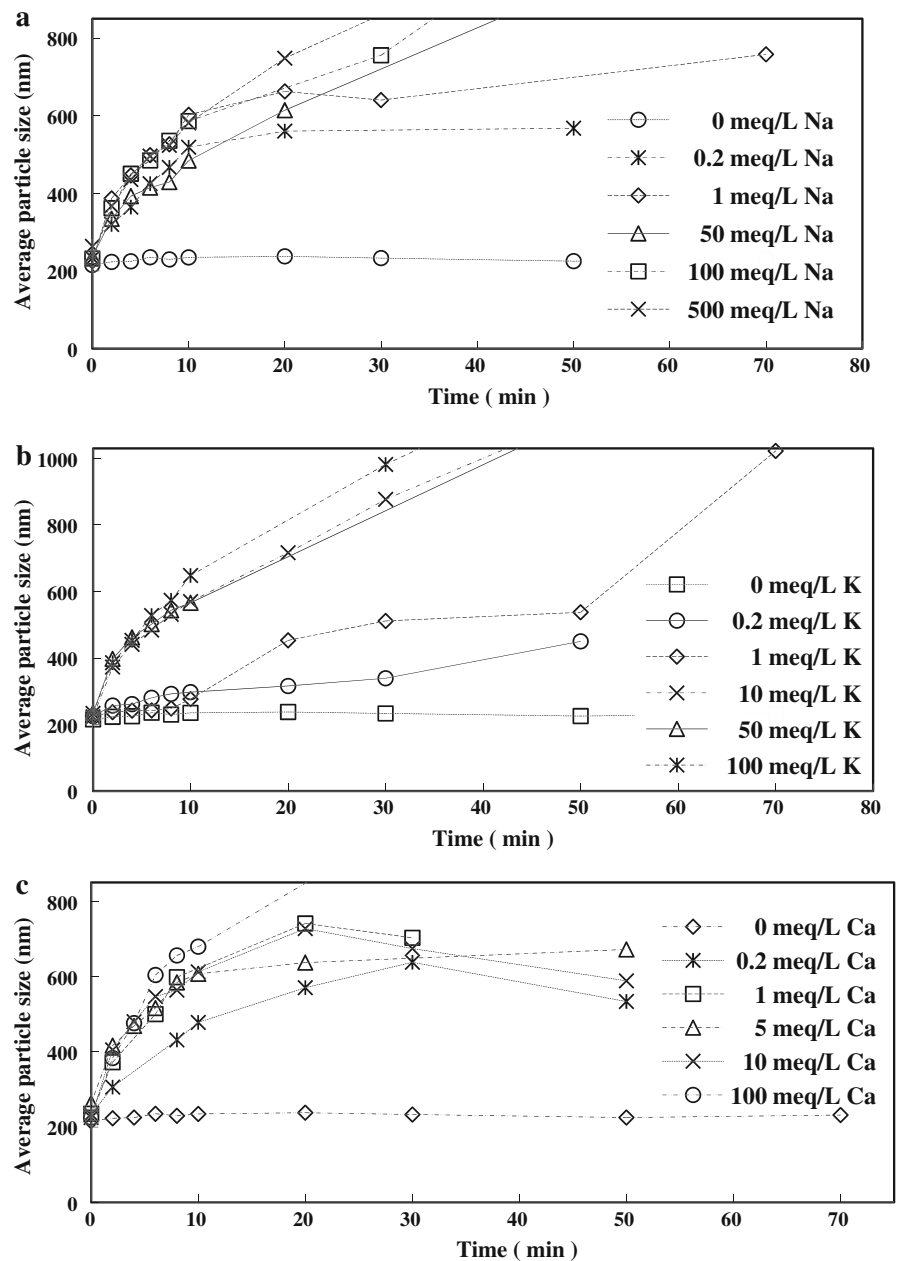
**Fig. 1** The SEM images of dry titanium dioxide NP powder

Aggregation kinetics of titanium oxide NP aggregates in the presence of sodium, potassium and calcium cations

The aggregation kinetics of the titanium dioxide NP aggregates was first studied in the absence of electrolytes (Fig. 2). In the absence of ions in solutions, the ultrasonicated titanium dioxide NP aggregates maintain their initial particle sizes during the experiments.

The particle size changes of the titanium dioxide NP aggregates in water as a function of electrolyte concentrations are also shown in Fig. 2. Beginning at low ionic strengths of three electrolytes, sodium chloride, potassium chloride, and calcium chloride, an increase in the ionic strength leads to a corresponding increase in the aggregation rate. However, increases in the ionic strength do not have a significant influence on the aggregation rate at higher ionic strengths for these

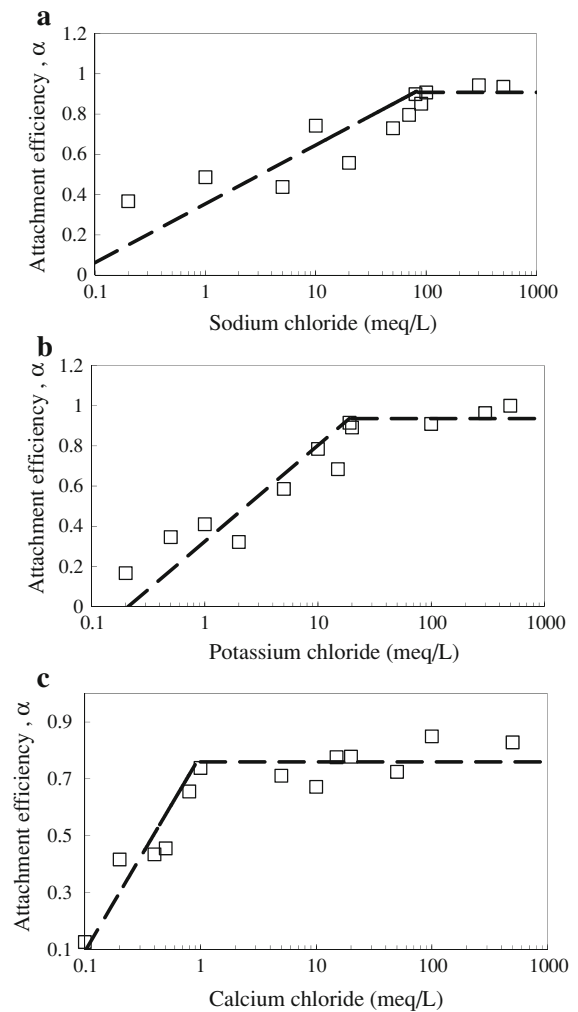
**Fig. 2** The particle size change of titanium dioxide NP aggregates at different concentrations of sodium chloride (a), potassium chloride (b) and calcium chloride (c) with time



three electrolytes. Distinct reaction-limited (slow) and diffusion-limited (fast) aggregation regimes are found for the titanium dioxide NPs in the presence of Na<sup>+</sup>, K<sup>+</sup>, and Ca<sup>2+</sup> chloride electrolytes. DLVO-type interactions mainly dominate the aggregation process for the titanium dioxide NP aggregates. This is also consistent with the aggregation observations of other NPs in different electrolytes (Chen and Elimelech 2006; Chen et al. 2006; Saleh et al. 2008b). In the presence of 100 meq/L sodium, the particle sizes of titanium dioxide aggregates rapidly increased (after 50 min) to larger than 1 μm (Fig. 2a). To directly quantify available charge and compare ionic strength for different valence of electrolytes, the normality unit (meq/L) instead of molarity (mmol/L) was used. Similar results were observed for potassium at 10 meq/L and calcium at 1 meq/L, respectively. Divalent cations are more effective than monovalent cations in reducing the electrostatic energy barrier to aggregation, as is commonly found for most colloids and NPs in aqueous solutions (Chen and Elimelech 2006; Zhang et al. 2008a; French et al. 2009).

The attachment efficiencies between NPs differ for each cation (Fig. 3). The attachment efficiencies are calculated from the aggregation kinetics using Eq. 1. The average of the aggregation rates in the diffusion-limited regime independent of the salt concentrations is taken as  $k_{fast}$ . By taking the initial slope of the attachment efficiencies at lower salt concentrations, the aggregation rates in this reaction-limited regime increase with the salt concentrations. When the salt concentration reaches the CCC [80 meq/L for sodium (Fig. 3a)], the attachment efficiency is close to 1 because the aggregation rate is a constant and nearing the fastest rate possible in the diffusion-limited regime. Extrapolating the intersections between the two regimes yields the CCC values of 19 and 1 meq/L for potassium and calcium, respectively (Fig. 3b, c).

The particle size distributions of titanium dioxide NP aggregates at their CCC initially and after 70 min were shown in Fig. 4. A mono-dispersed pattern of titanium dioxide NP aggregates was observed initially. After 70 min, the particle sizes at their CCC obviously increased to greater than microscale. In the presence of sodium, bimodal peaks at around 150 and 2000 nm were observed with most titanium dioxide NP aggregates in the range of 900 and 2700 nm (Fig. 4a). In the presence of potassium, titanium dioxide NP aggregates exhibited a similar aggregation tendency. Only a



**Fig. 3** The attachment efficiencies of titanium dioxide NP aggregates in different sodium chloride (a), potassium chloride (b) and calcium chloride (c) concentrations

small fraction is present around 400 nm and most particles were larger than 1 μm. For 1 meq/L calcium, a broad particle distribution was observed. The average particle size of 4200 nm for 1 meq/L calcium is significantly larger than the 2000 nm for 80 meq/L sodium and the 3100 nm for 19 meq/L potassium. Representative TEM images of the titanium dioxide NP aggregates in pure water after sonication and in the presence of three different electrolytes are shown in Fig. 5. In the presence of cations, the aggregates composed of NPs with a broad particle size distribution. The enhancement of particle aggregation in the presence of electrolytes was also confirmed by electron microscopy.

The zeta-potentials of titanium dioxide NP aggregates as a function of salt concentrations are shown in Fig. 6. The zeta-potentials generally increased with the increasing concentrations for these three different cations. The zeta-potentials rapidly increased from  $-2$  to  $30$  mV as the calcium chloride concentration increased from  $0.2$  to  $100$  meq/L at  $\text{pH } 7.5 \pm 0.6$ . In the presence of sodium at  $\text{pH } 7.7 \pm 0.6$ , the zeta-potentials were around  $-8$  mV for sodium concentrations less than  $20$  meq/L and then increased to positive values slowly as the sodium concentrations increased. The charge neutralization of sodium monovalent cations is less effective than that of calcium divalent cations, which contributed to a higher CCC of sodium than calcium. Addition of potassium chloride also resulted in an increase of ionic strength and zeta-potentials. Due to the fact that the aqueous pH ( $7.3 \pm 0.3$ ) was closer to the  $\text{pH}_{\text{zpc}}$  for potassium chloride than for the other two electrolytes, the zeta-potentials were close to zero and did not change significantly during the experiments. It may result in a smaller CCC of potassium than that of sodium.

#### Interaction energy of the titanium oxide NP aggregates with $\text{Na}^+$ , $\text{K}^+$ , $\text{Ca}^{2+}$

The interaction energies of NP aggregates in water can be analyzed using DLVO theory (Handy et al. 2008). DLVO theory accounts for two forces between particles: van der Waals attraction and electrical double layer (EDL) repulsion. The sum of these two forces can determine whether the net interaction between particle aggregates is either formed or not (Hiemenz and Rajagopalan 1997). The effects of different cations and concentrations on the representative DLVO calculations for titanium dioxide NP aggregates are shown in Fig. 7. The EDL repulsive energy is dominant and net repulsive energy barriers between the titanium oxide NP aggregates exist in solutions with very low ionic strength. As shown in Fig. 7a, the net energy barriers decreased with the increase of sodium concentrations. Comparing the concentrations from  $1 \times 10^{-5}$  meq/L (close to zero)  $\text{Na}^+$  to  $100$  meq/L  $\text{Na}^+$ , the net repulsive energy barrier decreased significantly. As the salt concentration closes to the CCC of the cation, the electrolyte concentration is high enough to completely eliminate the electrostatic energy barrier, resulting in particle aggregation. Similar results were also found for the

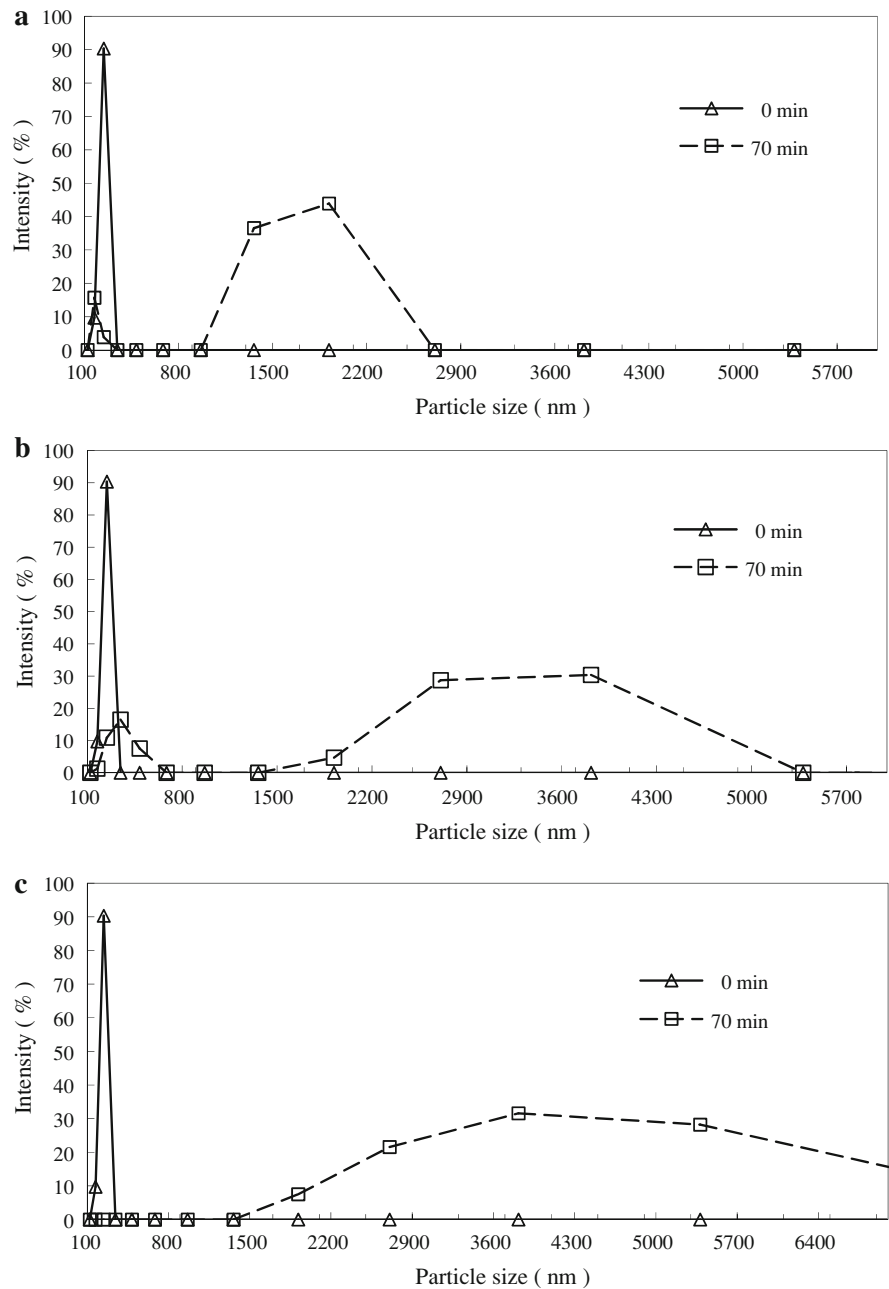
other two cations in Fig. 7b, c for potassium and calcium, respectively. Calcium diminishes the energy barrier at a lower concentration as compared to sodium and potassium. It indicates that the aggregation behavior of the titanium oxide NP aggregates in the presence of electrolytes is generally in agreement with the DLVO theory.

## Discussion

Commercial NPs are generally received as dry powder form. The particle size of titanium dioxide nanopowders from Aldrich in the nanoscale was confirmed by SEM (Fig. 1) although the observed particle size is bigger than the vendor reported. Zhang et al. (2008b) also observed titanium dioxide NP aggregates during storage as a dry powder. The aggregation of NPs was also found once these NP powders were dispersed into water. After several disaggregation approaches, it was found that several dry NP powders could only be disaggregated in water to sizes around  $500$  nm (Zhang et al. 2008b). Adams et al. (2006) also indicated that the true size of NPs in suspensions was significantly different from the advertised size of starting powders. We evaluated many disaggregation methodologies in our previous study (Shih and Tso 2012) and have adopted an ultrasonic method to disaggregate metal oxide powders in water to around  $200$  nm.

In the absence of electrolytes, DLS measurements did not show any significant aggregation of titanium oxide NP aggregates during the experiments at around  $\text{pH } 7$  (Fig. 2). With the increase of sodium concentrations, the aggregation process of titanium oxide NP aggregates was more pronounced and the particle size even increased up to microscales after  $50$  min in the presence of  $100$  meq/L NaCl (Fig. 2). French et al. (2009) also indicated that  $\text{TiO}_2$  particles with sizes of  $50$ – $60$  nm aggregated to microscale within  $15$  min at  $\text{pH } 4.5$  with increasing ionic strength to  $0.0165$  M NaCl. Similar enhancement of the aggregation process by increasing salt concentration was found, but with slightly slower aggregation kinetics of our  $\text{TiO}_2$  NP aggregates in our observations. Given that at  $\text{pH } 7.7$  in our study, the surface of  $\text{TiO}_2$  NPs has an overall negative charge,  $\text{Na}^+$  cations would act as electrostatic bridges between  $\text{TiO}_2$  particle aggregates to promote the aggregation process but not for  $\text{TiO}_2$  NPs at  $\text{pH } 4.5$  with positive charge in French et al.'s system (2009).

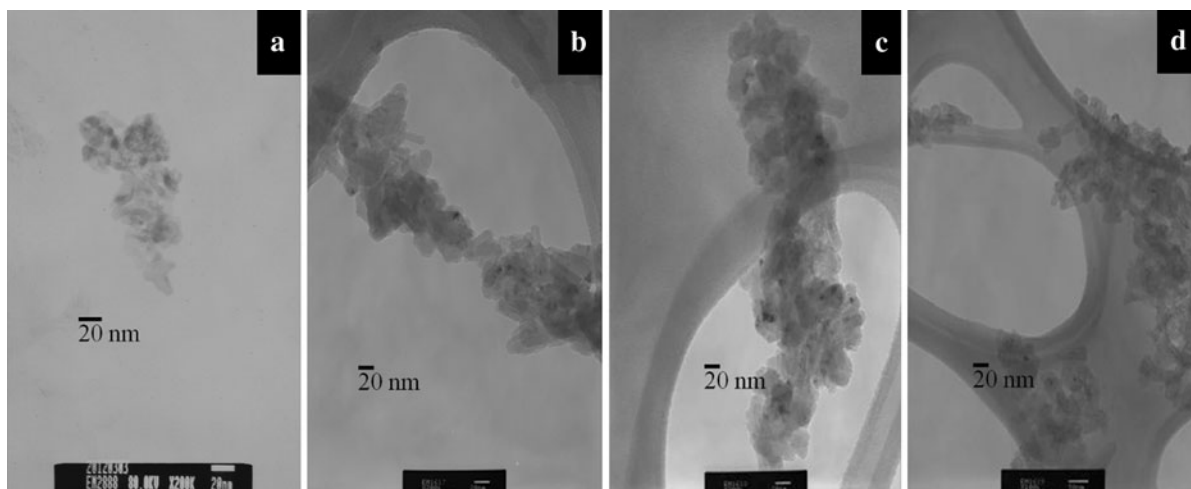
**Fig. 4** The particle size intensities of titanium dioxide NP aggregates with 80 meq/L  $\text{Na}^+$  (a), 19 meq/L  $\text{K}^+$  (b) and 1 meq/L  $\text{Ca}^{2+}$  (c) at different reaction time



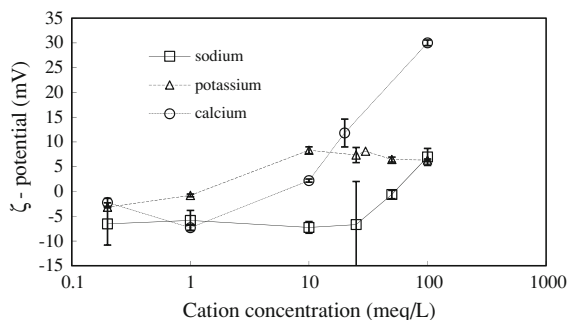
On the other hand, French et al.'s (2009) primary particle size was significantly fourfold smaller than our primary particle size of around 200 nm. Phenrat et al. (2008) indicated that the smaller the NP, the smaller the electrostatic repulsive interactions between them. The difference in size could result in the rapid aggregation of the smaller particles. Our powerful ultrasonication disaggregation method and

the different surface properties of NPs may also account for this observed discrepancy.

The aggregation kinetics and attachment efficiencies of the  $\text{TiO}_2$  NPs have been studied over sodium chloride and potassium chloride concentrations range from 0.2 to 500 meq/L and a calcium chloride concentration range from 0.1 to 500 meq/L (Figs. 2, 3). In the reaction-limited (unfavorable) regime, the



**Fig. 5** TEM images of titanium dioxide NP aggregations in pure water (a) and in the presence of calcium (b), potassium (c) and sodium (d) cations



**Fig. 6**  $\zeta$ -Potentials of titanium dioxide NPs aggregates under different cation concentrations

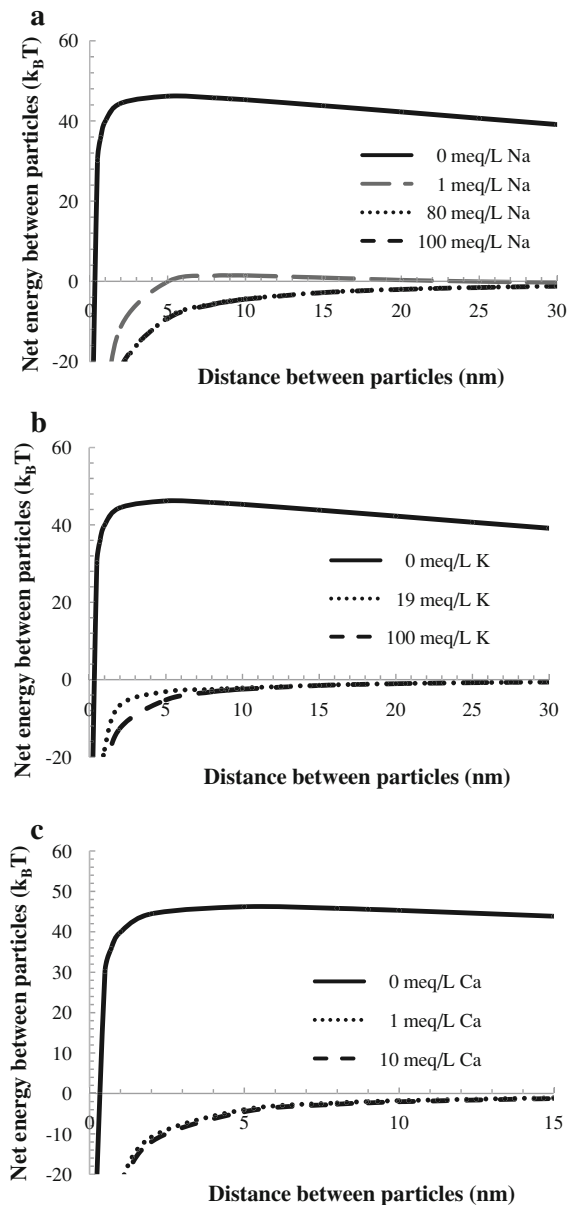
aggregation rates increased with the increase in electrolyte concentrations. The increase in the salt concentration decreases the surface charge of the  $\text{TiO}_2$  NPs, and diminishes the repulsive energy barrier between particles, thus promoting the aggregation kinetics. The attachment efficiency is dependent on the electrolyte concentration in this reaction-limited regime ( $\alpha < 1$ ). As the energy barrier is eliminated above the CCC concentration (80, 19, and 1 meq/L for  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Ca}^{2+}$ , respectively), it leads to diffusion-controlled aggregation ( $\alpha = 1$ ).

The lowest concentration of 1 meq/L calcium in this study was utilized to reach the favorable aggregation regime for  $\text{TiO}_2$  NPs. Due to the limited studies on the aggregation of  $\text{TiO}_2$  NPs, the CCC values from other nanomaterials were reported. Zhang et al. (2008a) also indicated that a low concentration of

1 meq/L calcium was required to induce the aggregation of CdTe quantum dots. Previously reported CCC value for single-wall carbon nanotube was 0.4 meq/L (Sano et al. 2001), which is close to our obtained value. We could not find any CCC value of KCl for any uncoated NPs, but no aggregation was observed for thioglycolated CdTe quantum dots up to 150 meq/L by Zhang et al. (2008a). For sodium ions, our derived CCC value of 80 meq/L for  $\text{TiO}_2$  NPs is close to a previously reported CCC value of 85 meq/L for fullerene (Mchedlov-Petrosyan et al. 1997). Due to different properties of these nanomaterials, various CCC values were observed. The CCC values for  $\text{Ca}^{2+}$  and  $\text{Na}^+$  are in the range from 0.4 to 12 meq/L (Zhang et al. 2008a; Chen and Elimelech 2007, 2006) and 20–160 meq/L (Mchedlov-Petrosyan et al. 1997; Chen and Elimelech 2007, 2006; Saleh et al. 2008b) for uncoated NPs, respectively, which is comparable to our result.

The CCC value of calcium is only 1/80th of  $\text{Na}^+$  and around 1/4th of  $\text{K}^+$  for titanium dioxide NPs. Calcium concentration was lower than both sodium and potassium because divalent cations are more effective in reducing the electrophoretic mobility of titanium dioxide NPs than monovalent cations like sodium and potassium. CCC dependence on counterion valence,  $z$ , ranges from  $z^{-2}$  to  $z^{-6}$ , which is in agreement with the Schulze–Hardy law. It indicates that the CCC values of salts for titanium dioxide NPs depend on cation valences and decreased with the increase in the valence of cations.





**Fig. 7** The net energy between particles of titanium dioxide in different sodium chloride (a), potassium chloride (b) and calcium chloride (c) concentrations

The particle size distribution of the NPs changed with time in the presence of these three cations. With the increase of cation valence, the mean aggregate size is larger and the size distribution is broader (Fig. 4). A broad particle size distribution observed in TEM images of the titanium dioxide NP aggregates corroborated the DLS measurements. In TEM images with sodium (Fig. 5), the subsequent linkage and gelation of original

NP aggregates into bigger aggregates may cause the bimodal distribution (Fig. 4). Compared to the original size distributions, the rapid aggregation and broad particle size distribution of nanoscale particles were observed in this study and other literatures (French et al. 2009; Zhang et al. 2008b; Chen and Elimelech 2007) in the presence of electrolytes.

The zeta-potentials generally increased with the increase of cation concentrations (Fig. 6). For these different ionic strengths, the zeta-potentials of TiO<sub>2</sub> with sodium are more negative than those with calcium. The zeta-potentials increased more rapidly in the presence of calcium as compared to two monovalent cations. This has also been observed by Zhang et al. (2008a) and may be related to the charge neutralization of divalent cations and therefore effective compression of the EDLs. The increase in ionic strength resulted in compression of the EDL and therefore a decrease in the EDL repulsive energy.

Theoretical DLVO prediction of titanium dioxide NP aggregates was calculated to elucidate the effect of EDL compression with different cations and concentrations (Fig. 7). Divalent cation Ca<sup>2+</sup> can effectively compress the EDL and then decrease the energy barrier at a lower ionic strength than monovalent cations. For potassium, a lower ionic strength can eliminate the energy barrier as compared to sodium, which is consistent with CCC observations. In the absence of electrolytes, our calculated energy barrier is around  $1.7 \times 10^{-19}$  J, which is similar to  $1.9\text{--}1.1 \times 10^{-19}$  J for commercial titanium oxide NP aggregates calculated by Zhang et al. (2008b). The energy barriers decreased with the increase of cation concentrations because the repulsive forces became weak with increasing cation concentrations. Thus, the aggregation of titanium dioxide proceeded easily. Sodium, potassium and calcium cations can compress the EDL of these NPs. The increase in ionic strength resulted in the compression of the EDL and then decrease in the EDL repulsive energy. For example, the calculated Debye layer thickness of titanium dioxide NPs,  $k^{-1}$ , decreased from 96 nm at  $1 \times 10^{-5}$  meq/L to 1.0 nm at 100 meq/L for sodium. Domingos et al. (2009) also found that the decrease of Debye layer thickness of NPs with the increase of sodium nitrate promoted the aggregation process. The increasing ion strength in estuarine systems would decrease the repulsive forces between particles and enhance aggregation. Consequently, the particle size rapidly increased with the increase of Na<sup>+</sup>, K<sup>+</sup>, and Ca<sup>2+</sup> concentrations.

## Conclusion

In aqueous systems, the investigations of the characteristics and stability of TiO<sub>2</sub> nanomaterials with different compositions and concentrations of cations indicated that the aggregation process of titanium dioxide NPs takes place quickly in aqueous solutions in the presence of cations. Even after the TiO<sub>2</sub> NP powders have been disaggregated by ultrasonication, the NP aggregates do not maintain their particle size in aqueous solutions containing electrolytes. The aggregation process of TiO<sub>2</sub> NP aggregates depends on the ionic composition and ionic strength of electrolytes in water. The increase of cation concentrations enhanced the aggregation rate of TiO<sub>2</sub> particles. Lowering the energy barrier at high cation concentrations allows the titanium dioxide NPs to more easily to aggregate. Three CCCs for different electrolytes on titanium dioxide NPs are 80 meq/L for sodium chloride, 19 meq/L for potassium chloride, and 1 meq/L for calcium chloride, respectively. Titanium dioxide particles aggregated more significantly in the presence of divalent cations than with monovalent ones. Based on the DLVO theory, the net energy barrier decreased rapidly in the presence of calcium which could contribute to the fast aggregation of titanium dioxide particles at a low concentration of calcium. The removal of titanium dioxide NPs can be more easily achieved by the rapid precipitation with multivalent electrolytes. The ionic composition and strength of electrolytes play an important role on NPs of titanium dioxide and affect their stability in water, as a result, the hazardous risk of titanium dioxide NP powder consequential decreases in aqueous environment.

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