Interpreting unique colloidal response of TiO$_2$ nanomaterials to controlled sonication for understanding of their assembly configuration in water

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ABSTRACT

It is important to determine the assembly configuration of engineered nanomaterials (ENMs) because assembly configuration influences their fate and transport behavior in the aquatic environment. Aggregated particles are more subject to segregation upon changes of environmental conditions (and vice versa) than agglomerated particles. As a strategic tool for investigating the time-resolved reversible segregating and assembling behavior of ENMs and thus estimating their assembly configuration, a controlled sonication process was proposed. It was hypothesized that the unique colloidal response of ENMs to sonication, with respect to changes in size, might be their intrinsic property associated with assembly configuration. As a model ENM, three different TiO$_2$ particles with unique properties (commercial P-25 and UV 100 and home-made (HM) TiO$_2$) were examined with programmed sonication processes under various environmental settings. When they were dispersed in water, all TiO$_2$ particles tested obviously assembled to form much larger clusters. Size of P-25 decreased immediately upon sonication and did not change under the subsequent quiescence step while sizes of UV 100 and HM gradually decreased and then slowly recovered back to their initial sizes. The trend was generally observed in all conditions tested. The unique colloidal response of TiO$_2$ could be explained by its properties associated with assembly configuration.

Key words | aggregation and agglomeration, aquatic fate and transport, environmental impact, nanomaterials, sonication, titanium dioxide

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INTRODUCTION

Engineered nanomaterials (ENMs) have been utilized in many new applications. Particularly, metal and metal oxide nanoparticles (NPs) are widely studied in the remediation of contaminated water and soil (Mueller & Nowack 2010). With the increasing usage of NPs in commercial products and environmental remediation areas, concern about their potential environmental risk has been also raised (Hessler et al. 2012). Since not all NPs released to the environment are available for exposure of human and living organisms to them, it is important to understand their colloidal behavior under various conditions, which controls their fate and transport in the environment (Sygouni & Chrysikopoulos 2015).

As one of the most important and widely used ENMs, titanium dioxide (TiO$_2$) has been studied as a photocatalyst and pigment. TiO$_2$ particles are insoluble in water and they assemble together naturally to form larger clusters like other ENMs. As a result, overall size of TiO$_2$ particles is much larger than their crystal size and thus they tend to precipitate quickly and filter out easily more than what is extrapolated based on their primary particle size (Keller et al. 2010). The reactivity, mobility, availability of TiO$_2$ particles can change significantly due to their assembling in aqueous media (Domingos et al. 2009). This implies the assembly configuration of TiO$_2$ particles should be always considered when their fate and transport behavior is assessed.

Many studies have been conducted to understand the stability and mobility of TiO₂ particles under various treatment conditions and in natural water resources (Zhang *et al.* 2008; Gottschalk *et al.* 2009; Keller *et al.* 2010; Brunelli *et al.* 2013). However, there have been few systematic studies to understand the assembly configuration of TiO₂ particles (i.e. how TiO₂ particles form assemblages and segregates over time), not to mention other ENMs. Particularly, it is important to determine whether particles are in aggregate configuration or agglomerate configuration because assembly configuration often has more influence on the fate and transport behavior of particles in the environment than their primary size.

As shown in Figure 1, particles at nanoscale are assumed to be present in either mono-dispersed (i.e. completely segregated) configuration, aggregated configuration, or agglomerated configuration. Aggregate can be defined as an assemblage of particles that are loosely and physically attached at their corners and edges, while agglomerate can be defined as an assemblage of particles that are rigidly bound at their faces. Configurations in Figure 1(a) and 1(b) might be easily interchangeable upon physical and chemical interactions between primary particles. Meanwhile, segregate configuration in Figure 1(a) transforms to agglomerate configuration Figure 1(c) by fusion, sintering, and/or crystal growth during synthesis of primary particles, and thus transformation of agglomerate configuration in Figure 1(c) back to segregate configuration in Figure 1(a) is less likely to occur. We assume that aggregated particles are more subject to segregation upon change of environmental conditions (and vice versa) and thus they might be more mobile and available, compared to agglomerated particles. Virkutyte *et al.* (2014) showed that TiO₂ particles with various assembly configurations exhibited their unique mobility through porous media.

An experimental approach is needed to investigate the segregating and assembling behavior of TiO₂ particles and thus to estimate their assembly configuration. In this study, we propose to use the sonication process to achieve the task. Sonication breaks particles in suspension via either erosion or fracturing. Erosion is effective to break weak bonds between particles mostly in aggregate configuration, while fracturing attacks weak structures mostly in agglomerated particles such as imperfections and cracks (Mandzy *et al.* 2005; Taurozzi *et al.* 2011). Sonication energy, once optimized, is believed to be strong enough to agitate particles mostly by mechanically segregating aggregated particles (i.e. from Figure 1(b) to 1(a)) but not enough to break down agglomerated particles (i.e. from Figure 1(c) to 1(a)).

We hypothesize that the unique colloidal response of TiO₂ particles to controlled sonication, with respect to changes in particle size, might be their intrinsic property associated with their assembly configuration. Based on the configurations shown in Figure 1, nanoscale particles in aggregate configuration might be more sensitive to sonication and more mobile in the environment and thus they can be practically called NPs in comparison to nanoscale particles in agglomerate configuration which can be called nanostructured particles (NSPs) (Virkutyte *et al.* 2014).

To prove the hypothesis, this study focuses on investigating the time-resolved reversible segregating and assembling behavior of TiO₂ particles under programmed sonication. Three different TiO₂ particles with unique properties were tested with programmed sonication processes (sonication followed by quiescence, sonication intensity) under different environmental settings (TiO₂ concentration and pH). Understanding the unique reversible segregating and assembling behavior of TiO₂ particles and thus their assembly configuration would be beneficial to interpreting their mobility, availability, and treatability in natural environmental systems as well as water and wastewater treatment facilities.
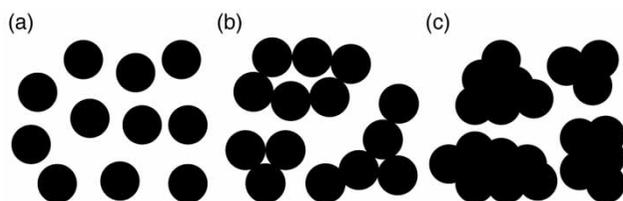

Figure 1 | Particle assembly configurations: (a) mono-dispersed (completely segregated) primary particles, (b) aggregated particles, and (c) agglomerated particles.

MATERIALS AND METHODS

Chemicals

Three types of TiO₂ ENMs were tested: P-25 (Degussa), UV 100 (Hombikat), and home-made (HM) TiO₂. P-25 purchased from Evonik Degussa GmbH, Germany shows

primary crystal size of 28.2 nm, specific surface area of 53.8 m^2/g, and mixture of 70% anatase and 30% rutile. P-25 is synthesized by flame hydrolysis. UV 100 purchased from Sachtleben Chemie GmbH, Germany shows primary crystal size of 5.50 nm, specific surface area of 292 m^2/g, and 100% anatase crystal phase. UV 100 is synthesized by the sulfate process. HM synthesized by the sol-gel process in our laboratory has surface area of 231 m^2/g and amorphous phase (Choi *et al.* 2006). Other chemicals include hydrogen chloride (HCl) and sodium hydroxide (NaOH) purchased from Sigma-Aldrich, USA.

Sonication process

Each of the TiO$_2$ ENMs (P-25, UV 100, and HM) was dispersed in water at a fixed concentration of 50 mg/l to briefly investigate their response to sonication and thus to estimate their assembly configuration. The sonication process was applied to the TiO$_2$ suspension to investigate how particles uniquely segregate and assemble as a function of sonication time followed by quiescence time. A sonicator (Misonix Sonicator S-4000) with the capability to accurately manipulate the total energy delivered to particle suspension was utilized. Based on preliminary studies, sonication was programmed at a probe energy intensity of 60 W and sonication for 15 min followed by quiescence for 15 min (standard conditions), where TiO$_2$ particles showed well-developed segregating and assembling behavior (Taurozzi *et al.* 2011).

The effect of concentration of TiO$_2$ particles in a range of 20–200 mg/L on their response to sonication was investigated. The test was conducted without pH control and thus pH was naturally maintained at 5.4 for P-25, 5.2 for UV 100, and 5.8 for HM. The experiment above under standard conditions was also resumed under controlled pH conditions in a range of 3–11 adjusted by adding HCl or NaOH in order to examine the effect of pH on the response of TiO$_2$ particles to sonication. Ionic species and strength was not controlled in this particular study. For the examination, variation of the zeta potential and hydrodynamic size of TiO$_2$ particles was monitored and their point of zero charge (pH$_{PZC}$) was also determined. Lastly, in order to investigate the effect of sonication energy, different probe sonication intensities were tested in a range of 30–100 W under standard conditions except for sonication time.

Instead of 15 min, 10 min for sonication and 10 min for quiescence were applied because high intensities caused severe erosion of the sonication probe tip.

Size measurement and zeta potential analysis

The hydrodynamic size and zeta potential (i.e. electric potential at the shear layer) of TiO$_2$ particles in suspension were monitored upon their segregation and assembling in response to sonication under different pH conditions. A particle size and zeta potential analyzer (SZ-100, Horiba, Japan) utilizing dynamic light scattering and laser Doppler electrophoresis, respectively, was applied. Based on light scattering of particles, their hydrodynamic diameter was calculated by using the Stoke-Einstein equation. Particle size was measured at the 173° detection angle. Zeta potential was calculated from the mobility by using the Smoluchowski model.

RESULTS AND DISCUSSION

Response of TiO$_2$ particles to sonication

In order to prove the hypothesis, the time-resolved reversible segregating and assembling behavior of TiO$_2$ particles under programmed sonication was investigated. TiO$_2$ particles under natural conditions start either assembling to make large assemblages or segregating to make small assemblages when they are dispersed in water. As shown in Figure 2, P-25 showed the smallest size at around 653 nm before sonication; UV 100 showed size at around 3,854 nm; and HM showed the largest size at around 6,284 nm. Considering that sizes of primary crystal particles are at 28.2 nm for P-25 and 5.50 nm for UV 100, TiO$_2$ particles obviously assembled to form much larger clusters.

Since TiO$_2$ particles are synthesized by different processes, they might exhibit inherently different assembly configurations and thus unique segregation behavior in response to sonication (Taurozzi *et al.* 2011). Size of P-25 decreased from 653 nm to around 210 nm immediately within 5 minutes of sonication and the size did not further decrease significantly. The similar result for P-25 was also observed by Jiang *et al.* (2009). They reported that size of P-25 decreased to 180 nm after 5 minutes of sonication and
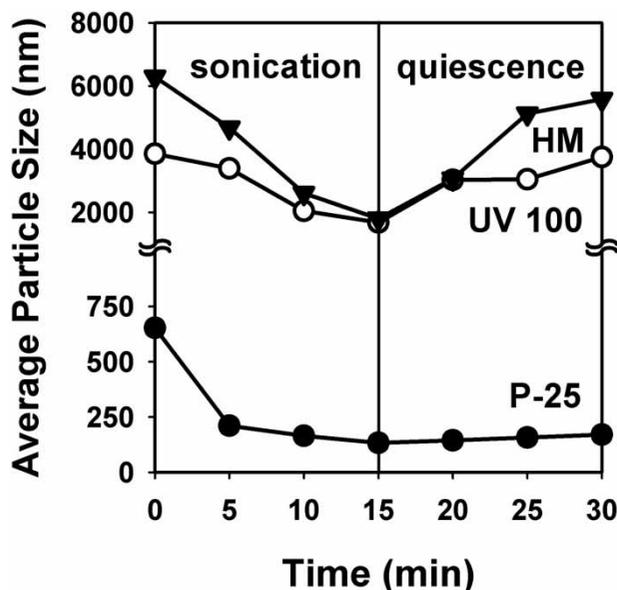
Figure 2 | Colloidal response of P-25, UV 100, and HM TiO$_2$ particles to sonication (TiO$_2$ concentration: 50 mg/l; sonication intensity: 60 W; pH: 5.2–5.8 with no control).

then became fixed. Taurozzi et al. (2011) pointed out that size of particles is stabilized after they break down to a specific size. Sonication increases collision frequency of particles and enhances particle-particle interactions, resulting in particle segregation (so-called peaking behavior) (Taurozzi et al. 2011). The response of UV 100 and HM to sonication was different from that of P-25. Their sizes kept decreasing over 15 minutes of sonication. Size of UV 100 almost continuously decreased from 3,854 nm to 1,675 nm and size of HM also continuously decreased from 6,284 nm to 1,797 nm. The result investigated under the specific sonic intensity implies that bindings between particles for UV 100 and HM might be stronger than particles for P-25. P-25 presumably in aggregate configuration segregated easily and immediately upon application of sonication energy while UV 100 and HM presumably in agglomerate configuration continued to disassemble over sonication time.

Size of P-25 at 133 nm after 15 minutes of sonication is relatively close to its primary crystal size of 28.2 nm. This implies that P-25 particles initially at 653 nm were effectively segregated upon sonication and several primary particles formed a small assemblage. The observation that P-25 particles were not completely broken to its primary particles might be explained by many factors associated with

their synthesis method, storage state, sonication intensity, and erosion mechanism (Ding & Pacek 2008; Zhang et al. 2008). Meanwhile, size of UV 100 at 1,675 nm after sonication is still much larger than its primary crystal size of 5.50 nm. This implies UV 100 is considered to be in agglomerate configuration although UV 100 successfully disassembled by both segregation and fracturing mechanisms during sonication. This also applies to HM.

Response of TiO$_2$ particles to quiescence conditions

After sonication, TiO$_2$ suspension stayed under quiescence conditions to investigate how TiO$_2$ particles re-assemble over time back to their initial size, as shown in Figure 2. Size of P-25 did not change significantly during the quiescence step. Size at around 133 – 170 nm was maintained, indicating no significant re-assembling. Taurozzi et al. (2011) and Horst et al. (2012) also observed the similar behavior. They explained that size of particles decreases only to size of their primary aggregates which are larger than their primary particles and those primary aggregates are hard to re-assemble. The result for UV 100 and HM is interesting. Their sizes under quiescence conditions increased almost back to their initial sizes before sonication. There was a continuous re-assembling process for UV 100 and HM. Those particles seemed unstable after sonication compared to stable P-25. The sonication intensity applied to this specific test might have physically and/or chemically altered the surface characteristics of TiO$_2$ particles differently (Taurozzi et al. 2011; Horst et al. 2012).

Effect of sonication intensity

The reversible segregating and assembling behavior of TiO$_2$ particles might change upon sonication intensity. In order to confirm whether the trends observed in Figure 2 are specific to the sonication intensity used for the study or not, the effect of sonication intensity on changes in size of TiO$_2$ particles was investigated, as shown in Figure 3. The similar trends to those shown in Figure 2 were also observed, regardless of sonication intensities at 30, 40, 60, and 100 W. Size of P-25 decreased steeply upon sonication and stayed the same upon quiescence conditions (Figure 3(a)) while sizes of UV 100 and HM decreased gradually and recovered
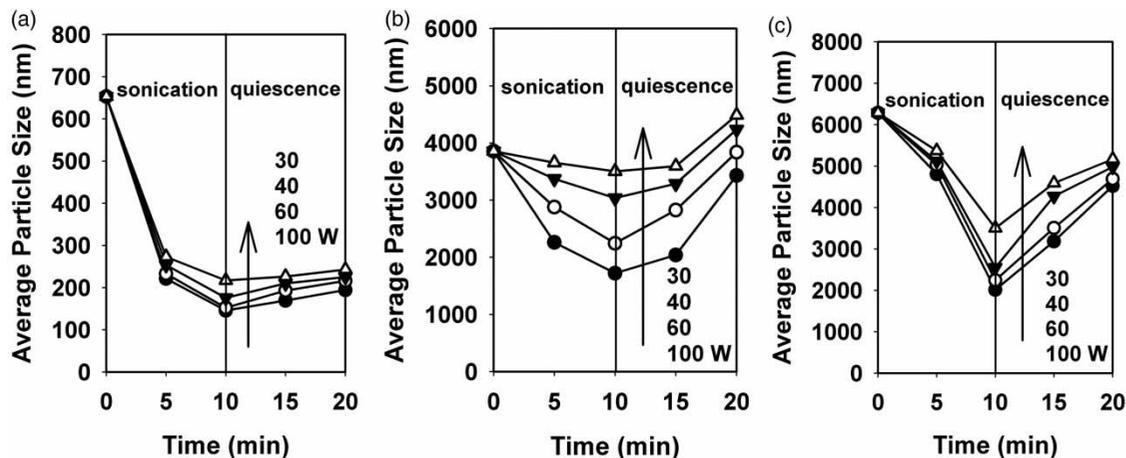
Figure 3 │ Colloidal response of (a) P-25, (b) UV 100, and (c) HM TiO₂ particles to sonication at intensities of 30, 40, 60, and 100 W (TiO₂ concentration: 50 mg/l; sonication intensity: 30–100 W; pH: 5.2–5.8 with no control). It should be noted that 10 min were used in this specific study instead of 15 min because a combination of 15 min and 100 W greatly damaged the sonication probe.

slowly back to their initial sizes (Figure 3(b) and 3(c)). As expected, higher intensities caused more breaking of particles, resulting in smaller sizes after sonication. Small particles made under high sonication intensities ended up with small particles under quiescence conditions.

The intensities investigated in this specific study, ranging 30 − 100 W, were not able to make any significant difference in the unique colloidal behavior of P-25. However, the intensities significantly impacted UV 100. High intensity at 100 W greatly changed size of UV 100 from 3,854 nm to 1,721 nm while low intensity at 30 W did not make any significant changes. P-25 was more sensitive to sonication even

at low intensities and thus P-25 seemed to be in aggregate configuration while UV 100 in agglomerate configuration was less sensitive, requiring high sonication intensities for particle segregation. The behavior of HM was similar to that of UV 100.

Effect of TiO₂ concentrations

In order to confirm whether the trends observed in Figures 2 and 3 are specific to the concentration used for the studies or not, different concentrations of TiO₂ particles at 20, 50, 100, and 200 mg/l were examined. As shown in Figure 4, higher
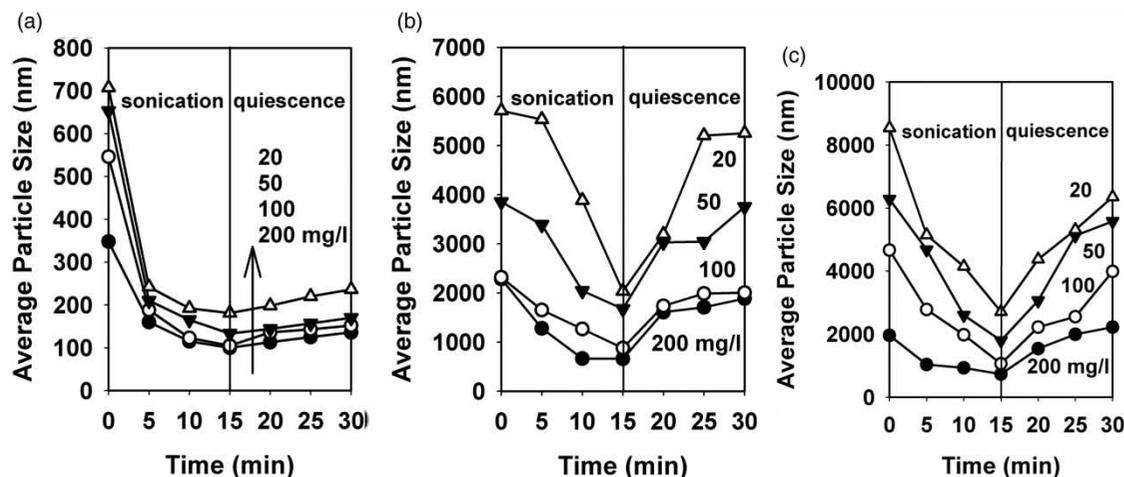

Figure 4 │ Colloidal response of (a) P-25, (b) UV 100, and (c) HM TiO₂ particles at different concentrations of 20, 50, 100, and 200 mg/l to sonication (TiO₂ concentration: 20–200 mg/l; sonication intensity: 60 W; pH: 5.2–5.8 with no control).

concentrations of TiO$_2$ particles generally induced smaller particles from the beginning. When mass concentration increased from 20 to 200 mg/l, particle size decreased from 707 to 348 nm for P-25, 5,708 to 2,285 nm for UV 100, and 8,540 to 1,960 nm for HM. This phenomenon was also observed in previous studies. Suttiponparnit *et al.* (2011) found that increase in TiO$_2$ concentration decreases pH and thus increased zeta potential inhibits particles from assembling. In addition, higher concentrations require less energy per unit mass for segregation (Ding & Pacek 2008). As shown in Figure 4(a), size of P-25 in all concentrations decreased immediately upon sonication. Size of P-25 after sonication was similar at 100 – 180 nm regardless of concentrations. Meanwhile, sizes of UV 100 and HM in all concentrations decreased gradually upon sonication and recovered slowly under quiescence conditions, as shown in Figure 4(b) and 4(c). As expected, low concentrations of TiO$_2$ particles seemed more sensitive to sonication, resulting in more significant changes in their size. The previously observed trends in the segregating and assembling behavior of TiO$_2$ were applicable to a wide range of TiO$_2$ concentrations.

Effect of pH conditions

To confirm whether the trends observed in Figures 2–4 are specific to the natural pH used for the studies or not and to investigate the effect of pH on the colloidal response of TiO$_2$ to sonication, different pH conditions were examined. First, particle size and zeta potential were measured over pH, as shown in Figure 5. Mandzy *et al.* (2005) pointed out that particles with zeta potential between -30 mV and $+30$ mV are unstable and subject to assembling due to van der Waals force. TiO$_2$ at acidic conditions has positive zeta potential due to adsorption of H$^+$ onto the surface of TiO$_2$. Point of zero charge of TiO$_2$ (pH$_{PZC}$) was determined to be at around 5.5 for P-25, 3.8 for UV 100, and 3.0 for HM. Small crystal UV 100 (5.50 nm) showed lower pH$_{PZC}$ at 3.8 than large crystal P-25 (28.2 nm) with pH$_{PZC}$ of 5.5, which was explained by Dunphy Guzman *et al.* (2006).

Based on the results shown in Figure 5, size of TiO$_2$ particles was generally correlated with zeta potential over pHs. At around the pH$_{PZC}$ of TiO$_2$, they showed the largest size due to particle attraction (i.e. negligible repulsion force between particles). When solution pH was far from the pH$_{PZC}$ (i.e. pH changed toward either more acidic or more basic), the size decreased due to increased particle repulsion. At pHs larger than 9, zeta potential did not further increase (rather it decreased) and thus size did not decrease (rather increased) in all TiO$_2$ solutions. Addition of NaOH to control such high pHs is known to increase ionic strength and compress the electric double layer, resulting in decreased particle repulsion (Jiang *et al.* 2009; Suttiponparnit *et al.* 2011; Horst *et al.* 2012). In comparison to size of P-25 at 653 nm under natural conditions (Figure 2), P-25 in the pH-controlled solutions showed larger size at 2,985–6,402 nm. In general, large size particles were formed in all pH-controlled TiO$_2$ solutions and thus settled out in a short time. Figure 6 shows the colloidal behavior of TiO$_2$ under sonication and quiescence
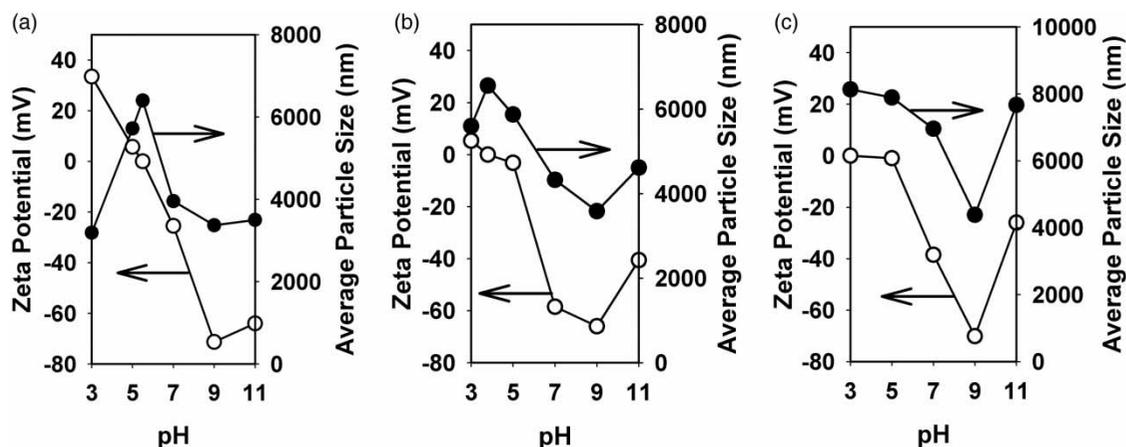

Figure 5 │ Effect of solution pH on the size and zeta potential of TiO₂ particles: (a) P-25, (b) UV 100, and (c) HM. In each TiO₂, pH_PZC (pH where zeta potential is zero) can be determined.
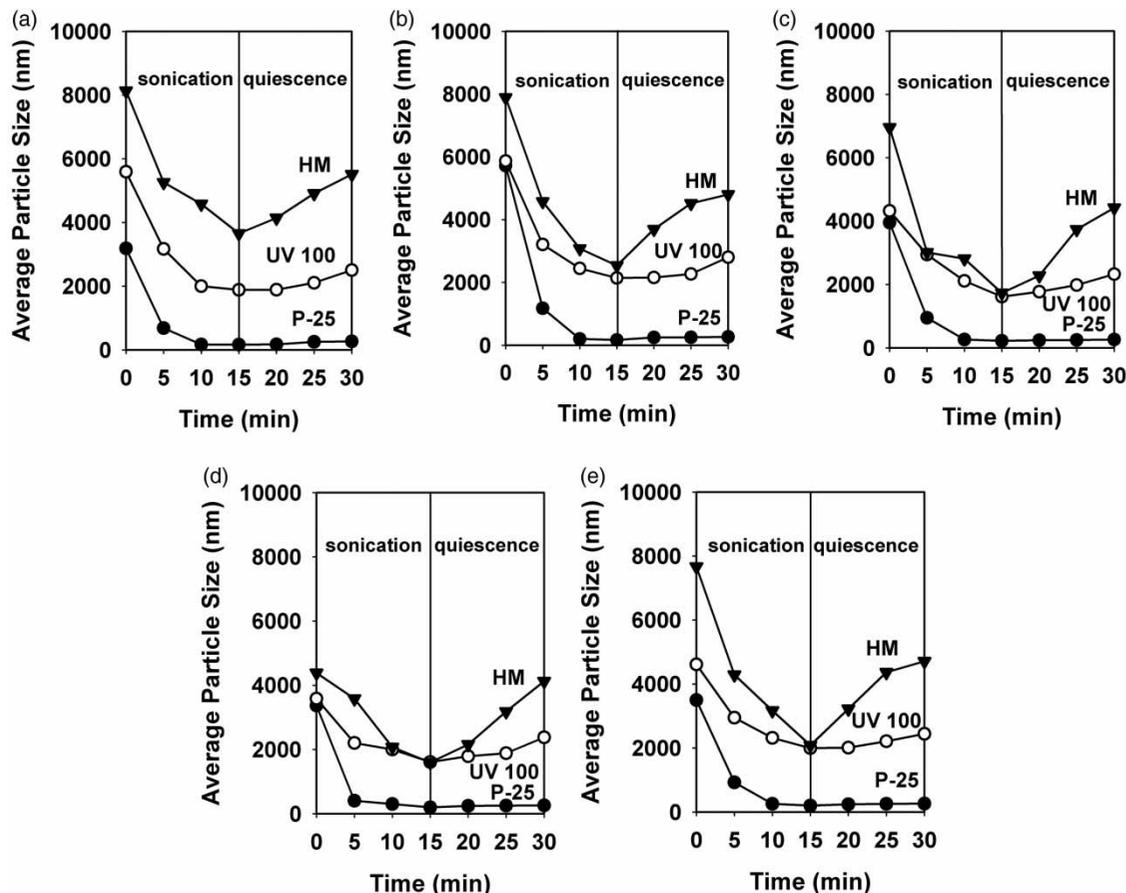
Figure 6 | Colloidal response of P-25, UV 100, and HM TiO$_2$ particles at different pHs of (a) 3, (b) 5, (c) 7, (d) 9, and (e) 11 to sonication (TiO$_2$ concentration: 50 mg/l; sonication intensity: 60 W; pH: 3–11).

conditions at different pHs. The behaviors were similar to the general trends observed in Figures 2–4. Particles at pHs of 3, 5, and 11 showed greater changes in their size. TiO$_2$ particles were more sensitive to sonication when their initial sizes were larger.

CONCLUSIONS

The time-resolved reversible segregating and assembling behavior of TiO$_2$ particles under a controlled sonication program was investigated to estimate their assembly configuration. When they were dispersed in water, all the TiO$_2$ tested obviously assembled to form much larger particles. Size of P-25 decreased immediately upon sonication and did not change significantly under subsequent quiescence conditions, while sizes of UV 100 and HM decreased gradually and then

recovered slowly back to their initial sizes. The trends were generally observed in all cases under different experimental conditions. The unique colloidal response of TiO$_2$ particles to sonication could be explained by their properties associated with assembly configuration. P-25 was in aggregate configuration while UV 100 and HM were in agglomerate configuration. This implies that P-25 particles can be practically called NPs while UV 100 and HM should be called NSPs. Those TiO$_2$ particles are expected to behave differently with respect to mobility, availability, and treatability in natural environmental systems as well as water and wastewater treatment facilities that work based on size-dependent exclusion and settling mechanisms, e.g. P-25, in comparison to UV 100 and HM, is obviously more mobile and available in the environment and is harder to remove by treatment processes. Examination on actual transport behavior of a series of TiO$_2$ particles under different colloidal states manipulated by the

controlled sonication should be followed in future. This study should also be extended to include more TiO$_2$ particles with different crystal phases and primary sizes and to test them under various ionic species and strengths so that we are able to set up a database for the aggregation and segregation behavior of a wide variety of TiO$_2$ particles in actual water matrix. Since TiO$_2$ was selected just as a model ENM for the concept demonstration, the hypothesis and the experimental approach might be widely applicable to many other ENMs assembled in various media to better understand and predict their colloidal behavior.

ACKNOWLEDGEMENTS

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