

## Stability of metal oxide nanoparticles in aqueous solutions

Chih-ping Tso, Cheng-min Zhung, Yang-hsin Shih, Young-Ming Tseng, Shian-chee Wu and Ruey-an Doong

### ABSTRACT

The application of nanoparticles in the processes of making commercial products has increased in recent years due to their unique physical and chemical properties. With increasing amount of commercial nanoparticles released into nature, their fate and effects on the ecosystem and human health are of growing concern. This study investigated the stability and morphology of three metal oxide nanoparticles in aqueous solutions. The commercially available nanoparticles, TiO<sub>2</sub>, ZnO, SiO<sub>2</sub>, aggregated quickly into micrometer-size particles in aqueous solutions, which may not threaten human health. Their changes in morphology and characteristics were further examined by dynamic light scattering (DLS) method and transmission electron microscopy (TEM). Among the several dispersion approaches, ultrasonication was found to be the most effective for disaggregating nanoparticles in water. For these three selected nanoparticles, ZnO could not remain stable in suspensions, presumably due to the dissolution of particles to form high concentration of ions, resulting in enhanced aggregation of particles. In addition, the existence of dissolved organic matters stabilized nanoparticles in lake water and wastewater for several hours in spite of the high concentration of cations in these real-water samples. The fate of metal oxide nanoparticles in natural water bodies would be determined by the type and concentration of cations and organic matters. Results obtained in this study revealed that the stability of nanoparticles changed under different aqueous conditions and so did their fate in the environment.

**Key words** | aggregation, aqueous phase, commercial nanoparticle powders, dispersion, organic matter

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### INTRODUCTION

Nanoparticles (NPs) have been used in many commercial applications and entered inevitably into aquatic ecosystems. The toxicity and effects of nanoparticles on human health have received much attention in recent years. Some studies have shown that metal oxide NPs can enter human bodies and exhibit toxicity (Brunner *et al.* 2006; Jeng & Swanson 2006). The fate of commercial NPs in the environment is of significance to the ecosystem and human health. Human exposure to commercial nanoparticles is determined by their fate and transport in the environment.

Furthermore, the fate of commercial nanoparticles in aqueous environments depends on their physical and chemical properties such as surface characteristics and sizes, as well as other chemical species in water.

Commercial nanoparticle products are often shipped as dry powders. Dispersed in water, commercial nanoparticle powders could not be kept in nanoscale range. The aggregation of NPs plays a key role in their fate in aqueous environment. Several parameters of water bodies including pH and ionic composition dominate the interactions of NPs

in water (Guzman *et al.* 2006; Zhang *et al.* 2008a,b). The size distribution of aggregated nanoparticles is usually not unimodal and the aggregated sizes generally increase as the pH approaches that of the zero point of charge ( $\text{pH}_{\text{zpc}}$ ). The determination of whether NPs can be dispersed as primary nanoparticles is also a key step in understanding their behavior in water. In addition, there are very few reports on the behavior of commercial NPs in wastewaters and natural water bodies in the literature.

This study examined the characteristics and behavior of three commercial metal oxide nanoparticles ( $\text{ZnO}$ ,  $\text{TiO}_2$ , and  $\text{SiO}_2$ ) in water. The stability of these three NPs in various particle concentrations, different pHs, and real-water samples was also evaluated to better understand the aggregation and stability of commercial nanoparticles in real-water samples and to facilitate the prediction of their fate in the environment.

## MATERIALS AND METHODS

### Nanoparticles

Commercial nanocrystalline titania ( $\text{TiO}_2$ ) with particle size of less than 25 nm was purchased in powder form from Aldrich. Two dry commercial nanoparticle powders, silicon dioxide ( $\text{SiO}_2$ ) at around 40 nm and zinc oxide ( $\text{ZnO}$ ) at around 20 nm, were obtained from Bio-Tech. Nanoparticle stock suspension at a final concentration of 0.1 g/L was prepared by adding 0.1 g of nanopowder to 1 L of pure water before each experiment. The suspensions were stirred with different approaches and stored at 4°C for no longer than 2 days before being used in all experiments. Pure water was double-distilled and deionized with a Milli-Q water purification system (Millipore,  $18.3 \text{ M}\Omega \text{ cm}^{-1}$ ). Nanoparticle crystalline was determined using powder X-ray diffraction (XRD), (PANalytical X'Pert Pro MRD). Field-emission scanning electron microscope (FE-SEM, JOEL JSM-6700F) was employed to obtain images of nanoparticles.

### Characterization of nanoparticles in water

Particle size analysis was performed using photon correlation spectroscopy (PCS P5, Beckman coulter, UK)

of suspended particles and particles aggregated under different experimental conditions with time. Photon correlation spectroscopy, also known as dynamic light scattering (DLS), utilizes a laser beam to probe particles' Brownian motion in particle suspensions. Various methods were employed to disaggregate commercial nanoparticles. Sonication (40 kHz, 280 W), stirring, and ultrasonic disruptors (Misonix Sonicator 3000, 30 W) under different conditions were utilized to disaggregate nanopowders in water under different conditions. Zeta-potential was measured by a Zetasizer Nano ZS (Malvern) at 25°C. The zeta potentials of nanoparticles were determined from their electrophoretic mobilities according to Smoluchowski's equation (Huter 1981). The pH of these nanoparticle suspensions was adjusted between 1 and 11 using HCl or NaOH solutions.

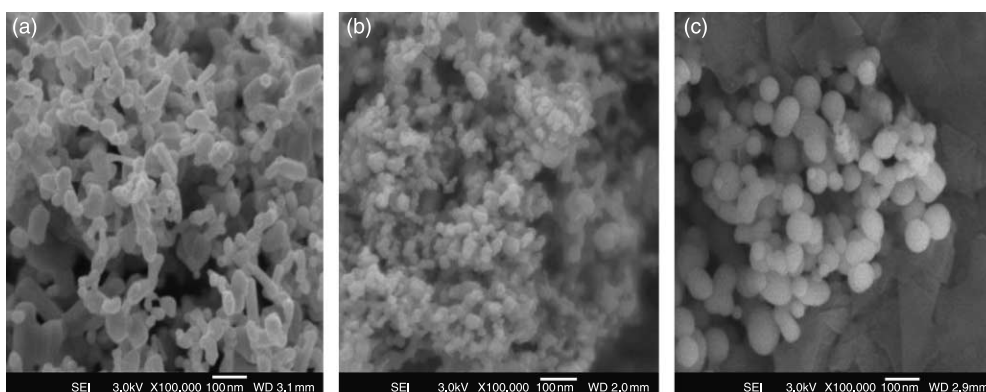
### Stability of nanoparticles in water

The effect of particle concentration on their stability was evaluated by adding different amounts of nanoparticles into water. Diluted nanoparticle suspensions were used in the disaggregation experiments and the subsequent stability analysis. The nanoparticle suspensions were adjusted to the desired pH to examine the pH effect. The changes in particle sizes with time in all experiments were monitored. Two real-water samples including the lake water of Yang Ming Reservoir in Kinmen County, Taiwan, and the wastewater from a hi-tech manufacturing factory in Hsinchu County, Taiwan, were examined to investigate the stability of nanoparticles in real-water samples. Nanoparticles at suitable concentration of around 1 mg/L were added to observe the change in particle sizes with time.

## RESULTS AND DISCUSSION

### Properties of commercial nanoparticles

Figure 1 shows the SEM images of the three selected nanoparticles. The particle sizes of dry  $\text{TiO}_2$ ,  $\text{SiO}_2$ , and  $\text{ZnO}$  nanoparticles observed in FE-SEM images are about 40, 35, and 70 nm, respectively; indicating that these commercial metal oxide particles are in the nanoscale

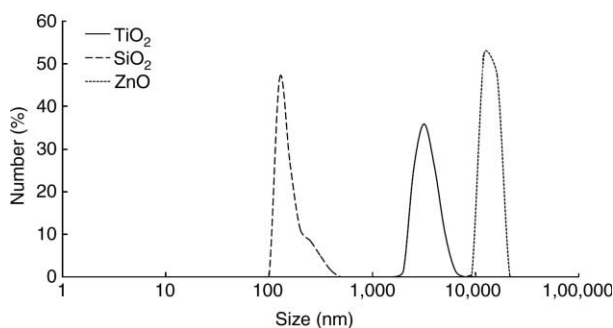


**Figure 1** | FE-SEM images of nanoparticle powders: (a) ZnO, (b) TiO<sub>2</sub>, and (c) SiO<sub>2</sub>.

range. However, the particle sizes of these commercial nanoparticles determined from SEM images are slightly larger than those reported by the manufacturers. Such discrepancy could be attributed to the aggregation of metal oxide nanoparticles when stored for a long time.

The crystallinity of the selected nanoparticles was further examined. According to the XRD patterns of these three nanoparticle powders, the main ZnO nanoparticle structure is hexagonal wurtzite. The TiO<sub>2</sub> nanoparticles are primarily anatase. The received SiO<sub>2</sub> nanoparticles are mainly in amorphous form.

Different from those in dry form, the average sizes of these three commercial NPs in pure water were in the range of 200–17,000 nm, which were much larger than the sizes reported by the manufacturers (Figure 2). Although SEM images (Figure 1) of these three nanoparticles show that they were nano-sized particles, their primary nanoparticles aggregated rapidly in aqueous solutions (Figure 3). Considerable particle aggregation was

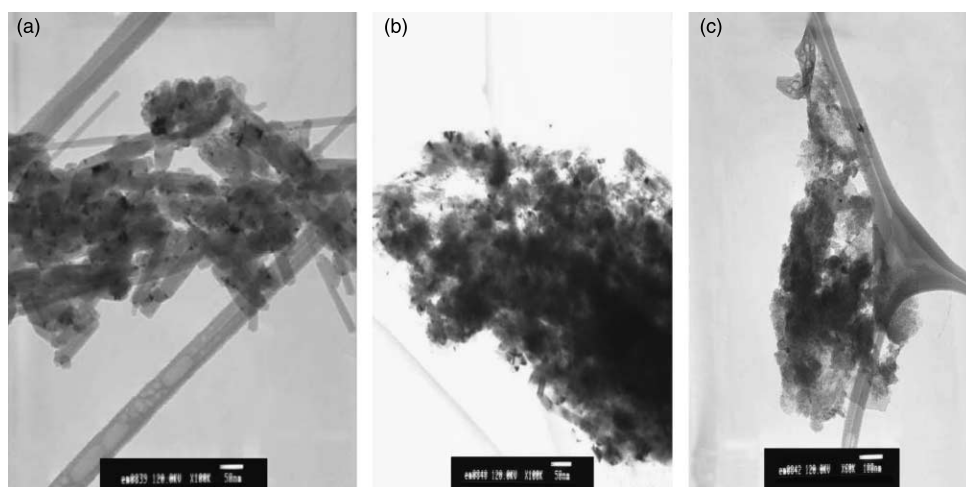


**Figure 2** | Particle size distribution of TiO<sub>2</sub>, SiO<sub>2</sub>, and ZnO nanoparticle powders in pure water.

observed for each NP, resulting in the formation of flocs. These metal oxide NPs seem to comprise aggregates of primary NPs. The number of NPs larger than 3 μm, as estimated by the filtration method, exceeded 90%. In addition, when added into water, the particle size of these NP aggregates, determined by the static laser particle analyzer, was in the micrometer scale, presumably due to the hydrophobic nature of the NP surface and electrostatic attraction of the NP powders used in this study. Therefore, these commercial nanoparticles would aggregate in water with particle sizes exceeding nanoscale and even reaching micrometer scale. The zero points of charge (pH<sub>zpc</sub>) of the NPs were obtained from the measurement of zeta potentials as a function of pH. The determined pH<sub>zpc</sub> of ZnO, TiO<sub>2</sub>, and SiO<sub>2</sub> are about 8.0, 5.9, and 3.1, respectively. TiO<sub>2</sub> and SiO<sub>2</sub> nanoparticles represent a negatively charged surface at neutral pH, whereas the surface of ZnO is positively charged at neutral pH. It is noted that the reported pH<sub>zpc</sub> of ZnO, TiO<sub>2</sub>, and SiO<sub>2</sub> are 9–9.6, 5–7 and 2–4, respectively (Lewis 2000; Ishikawa *et al.* 2005; Sverjensky 2005), which are in good agreement with the results obtained in this study. Finnegan *et al.* (2007) reported that the pH<sub>zpc</sub> of nanoparticles changes with nanocrystalline size, with the smaller particle sizes exhibiting a lower pH<sub>zpc</sub>. For ZnO nanoparticles, the pH<sub>zpc</sub> lower than the reported value could be attributed to its nanoparticle size.

#### Effect of particle concentrations on nanoparticle size

The hydrodynamic diameters of NP in aqueous solution, determined by DLS, demonstrate that the particle sizes



**Figure 3** | TEM images of (a) TiO<sub>2</sub>, (b) SiO<sub>2</sub>, (c) ZnO nanoparticle aggregates in pure water.

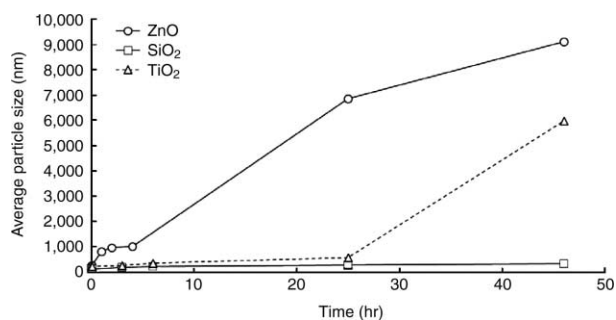
of ZnO and TiO<sub>2</sub> in solutions generally increase with their mass concentration ranging from 1 to 100 mg/L within 10 min. The average particle sizes of ZnO at concentrations of 1, 10, and 100 mg/L are 2,990, 6,820, and 11,400 nm, respectively, which are positively correlated with the concentrations of ZnO added. Although the regression between the concentration and average particle size yields a good coefficient of 0.86, statistical significance was not suggested due to the broad particle size distribution. Furthermore, TiO<sub>2</sub> particles at concentrations of 1, 10, and 100 mg/L have sizes around 1830, 956, and 2,030 nm, respectively, showing that particle concentration has little influence on the particle size of TiO<sub>2</sub>. Similar behavior was also observed for SiO<sub>2</sub>.

The number concentration of NPs did not seem to significantly affect the size of NPs. It may be due to the measurement uncertainties and rapid aggregation of NPs. Since the intensity is strongly dependent on particle radius, uncertainties in the measured intensity would be greatly magnified in the calculated number distribution (Zhang & Buffle 1995). Smaller particles have a higher number concentration and a larger diffusion coefficient as compared with larger ones at the same mass concentration, which aggregated rapidly in water by Brownian motion. Clearly, these nanoparticles with high surface energies increase quickly their size into the microscale range in water due to rapid particle collision, Van der Waals attraction, water bridging, and high surface energy.

#### Disaggregation of commercial nanoparticles in water

Three commercial metal oxide, ZnO, TiO<sub>2</sub>, and SiO<sub>2</sub> powders were used as representative commercial nanoparticles at different particle concentrations to determine whether commercial nanoparticles in water could be disaggregated by stirring and sonication. Prior to sonication, the average sizes of the three commercial nanoparticles in water at 1 g/L were larger than 1 μm. After sonication for different durations, these three nanoparticle aggregates are still more than 1 μm. Similar result was observed for disaggregating NPs at different concentrations with either sonication or magnetic stirring. Several stirring speeds were tested but all failed to separate the aggregates. Two high stirring speeds of around 15,000 rpm were also employed. Only SiO<sub>2</sub> aggregates could be broken down to around 160 nm. The estimated particle sizes of TiO<sub>2</sub> and ZnO aggregates changed slightly and were often not detected because the aggregates settled down before detection. Clearly, sonication and stirring failed to break down these aggregates.

The ultrasonic disruptor is an effective tool for dispersing NP in aqueous solution. The particle sizes of SiO<sub>2</sub>, TiO<sub>2</sub>, and ZnO could be broken down to 146, 225, and 244 nm, respectively, after running the ultrasonic disruptor for 10 min. Furthermore, the average particle size changed with time after ultrasonication (Figure 4). The sizes of SiO<sub>2</sub> and TiO<sub>2</sub> particles could be kept in close nanoscale ranges in one day. SiO<sub>2</sub> particle size was around 350 nm after the



**Figure 4** | Changes in average particle size of three commercial nanoparticle solutions at 10 mg/L after 10 min of ultrasonication.

suspension has remained still for 40 h. However, the TiO<sub>2</sub> particle size increased to micrometer scale after 25 h, while the ZnO particle aggregated speedily to become larger than 1  $\mu\text{m}$  after 2 h in water. These results indicate that ultrasonication can effectively disperse NPs in water.

Although the ultrasonic disruptor can disperse SiO<sub>2</sub> and TiO<sub>2</sub> aggregates into smaller sizes, ZnO particles cannot keep their particle size and still aggregate seriously even after strongly physical stirring. Degen & Kosec (2000) found that ZnO suspensions could not be electrostatically stabilized because the colloidal zinc oxide particles were transformed into zinc ions. For ZnO nanoparticles, agglomeration becomes more serious within increase in reaction time. It may be due to the gradual change of the particles from soft agglomeration, which depends mainly on physical absorption, to hard agglomeration, which is mainly dependent on chemical bonds (Ishikawa *et al.* 2005).

### Effect of pH on commercial nanoparticles

pH is an important parameter for controlling the particle sizes of colloids because it affects the stability of surface charge and particle interactions. Owing to the rapid and serious aggregation of these three nanoparticles in the presence of cations, electrolytes were not added to control the ionic strength of solutions during the experimental

courses of pH effect. However, HCl or NaOH solution was employed to adjust the pH values. Nanoparticle aggregation and settling of aggregates varied with their initial pHs. Over a pH range from 2.2 to 10.4, the stability of a typical suspension of SiO<sub>2</sub> was maintained at pH 4.3–8.5 for 1 h. However, coagulation of SiO<sub>2</sub> nanoparticles was also observed and the particle sizes increased to 1.5  $\mu\text{m}$  within 60 min at pH 2.2. This may be primarily because the zeta potential of SiO<sub>2</sub> is close to 0 (about 2 to 3 mV) and the experimental pH is close to its  $\text{pH}_{\text{zpc}}$ . The particle size exceeded 1.8  $\mu\text{m}$  after 14 min at pH 10.4, which may be induced by excessive Na from the additional NaOH for pH adjustment.

For TiO<sub>2</sub>, the initial particle sizes are between 280 and 477 nm after adjusting the initial pH to the range of 2.0–8.1. TiO<sub>2</sub> nanoparticles remained suspended in solution after 60 min; however, this condition did not remain for days. At initial pH of 10.4, particle sizes increase from 389 to 2,900 nm after 60 min due to the excessive Na from the pH adjustment. In this study, the effect of cations in water is more important than that of pH. Further studies on maintaining simultaneously the ionic strength and particle size are needed.

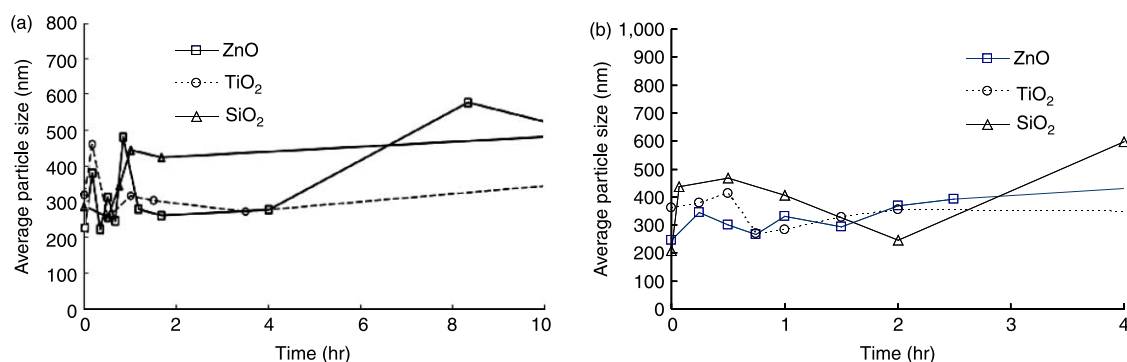
For ZnO, all final pH values tend to become neutral gradually after 60 h when the initial solution pH was in the range of 5.1–10.1, indicating that ZnO has a high degree of pH buffer capacity. ZnO nanoparticles aggregated rapidly when pH is lower than 5.1, which can be attributed to the existence of dissolved zinc species. Although particle sizes of ZnO are around 234–351 nm within 1 h at the initial pH larger than 7.5, the average particle sizes of ZnO exceeded 1,000 nm after 60 h.

### Stability of commercial nanoparticles in real-water samples

Rapid aggregation of NPs was found in the presence of cations and enhanced with the valence of cations as well

**Table 1** | Aqueous properties of lake water and wastewater in this study

	pH	TOC (mg/L)	Cl <sup>-</sup> (mg/L)	NO <sub>3</sub> <sup>-</sup> (mg/L)	SO <sub>4</sub> <sup>-</sup> (mg/L)	Ca <sup>2+</sup> (mg/L)	Mg <sup>2+</sup> (mg/L)	Al <sup>3+</sup> (mg/L)
Yang-ming lake	6.54	14.0	22.59	1.17	16.62	47.3	2.92	ND
Wastewater	7.11	23.8	241.1	11.8	682.9	13.9	3.17	ND



**Figure 5** | Change in sizes of three commercial nanoparticles in lake water (a) and wastewater (b) with time.

as their concentrations (Zhang *et al.* 2008b; Zhuang *et al.* 2009). The cation concentrations and other aqueous properties of the lake water and wastewater are shown in Table 1.

Their electrical conductivities of Yang-ming lake water and wastewater are 117 and 1,380  $\mu\text{S}$ , respectively. These three nanoparticles were expected to aggregate quickly in these two real-water samples. However, the particle size of these three commercial nanoparticles in lake water after 10 h was in the range of 200–600 nm (Figure 5a). Zhang *et al.* (2008b) and Zhuang *et al.* (2009) indicated that cations in natural water (e.g.  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) could neutralize the negative charge on the nanoparticle surfaces. However, the existence of humic substances could prevent the nanoscale particles from agglomerating. These phenomena have been reported for NPs in water with natural organic colloids, e.g. natural organic matter (Hyung *et al.* 2007; Xie *et al.* 2008).

Figure 5b shows that  $\text{SiO}_2$  nanoparticle increased from 200 to 500 nm in the beginning and to around 600 nm after 4 h. However, the particle sizes of  $\text{TiO}_2$  and ZnO remained unchanged between 200 and 400 nm. After 20 h of suspension,  $\text{TiO}_2$  and ZnO particles remained stable in wastewater with size between 200 and 800 nm. Although there are often high concentrations of cations in wastewaters, surfactants discharged from factories may effectively preserve the stability of nanoparticles in these water bodies.

The pH and electrical conductivities of these two water samples showed no obvious change after addition of nanoparticles (Table 2). Owing to the higher conductivity of the wastewater sample compared with that of the lake

water sample, the particle size of three NPs increased slightly faster in the wastewater than in Yang-ming lake water. The zeta potentials of  $\text{SiO}_2$ ,  $\text{TiO}_2$ , and ZnO particles in water at pH 7 were around  $-28$ ,  $-29$ , and  $18$  mV, respectively. The zeta potentials of  $\text{SiO}_2$  and  $\text{TiO}_2$  in these two water samples did not change significantly. However, the negative surface charge of ZnO was observed in these two real waters, indicating that humic substances and surfactants could be shielding ZnO nanoparticles with negative charge to keep them stable. O'Connell *et al.* (2002) observed the same phenomenon and indicated that humic polymers and surfactants could create more thermodynamic favorable surfaces and induce steric and electrostatic stabilization.

The greater negative surface charges on ZnO in the lake water than in the wastewater may be attributed to the more effective functional groups on natural humic substances in the lake water than the surfactants in the wastewater, despite the higher total organic carbon content of the wastewater. Hyung *et al.* (2007) also indicated a better stabilizing capacity of Suwannee river water including natural organic matter for carbon nanotubes than a commonly used surfactant, sodium dodecyl sulfate.

**Table 2** | Properties of the three NPs in lake water and wastewater

	Yang-ming lake			Wastewater		
	pH	EC ( $\mu\text{S}$ )	Zeta potential (mV)	pH	EC ( $\mu\text{S}$ )	Zeta potential (mV)
$\text{SiO}_2$	7.6	84.5	$-27.9$	7.5	1,220	$-23.1$
$\text{TiO}_2$	7.4	100.2	$-16.2$	7.7	1,247	$-18.4$
ZnO	6.9	105.4	$-23.4$	7.7	1,223	$-7.61$

## CONCLUSIONS

Three selected types of nanoparticle powders aggregated rapidly into microscale aggregates and even settled down obviously in pure water, thus reducing their threat to the ecosystem. Among the methods for dispersing NPs used in this study, ultrasonication could effectively break these aggregates up into their primary particles in water. pH affected the stability of nanoparticles in water; however, the effect of particle concentrations on aggregation was not readily apparent. After ultrasonication, SiO<sub>2</sub> and TiO<sub>2</sub> suspensions were more stable than ZnO suspension. ZnO nanoparticles aggregated quickly because of electrostatic instability from the dissolution of colloidal ZnO nanoparticles into dissolved ion species. In real-water samples such as lake water and wastewater, the particle size of NPs increased more slowly than that in pure water due to the existence of organic colloids such as humic substances or surfactants. Natural organic colloids and surfactants in natural waters and industrial wastewater can overcome the aggregation process of NPs after neutralization of counterions in real-water samples. The fate of metal oxide nanoparticles in water depends significantly on the presence of organic colloids in the aqueous environment.

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