Aggregation and Dissolution of ZnO Nanoparticles in Solutions

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In the present study, aggregation and dissolution of 30 nm ZnO nanoparticles with concentration of 10 mg/L in different solutions were investigated. The solutions used were four types, three of among, which were double distilled water with the pH values adjusted to 5.5 (acid), 7.0 (neutral) and 8.5 (alkaline), respectively. The forth solution is modified Hoagland's solution. Changes of particle size of the ZnO nanoparticles in the solutions were determined and the concentrations of Zn^{2+} at 96 h were detected. The results show that aggregation occurred immediately after preparation and there were basically no ZnO nanoparticles in the supernatants after 12 h excerpt for the alkaline solution, suggesting pH value and ionic strength may influence the aggregation. Dissolution of the nanoparticles was highly pH-dependent. Acid facilitated and accelerated the process. Present results could provide supports for the ecotoxicological tests of the ZnO nanoparticles.

Key Words: Aggregation, Solubility, Solutions, ZnO nanoparticles.

INTRODUCTION

Manufactured nanoparticles have been defined as new materials with at least one dimension between 1 and 100 nm[1]. Unique properties of nanoparticles are due to small size and corresponding enormous surface area and may differ substantially from respective bulk ones. This makes them attractive for a wide range of novel applications in the electronics, healthcare, cosmetics, technologies and engineering industries[2-4]. According to conservative estimates, the number of consumer products on the market containing nanoparticles or nanofibers now exceeds 800 and is growing rapidly[5].

The rapid discovery and production of nanoparticles will undoubtedly increase the potential for human and environmental exposures. Many studies reported the potential risk to human health from nanoparticles, including inflammatory reactions caused by ferric oxide nanoparticles in rats[6] and toxic effects of silica nanoparticles on fibroblast and tumor cells[7]. At present, investigations on the ecotoxicology of nanoparticles are emerging rapidly, with a goal of assessing nanoparticles' harmful effects to the ecosystem[8,9].

Water environment is the most important and may be the ultimate destination of nanoparticles released in the environment despite their sources. Therefore, many studies focused on toxicity of nanoparticles on aquatic organisms[10,11]. However, there is a lack of knowledge on the fate and behaviour of manufactured nanoparticles in water. Do they retain their nominal nanoscale size and original structure and reactivity in aquatic systems? What causes the toxic effects to organisms, the nanoparticles themselves or the ions released? Before operation of the ecotoxicological tests, such questions should be clarified. Hence, aggregation and dissolution of nanoparticles in the aquatic environment need to be better understood.

Nanoparticles of zinc oxide (ZnO) are widely used in cosmetics and sun care products[12], as well as self-cleaning coatings[13]. According to "The Nanotechnology Consumer Products Inventory"[14], the most common metal oxide nanoparticles material mentioned in the product descriptions was titanium dioxide (TiO_2), followed by ZnO. During the life cycle of these commercial products, ZnO nanoparticles may be released to the environment and become a threat to the ecosystem.

The main objective of this study is to explore the physical and chemical changes of the ZnO nanoparticles in water. Investigation to the aggregation and dissolution of the nanoparticles in solutions with different pH values and constituents is conducted for the purpose of providing supports for the ecotoxicological researches of the selected nanoparticles.

EXPERIMENTAL

Characterization of ZnO nanoparticles: ZnO nanoparticles were purchased from Aipurui Co. Ltd., Nanjing, China. The surface area of the nanoparticles was further

determined using the multipoint Brunauer-Emmett-Teller (BET) method. The morphology of the nanoparticles was examined using transmission electron microscopy (H-7500, HITACHI, Japan).

The solutions used in this study were four types, three of among, which were double distilled water with the pH values adjusted with 0.1 N HCl or NaOH to 5.5 (acid), 7.0 (neutral) and 8.5 (alkaline), respectively. The forth solution is modified Hoagland's solution[15], the chemical composition of which was as follows (in mg/L): $Ca(NO_3)_2 \cdot 4H_2O$, 118; KNO_3, 5.055; $MgSO_4 \cdot 7H_2O$, 4.932; KH_2PO_4, 0.68; $FeSO_4 \cdot 7H_2O$, 0.307; K_2SO_4, 0.348; H_3BO_3, 0.286; $MnSO_4 \cdot 7H_2O$, 0.155; $ZnSO_4$, 0.022; $CuSO_4$, 0.0079; $NiSO_4 \cdot 7H_2O$, 0.00478; $NaWO_4 \cdot 2H_2O$, 0.00179; $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, 0.0128; $Co(NO_3)_2 \cdot 6H_2O$, 0.0049. The pH was adjusted to 6.5 by addition of NaOH 0.1 N. The four solutions, which contained in 500 mL beakers with volume of 350 mL were prepared for the succeeding experiments. Three replicates were considered in all the experiments.

Prior to the test, ZnO nanoparticles were added to each solution and got a final concentration of 10 mg/L. There were no cosolvents used in this study. Subsequently, the solutions were treated by a sonicator (Vibra-Cell TM, USA; 50 Hz, 10 s pulse and 5 s interval) for 10 min and then the beakers were placed in an incubator at 25 ºC with no disturbing.

Detection methods: Particle size of the ZnO nanoparticles in the solutions was determined with a Nanotrac 250 particle analyzer (Microtrac Inc., USA). The 10 mL water samples were taken from the upper layer of the solutions carefully to avoid disturbing at 0, 0.25, 0.5, 0.75, 1, 2, 3, 4, 5, 6, 12 and 96 hour (h) for the test. The concentrations of Zn^{2+} at 96 h were detected by ICP-OES (VISTA-MPX, USA).

RESULTS AND DISCUSSION

Characteristics of ZnO nanoparticles: Table-1 shows the results of characterization of the nanoparticles and the TEM image is given in Fig. 1. The results reveal the shape is mainly sphere and the size of the single sphere particle was about 30 nm with surface area of 90 m^2/g.

TABLE-1
CHARACTERISTICS OF ZnO NANOPARTICLES
USED IN THE PRESENT STUDY

Sample	Diameter (nm)	Purity (%)	Crystalline phase	Surface area (m^2/g)
ZnO	30	99.6	Rutile	90

Changes of particle sizes of ZnO nanoparticles in different solutions: Fig. 2 depicts particle size distribution of 30 nm ZnO nanoparticles in different solutions (neutral, acid, alkaline and Hoagland) over 4 days. The similar variation trend can be found in these results. After sonication, the solutions were homogeneous mixed and the particle size was about 30 nm. However, aggregation occurred immediately after preparation and the particle size could reach more than 4 µm. Over the initial 6 h tested, there were no regular patterns of aggregation could be detected. After 12 h, the data of the particle sizes were reduced to lower than 1 nm except for alkaline group, suggesting that there were no ZnO nanoparticles in the supernatants. The white aggregations could be

found at the bottom of the beakers. At the same time, there were visible floats on the surface of the alkaline solution. Based on the data of alkaline solution at 1 h and 96 h, there were still ZnO nanoparticles left in the supernatant. According to observation to the experiments, it is speculated that the nanoparticles are mainly from the floats.
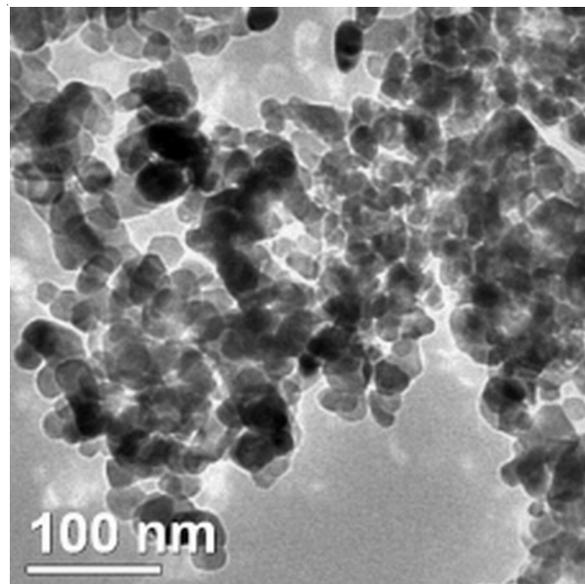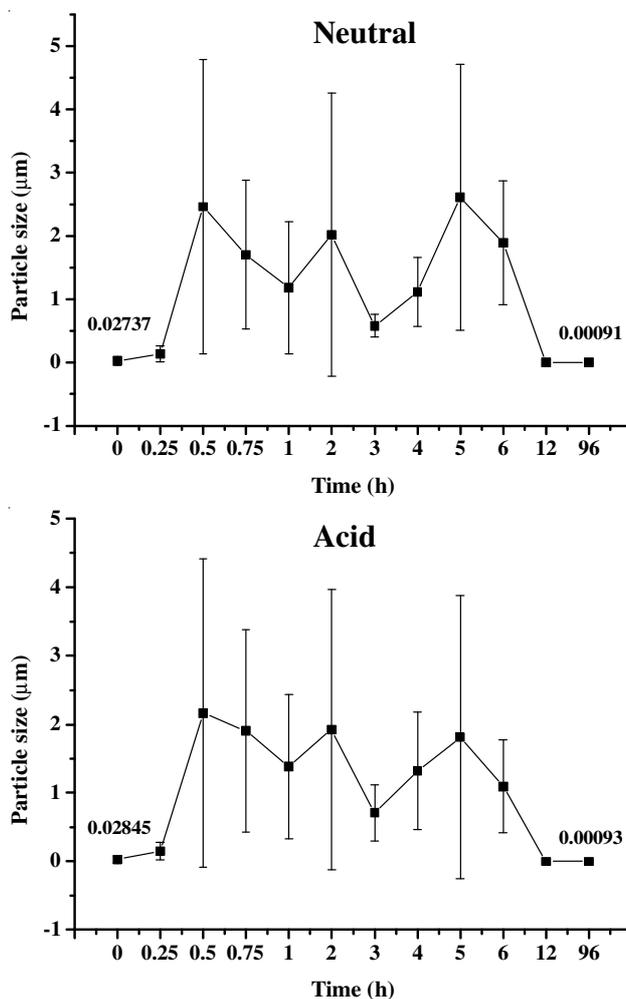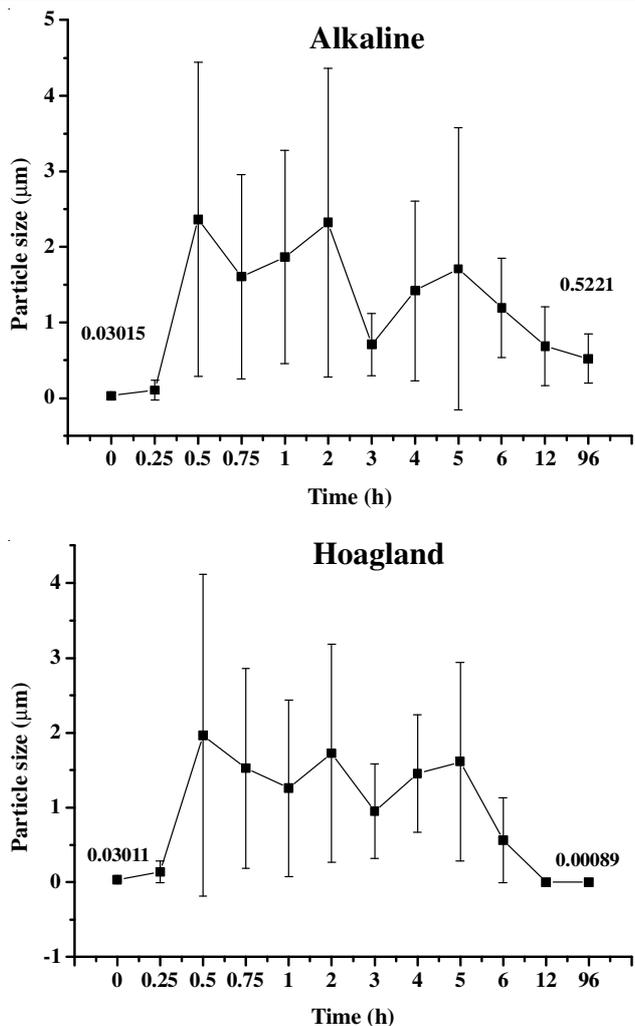

Fig. 1. SEM of ZnO nanoparticles

Fig. 2.　Particle size distribution of 30-nm ZnO nanoparticles over 96 h (show mean value and SD, mean values of 0 h and 96 h are also marked)

Changes of dimension distribution of ZnO nanoparticles as the time goes on after preparation of the neutral solution are shown in Fig. 3. It displays that the particle size reduced to lower than 1 nm when the solution was laid for 12 h.

In aquatic systems, colloid is the generic term applied to particles in the 1 nm to 1 μm size range. Therefore, ZnO nanoparticles existed in the solutions as colloid first and then aggregated to large paticles and deposited to the bottom. It was reported that colloidal fate and behaviour are dominated by aggregation[16,17] and colloids will ultimately aggregate to particles (> 1 μm) that are sufficiently large that their transport is dominated by sedimentation. This process has been already characterized to understand trace metal behaviour[18]. It is important in the self-purification of water bodies and results in pollutant loss from surface waters and accumulation in the sediments and is analogous to the likely behaviour of manufactured nanoparticles, with aggregation and subsequent sedimentation an important process in their ultimate fate.

Nanoparticles and natural colloids will interact and this will affect nanoparticle behaviour in the natural environment. To our best of knowledge, at present, no direct published data are available on the concentrations of nanoparticles in natural waters, but a recent report using a simplified box model and known current uses suggested environmental concentrations is approximately 1 to 100 μg/L[19], whereas typical dissolved and colloidal organic matter in freshwaters may be found at 1 to 10 mg/L concentrations. In this study, we used 10 mg/L as test concentration in order to investigate the fate of the selected nanoparticles under the laboratory conditions. Disturbing in the actual aquatic environment may also influence the aggregation of the nanoparticles.

Dissolution of the ZnO nanoparticles: According to the results of ICP-OES (Fig. 4), Zn^{2+} concentrations in the 4 solutions exhibit great differences with the solubility of 15.0 % (neutral), 72.2 % (acid), 40.6 % (Hoagland) and 5.2 % (alkaline),
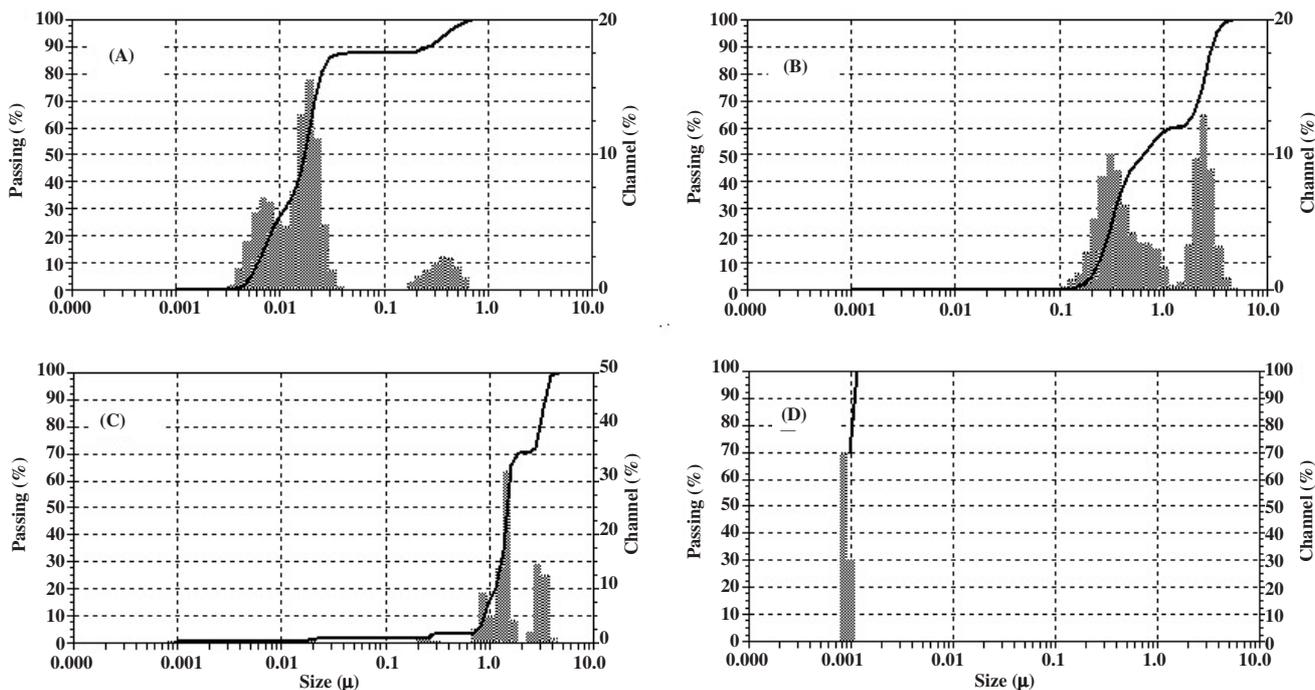

Fig. 3. Dimension distribution diagrams of ZnO nanoparticles at the times (h) after preparation of the neutral solution. (A) 0 h; (B) 1 h; (C) 6 h; (D) 12 h

respectively. This suggests that the dissolution of ZnO is highly pH-dependent. Acid could facilitate and accelerate the process, while alkaline hinders it. As to the Hoagland solution, acid property and high ionic strengths may increase dissolution of the nanoparticles.
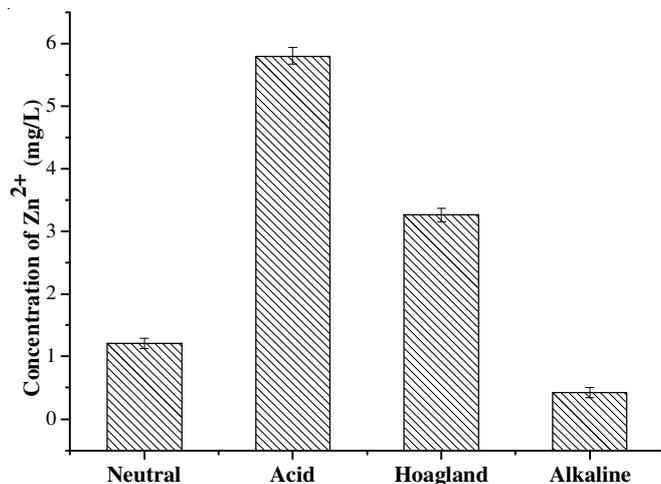

Fig. 4. Concentration of Zn^{2+} in the different solutions at 96 h

It has been assumed that the predominant bioavailable portion of the total contaminant was the soluble form[20]. Whereas, few studies could be found on the relationship between the dissolved portion and the toxicity of the metal oxide nanoparticles[21]. Present results are consistent with Shi *et al.*[22], which investigated the dissolution of CuO nanoparticles. In the further ecotoxicological researches of the nanoparticles, solubility is likely to be an important aspect and should be considered.

Conclusion

Ecotoxicological studies of the metal oxide nanoparticles in the aquatic environment need more knowledge about their behaviour and fate. This study provides a preliminary data on aggregation and dissolution of ZnO nanoparticles in four different solutions under the laboratory condition. The results show that aggregation occurred immediately after preparation and there were basically no ZnO nanoparticles in the super-natants after 12 h excerpt for the alkaline solution. The white aggregations could be found at the bottom of the containers. Dissolution of the nanoparticles is highly pH-dependent. Acid

could facilitate and accelerate the process. Present results indicate that pH value and ionic strength may significantly influence the aggregation and dissolution of the selected nanoparticles.

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