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Role of morphology in the aggregation kinetics of ZnO nanoparticles

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ABSTRACT

The aggregation kinetics of two types of ZnO nanoparticles were investigated under various conditions. Distinct differences in aggregation kinetics were observed between the two ZnO particles. The aggregation of the nearly spherical ZnO (denoted as Me ZnO) exhibited strong dependence on the ionic strength (IS) of the solution; while minimal influence of IS was seen on the irregularly shaped ZnO (mixture of slab-like and rod-shaped particles, denoted as Mk ZnO) in the IS ranged tested. It is postulated that Mk ZnO possesses a critical coagulation concentration (CCC) below the lowest electrolyte concentration tested (1 mM NaCl) due to the interactions between various surfaces. The CCC of ZnO was found to be a function of pH; the CCC increased significantly as the pH was further away from the point of zero charge. Natural organic matter (NOM) was found to substantially hinder the aggregation of both types of ZnO particles (above 10 mg/L for Me ZnO and above 1 mg/L for Mk ZnO). A Langmuir adsorption model was used to describe the NOM to ZnO nanoparticle adsorption isotherms. To our knowledge, this is the first study to report the effect of particle morphology on nanoparticle aggregation, which outlines the importance of accounting morphology into environmental transport assessment of nanoparticles.

1. Introduction

Nanostructured ZnO materials have applications in various fields (e.g. sunscreens, cosmetics, coatings, optics and electronics, etc) because of their distinct electronic, optic and photonic properties (Wang, 2004; Dange et al., 2007). However, the potential toxicity of nanosized ZnO has generated concern from both the scientific community and the public. In the past few years various adverse effects of nanosized ZnO to plants, phytoplankton, mammals, and even human cell lines have been reported (Xia et al., 2008; Franklin et al., 2007; Lin and Xing, 2008). To fully assess the environmental risk of these nanomaterials, information of how these materials transport and transform in the environment, and in which form these materials reach organisms and cause negative effects is indispensable. In the past few years, a number of investigators have looked into the fate and transport of nanoparticles (e.g. Chen et al., 2007; Saleh et al., 2008; Zhang et al., 2009; Xie et al., 2008; Phenrat et al., 2007; Smith et al., 2009). In the aqueous environment, nanoparticles (NPs) tend to attract each other and form aggregates (Chen and Elimelech, 2006). This process influences the mobility of NPs, and can determine their final sink.

The aggregation of metal oxide nanoparticles has been studied by several investigators. Multimodal size distribution was seen in titanium dioxide nanoparticles aggregates after equilibration for 3 months, and the suspended particle size displayed dependence on pH – pH_{pzc} (point of zero charge)

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(Guzman et al., 2006). Titanium dioxide nanoparticles with a primary particle size of 5 nm were observed to form stable aggregates (50–60 nm) under relatively low ionic strength (IS), but form micron-sized aggregates within 15 min at elevated salt concentration (French et al., 2009). Interstitial Zn and the presence of carbonate groups on the ZnO surface was shown to have no influence on ZnO particle aggregation, while a strong correlation between the zeta-potential and aggregation rate was observed (Logtenberg and Stein, 1986).

Adsorbed species have been shown to impact aggregation and stabilize metal oxide nanoparticles. At low pH (4.7) multiply charged pyrophosphate ion ($P_2O_7^{4-}$) was found to stabilize TiO_2 nanoparticles by adsorbing to the particle surface and increasing the surface charge (Jiang et al., 2009). Zhang and his colleagues investigated the impact of Suwannee River natural organic matter (NOM) on five engineered metal oxide nanoparticles, and their results showed that 4 mg/L NOM was sufficient to stabilize most of the five nanoparticles (Zhang et al., 2009). Suwannee River fulvic acid (SRFA) showed the opposite effect on TiO_2 aggregation under varying pH and IS conditions (Domingos et al., 2009). Below the pH_{pzc}, TiO_2 nanoparticles were completely stabilized in the presence of SRFA regardless of the electrolyte concentration; in contrast, SRFA facilitated TiO_2 aggregation at low IS when the pH was above pH_{pzc}, which was ascribed to the bridging effect of SRFA caused by the increased molecular rigidity of SRFA (Domingos et al., 2009). Complicated behavior was also observed in the case of alginate-coated hematite aggregation (Chen et al., 2006). In the presence of $CaCl_2$, the aggregation of alginate-coated hematite was abnormally faster than that predicted by conventional theory for diffusion-limited aggregation. An alginate-gel-network-formation mechanism in the presence of Ca^{2+} ion was proposed to account for the phenomenon.

There have been few studies (Vold, 1954; Kozan and Sunkara, 2008) that studied the effect of colloid morphology in particle aggregation. Vold (1954) provided a theoretical analysis of the van der Waals attraction energy for particles with different morphology, while Kozan and Sunkara (2008) studied the role of particle morphology in controlling the aggregate compactness. In this study, two ZnO nanoparticles with distinct morphology were selected. Since the solubility of ZnO increases sharply when pH is below 7 or above 11 and it becomes completely dissolved around pH 6 and 12 (Dange et al., 2007), all the experiments in this study were conducted in the pH range of 7–11 to minimize dissolution. The aim of this study was twofold. First, to examine the aggregation kinetics of ZnO under varying solution chemistries. Second, to investigate the role of particle morphology in ZnO NP aggregation by comparing the aggregation processes of two differently shaped ZnO NPs.

2. Theory

2.1. Attachment efficiency

The early-stage aggregation kinetics (in practice treated as the time in which the aggregate's mean diameter grows by 25%) is believed to reflect the formation of doublets (Chen et al., 2006),

$$\left(\frac{da_h(t)}{dt}\right)_{t\to 0} \propto k_{11}N_0 \tag{1}$$

where $a_h(t)$ is the hydrodynamic diameter of aggregates as a function of time t, N_0 is the initial number concentration of primary particles, and k_{11} is the doublet formation rate (Chen et al., 2006). As the electrolyte concentration increases, the doublet formation rate becomes faster because of decreased interparticle repulsion. When the interparticle energy barrier is completely diminished, k_{11} will be equal to the Smoluchowski aggregation rate (diffusion-limited aggregation rate), which is given by $k_{Smol} = 8\ kT/3\ \mu$ (Kim and Berg, 2000), where k is Boltzmann's constant, T is the absolute temperature and μ is the liquid's viscosity. The stability ratio, $\alpha = k_{11}/k_{Smol}$, is used to describe the aggregation kinetics. The diffusion-limited (DLCA) and reaction-limited (RLCA) clustering aggregation regimes can be identified in a plot of electrolyte concentration vs. α.

2.2. Fractal dimension

It has been recognized that many aggregation processes are fractal in nature (Kim and Berg, 2000). Most aggregates can be characterized by a non-integer dimensionality, i.e., the mass of a fractal aggregate, $m(R)$, is proportional to its hydrodynamic radius, a_h, to a power d_F, the fractal dimension (Burns et al., 1997):

$$m(R) \propto a_h^{d_F} \tag{2}$$

Experimental d_F values are in the range of 1.7–2.5 (Burns et al., 1997). The fractal dimension is related to the aggregation rate, the slower the aggregation, the more particles have time to configure themselves into a more compact structure, and the higher the fractal dimension. Typical DLCA aggregates possess a d_F of 1.7–1.8, while RLCA aggregates often exhibit a d_F value around 2.1 (Burns et al., 1997).

Dynamic light scattering (DLS) measurement can be used to determine d_F for particles with spherical primary particle shape. The theoretical basis of the DLS technique is that a relationship between hydrodynamic size a_h and time t exists as follows (Berka and Rice, 2005):

$$a_h(t) \propto (1 + t/t_a)^{1/d_F} \tag{3}$$

where t_a is the characteristic Brownian aggregation time for doublet formation, given by:

$$t_a = 1/(k_{11}N_0) \tag{4}$$

3. Materials and methods

3.1. Materials

ZnO nanoparticles were obtained as dry powder from two sources: Meliorum Technologies (denoted as Me ZnO) (Rochester, NY) and M.K. IMPEX Canada (denoted as Mk ZnO) (Mississauga, Canada). X-ray diffraction (Bruker D8 Advance, Madison, WI), Scanning electron microscopy (SEM) (FEI XL40, FEI company, Hillsboro, OR), Transmission electron microscopy (TEM) (FEI Tecnai G2 Sphera Microscope, FEI company,