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Sensitivity of nanoparticles' stability at the point of zero charge (PZC)

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ABSTRACT

Since bare-nanoparticles (NPs) without stabilizers in aqueous phase are stabilized by electrostatic forces, pH control is easily used to influence the surface charge and hence the formation of aggregates or agglomerates. Therefore, herein, the sensitivity of bare-NPs' stability in aqueous phase was analyzed close to the point of zero charge (PZC) using six model NPs. The results demonstrated that the sensitivity of NPs' agglomeration/aggregation could be estimated by the diameter ratio (R_D) between the primary and secondary particle sizes. Namely, if the primary particle size was almost identical to the hydrodynamic diameter (HDD), the agglomeration proceeded aggressively.

1. Introduction

The number of potential applications of nanoparticles (NPs) is growing rapidly because of their unique electronic, optical, magnetic and catalytic properties, compared with the corresponding bulk material [1–3]. Controlling the particle size distribution (PSD) and the dispersion state of NPs is a key criterion to good product quality, because the desired product properties can be affected by particle size and the degree of aggregation or the aggregate structure [4,5]. Among the various preparation methods for NPs, wet chemical preparation is a promising method for the economic production of commercial quantities of NPs as it is fast and operable at ambient conditions [6].

Numerous stabilizers or capping materials are used to control the growth of the nanoclusters formed initially and to prevent them from agglomeration and/or aggregation. However, not all of the NPs necessarily need to be surface treated with stabilizers. Such untreated NPs are called bare-NPs, and are produced by metal vapor techniques. NPs in the dry state take two forms: aggregated (hard bonds between primary particles due to sintering) and agglomerated (held by weaker van der Waals forces) [7]. When bare-NPs in powder form are dispersed in solutions, aggregation and/or agglomeration between neighboring bare-NPs easily occur due to the change of pH, temperature, agitation, and light. Namely, they can remain as singlets (primary particles) or form agglomerates or aggregates (secondary particles) surrounded by an electrical double layer. While primary particles show individual movement in solutions, secondary particles show population behavior. The size and PSD of primary and secondary particles in aqueous phase can be analyzed by transmission electron microscopy (TEM) and dynamic light scattering spectroscopy (DLS), respectively [8]. When highly dispersed in solutions, the size of secondary particles approaches that of primary particles.

Proper dispersion of colloidal systems in aqueous media is often achieved by controlling the zeta potential on the NPs via variation of pH or electrolyte. Therefore, the measurement and control of the surface charge and zeta potential of NPs may be used to control the properties of NPs solutions [9]. The stability of an aqueous dispersed system can be tailored by generating like charges of sufficient magnitude on the surface of NPs. Since bare-NPs in aqueous phase are stabilized by electrostatic forces, pH control is easily used to influence the surface charge and hence the formation of aggregates or agglomerates. The point of zero charge (PZC), defined as the pH value at which the net proton charge equals zero, is an important parameter for understanding the aggregation/agglomeration feature of NPs [10]. When bare-NPs are dispersed in solutions at pH_{PZC}, the surface charge of NPs approaches zero and the electrostatic force is diminished, followed by the formation of agglomeration/aggregation between NPs.

Therefore, in this work, we attempted to investigate the dependence of the surface charge on the diameter ratio (R_D) between primary (singlets) and secondary particles (aggregates/agglomerates). Namely, the sensitivity of NPs' stability in aqueous phase was analyzed at pH values near pH_{PZC}. As model NPs, two kinds of TiO_2 and four kinds of SiO_2 were dispersed in solutions of pH 1–12 to determine the hydrodynamic diameter (HDD) and zeta potential.

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2. Experimental

Two kinds of TiO_2 were purchased from Evonik (**TE**, Germany) and Daejoo (**TD**, Korea), and two kinds of SiO_2 from Sigma (**SS**, American) and SukgyungAT (**SA**, Korea). The remaining two kinds of SiO_2 were prepared by the modified Stöber method [11], which afforded 36 and 80 nm sized SiO_2, referred to as **S1** and **S2**, respectively. None of the metal oxides were surface treated with stabilizers, and their diameters were measured by TEM and DLS; the results are summarized in Table 1. After bare-NPs with 100 ppm were dispersed in deionized water (DW) by ultrasonic-generator (Ulh700S, ULSSO Hi-Tech), the solution pH was adjusted by adding HCl and NaOH as needed.

The morphological properties of the NPs were observed by TEM (JEM-1010, JEOL), and HDD and zeta potential were analyzed by DLS (ELS-Z, Photal). The PSD of bare-NPs dispersed in various pH solutions was analyzed by ImageJ™ software (NIH) based on the TEM images.

3. Results and discussion

Various methods have been published on how to avoid the formation of coarse agglomerates of NPs dispersed in liquid phase. The importance of the correct ultrasound energy and of the use of dispersion stabilizers was emphasized for the optimal de-agglomeration of NPs [12]. Sonication preceding the addition of a dispersion stabilizer to the NP dispersion has been shown to be more effective than sonication afterwards. However, herein, a simple sonification procedure without any stabilizer addition was used as the stabilizing method to consider the effect of surface charge of the NPs on the aggregation or agglomeration.

After the dispersion of NPs in DW, PSD and diameter were analyzed with TEM and DLS. As shown in Fig. 1, **TE** and **SA** showed aggregated and agglomerated forms, respectively. Despite being well dispersed with ultrasonification, **TD** and **SS** also exhibited an aggregated form, whereas **S1** and **S2** showed an agglomerated form (Fig. S1). Typically, when agglomerated NPs are added to a liquid they can be separated by overcoming the weaker attractive forces by sonification, whereas the aggregated NPs cannot be separated easily [7].

After image analysis with ImageJ software based on several TEM images of the NPs, the PSD for the primary particle size could be obtained (Fig. 1b and e). The PSD of the secondary particles, HDD (D_0), was simply analyzed by DLS (Fig. 1c and f). The average diameter of all the NPs is summarized in Table 1. Even if the HDD of the NPs suspended in aqueous media is determined to be larger

Table 1
PZC, diameter (TEM and DLS), diameter ratio (R_D), and equation constants of the six NPS.

Type	Samples	PZC	Diameter (nm)		Diameter ratio, R_D	Equation constants	
			TEM	DLS (D_0)		D_a (nm)	S (1/mV)
TiO_2	TE	6.7	27	200	0.14	5528	0.198
	TD	7.8	15	175	0.09	10,960	0.219
SiO_2	SS	2.5	11	176	0.06	3.1	3.7E-9
	SA	1.9	47	170	0.28	3387	0.196
	S1	2.2	36	61	0.59	113	0.487
	S2	2	80	84	0.95	151	1.518

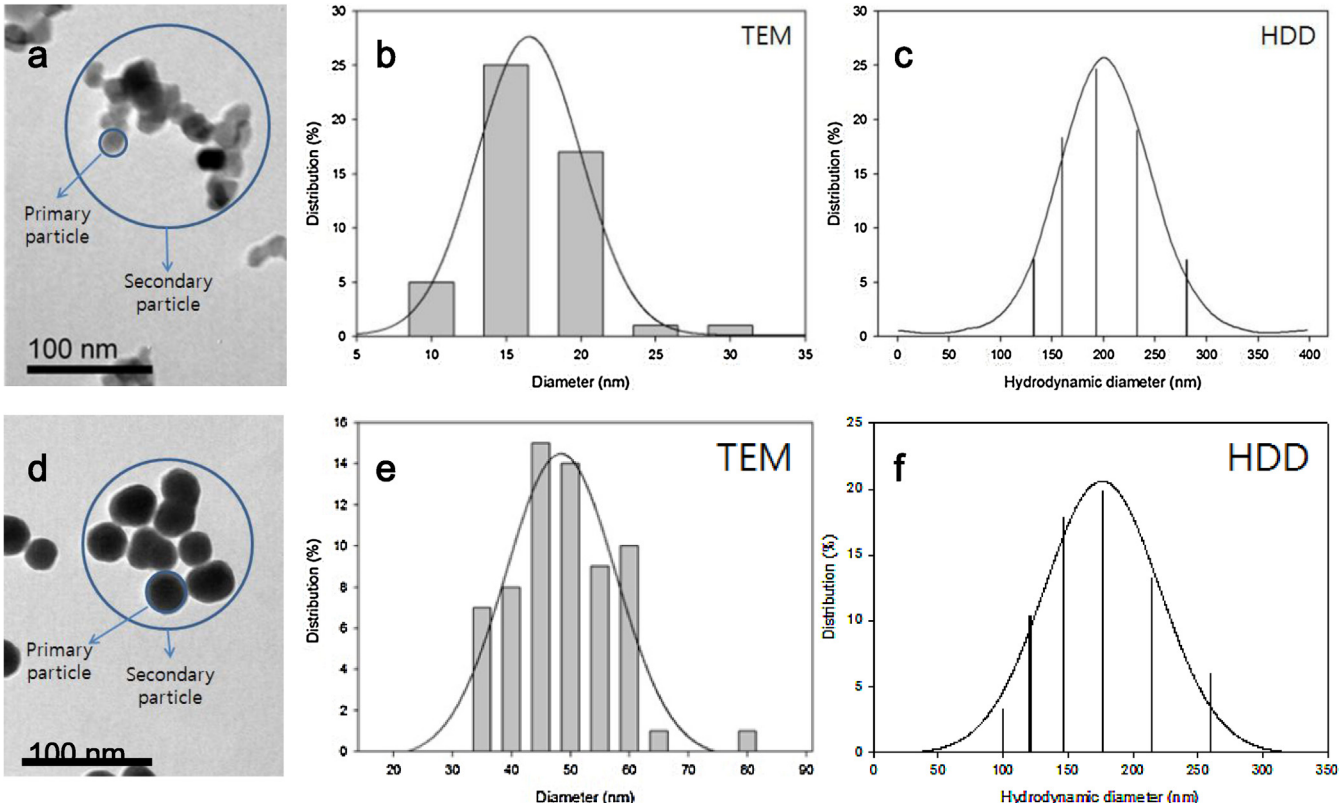

Fig. 1. TEM image and particle size distribution (PSD) analyzed by TEM and DLS for (a–c) **TE** and (d–f) **SA** NPS.