Influence of metal oxide nanoparticles concentration on their zeta potential

Nan Wang [a,b], Chien Hsu [a], Lihua Zhu [b,*], Shiojenn Tseng [c,*], Jyh-Ping Hsu [a,*]

[a] Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan
[b] College of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, PR China
[c] Department of Mathematics, Tamkang University, Tamsui, Taipei 25137, Taiwan

ABSTRACT

In an attempt to estimate the zeta potential of various metal oxide nanoparticles (NPs) dispersed in water, it is interesting to observe that both the magnitude and the sign of this property depend highly upon their concentration. For example, in the case of naked TiO_2 at pH 6, the zeta potential increased from -6.7 to 8.2 mV as the particle concentration varied from 0.5 to 5 mg L^{-1}. As a result, the isoelectric points of naked TiO_2, Fe_3O_4, $Fe(OH)_3$, and Al_2O_3-coated TiO_2 could deviate ca. one, one, two, and three pH units, respectively, depending upon the particle concentration. We showed that these behaviors arise mainly from that the dissolved ambient CO_2 reacts with the particle surface functional groups to form $>MOCO_2^-$, which neutralizes or even overcompensates the particle surface charge. The surface density of $>M-OCO_2^-$, $[>M-OCO_2^-]_S$ depends upon the particle concentration; if it is sufficiently high, $[>M-OCO_2^-]_S$ becomes negligible, so is its influence on the zeta potential. We concluded that the zeta potential measurements for the tested NPs are reliable only if their concentration exceeds a certain level. This also applies to other metal oxides or hydroxides, the surface of which reacts appreciably with dissolved CO_2. The results gathered are of practical significance in estimating the surface properties of unknown and/or newly synthesized NPs since conventional measurements are usually made at dilute particle concentrations.

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1. Introduction

Nanoparticles (NPs) exhibit unique chemical and physical properties, which depend upon their shape, size, and local environment. Often, these particles are applied in wet atmosphere, resulting in potential physicochemical changes such as their sizes and charged conditions due to aggregation and surface reactions, respectively. The surface charge of NPs influences significantly their aggregation behavior, reactivity, and toxicology [1,2]. However, available techniques are unable to measure accurately this property, and it is commonly estimated by the corresponding zeta potential, the electric potential of a particle on the inner boundary of its diffuse layer. Zeta potential is closely related to suspension stability and particle surface morphology and is widely used in relevant studies [3–9]. Sun, for example, found that the dispersion quality of surfactant-stabilized single-walled carbon nanotubes scaled very well with their zeta potential [10]. Zeta potential measurements also provided a simple and rapid "direct-on particle" approach to analyze the multistep chemical reaction sequences carried out on

nano- and micro-sized particles in heterogeneous catalysis [11]. In cell biology, the concept of zeta potential has been used to study cell biological activation, cell agglutination, and cell adhesion [1,2,4]. Zhang proposed a theoretical zeta potential model to predict the interaction of iron oxide NPs with normal and cancer human breast epithelial cells [4].

Among the methods for zeta potential measurement, electrophoretic light scattering, capillary electrophoresis, acoustic, and electroacoustic, the first one is commonly used due to its sensitivity, accuracy, and versatility [12]. Both theoretical and experimental results have confirmed that zeta potential is affected not only by the suspension conditions such as pH, temperature, ionic strength, and even the types of ions in the suspension [13–16], but also by the particle properties such as size and concentration. Experimental observations revealed that the isoelectric point (IEP) of NPs depended upon the particle size [17,18], and the zeta potential could be particle concentration dependent [12,19,20]. Low particle concentrations may seriously degrade the signal-to-noise ratio, resulting in noisy and inconsistent results. Tantra et al. [19] reported that below a certain particle concentration, the zeta potentials of Ludox (silica), multi-walled carbon nanotubes, and gold NPs have an apparent shift to a less negative value. This was due to a significant contribution of the signal from extraneous

* Corresponding authors. Fax: +886 2 2362 3040 (J.-P. Hsu).
E-mail addresses: lhzhu63@yahoo.com.cn (L. Zhu), topology@mail.tku.edu.tw (S. Tseng), jphsu@ntu.edu.tw (J.-P. Hsu).

particles. On the other hand, particle interactions, multiple scattering, and turbidity effects become significant at high concentrations. As pointed out by Xu [12], electrophoretic light scattering is inapplicable as the particle concentration exceeds 0.01%. In fact, even if the particle concentration takes a medium high value, the measured zeta potential can still be affected by that concentration. For example, when dispersed in very dilute solutions of cetyltrimethylammonium bromide (CTAB, 4×10^{-7} mol L^{-1}), the zeta potential of hexadecane particles decreased from 60 to −60 mV as their concentration increased from 100 to 2000 mg L^{-1} [20]. This was explained by that the higher the particle concentration, the smaller the averaged amount of CTA^+ ions adsorbed on each particle surface [20]. Suttiponparnit observed that the zeta potential of TiO_2 particles increased from 29 to 38 mV as their concentration increased from 15 to 500 μg mL^{-1}, due to the increase in the total surface area of titania particles [18]. These strongly suggest that a detailed study on the dependence of zeta potential upon particle concentration is necessary, so that the results obtained are reliable and of practical value. However, a thorough survey reveals that there is a lack of such information.

Due to its various potential applications in biomedical, optical, electronic, and environmental fields, nanotechnology is currently an area of intense scientific research. For example, titanium dioxide (TiO_2) NPs are widely used in photocatalysis, and sunscreen [21,22], ferrosoferric oxide (Fe_3O_4) NPs have potential applications in magnetic storage media, biosensing, and Fenton catalysis [23,24]. In an attempt to estimate the zeta potential of the aqueous dispersion of these particles, it is interesting to observe that both its magnitude and sign depend upon their concentration. Since the ionic species in the liquid phase are inert, the mechanism of Medrzycka [20] is insufficient for the explanation of that behavior. This study focused on a systematic study on the influence of the concentration of various metal oxide NPs on their zeta potential. Possible mechanism involved in zeta potential measurement is proposed and justified by experiments.

2. Experimental section

2.1. Reagents and chemicals

Ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$), ferric trichloride hexahydrate ($FeCl_3 \cdot 6H_2O$), sodium bicarbonate ($NaHCO_3$), calcium carbonate ($CaCO_3$), sodium hydroxide (NaOH), ammonium hydroxide (NH_4OH), hydrogen chloride (HCl) (Showa Chemical Industry, Japan), and NaCl (J.T. Baker-Mallinckrodt, USA) of reagent grade were used. Two kinds of commercial TiO_2 powders were used: Degussa P25 (80% anatase and 20% rutile; primary average particle diameter, 20–30 nm) and TTO-51A (rutile; primary particle diameter, 10–30 nm; surface treated with Al_2O_3; TiO_2 content, 76–83 wt.%; Ishihara Sangyo Kaisha). XPS measurement showed the molar ratio of Al/Ti is about 3:5 on the surface of TTO-51A TiO_2 (Fig. S1a in Supplementary materials). For convenience, Degussa P25 and TTO-51A were defined as naked TiO_2 and Al@TiO_2, respectively. All other reagents were used analytical grade. Deionized (DI) water with a resistivity of 18.2 MΩ cm was used. To avoid the influence on solution pH due to the dissolution of atmospheric CO_2, fresh DI water was left standing overnight to reach equilibrium with atmospheric CO_2 before use. The concentration of dissolved CO_2 was controlled at 1.1×10^{-5} mol L^{-1}, as was confirmed by that the solution pH is kept at 5.5.

2.2. Preparation and characterization of NPs

$Fe(OH)_3$ NPs were synthesized by a reverse precipitation method [25] using NH_4OH and $FeCl_3$ as the precipitator, and the source

of Fe^{3+}, respectively. Fe_3O_4 NPs were prepared by an advanced reverse co-precipitation method assisted by ultrasound irradiation [26]. The NPs obtained were water washed to neutral pH, re-dispersed in water, and then stored at 5 °C. The concentration of total iron and the Fe^{2+}/Fe^{3+} molar ratio in NPs was determined by a 1,10-phenanthroline method (GB/T 14427-2008, China) after they were completely dissolved in 6 mol L^{-1} HCl [26]. The dissolved samples were mixed with 1,10-phenanthroline, followed by adding the NaAc buffer, and then, the amount of Fe^{2+} was estimated by measuring the absorption at 510 nm on a Cary 50 UV–vis spectrophotometer (Varian, USA). Total iron was similarly quantified after adding hydroxylamine hydrochloride to the dissolved samples. The Fe^{2+}/Fe^{3+} molar ratios were 0:1 and 1:2 for $Fe(OH)_3$ and Fe_3O_4, respectively. The chemical composition of Fe_3O_4 is almost unchanged after being stored in a nitrogen atmosphere at dark for 2 weeks. On the basis of the total iron concentration, the estimated mass concentrations of NPs were 5.5 and 5.6 g L^{-1} in $Fe(OH)_3$ and Fe_3O_4 stock suspensions, respectively.

The morphology of iron-bearing NPs was observed by scanning electron microscope (SEM, Hitachi S-4800, Japan) at an accelerating voltage of 5–7 kV, and the corresponding averaged diameters of $Fe(OH)_3$ and Fe_3O_4 primary NPs are ca. 7 and 40 nm, respectively (Fig. S2). Their hydrodynamic size was characterized by ZetaSizer Nano ZS (Malvern Instruments, UK) at 633 nm red laser, based on dynamic light scattering. In the size measurements, dispersions were ultrasonicated for 2 min and then immediately measured.

2.3. Zeta potential measurements

The electrophoretic zeta potential of NPs was also measured by ZetaSizer Nano ZS with a laser Doppler electrophoresis technique. The net electrophoretic mobility of a particle, μ, was measured, which is converted to its zeta potential, ζ, by Henry's approximation [27]

$$\mu = \frac{2\varepsilon_0 \varepsilon_r \zeta f(\kappa r)}{3\eta}, \tag{1}$$

where ε_0, ε_r, κ, r, η, and $f(\kappa r)$ are the permittivity of a vacuum, the medium dielectric constant (or permittivity), the Debye–Hückel parameter (or reciprocal double layer thickness), the hydrodynamic radius of particle, the medium viscosity, and the Henry's function, respectively. $f(\kappa r) \rightarrow 1.5$ as $\kappa r \rightarrow \infty$ (infinitely thin double layer) (Smoluchowski approximation) and $f(\kappa r) \rightarrow 1$ as $\kappa r \rightarrow 0$ (infinitely thick double layer) (Hückel approximation). The Debye–Hückel parameter κ is calculated by

$$\kappa = \left(\frac{2000F^2}{\varepsilon_r \varepsilon_o RT}\right)^{1/2} \sqrt{I}, \tag{2}$$

where F, R, T, and I are Faraday constant, gas constant, the absolute temperature, and the ionic strength (mol L^{-1}), respectively.

The measurements were made at 25 °C, and unless specified otherwise, the solvent was DI water containing 1 mmol L^{-1} NaCl, the natural pH of which was 5.5. The solution pH, which ranged from 3 to 11, was adjusted by either 0.1 mol L^{-1} HCl or NaOH. After preparation, the NaCl solution was kept in a glass vial with screw cap and used within 2 h. In the electrophoretic measurements, about 10–400 μL of NPs stock dispersion was rapidly introduced to 10 mL of NaCl solution in a glass vial with screw cap, and ultrasonicated for 1 min. Then, an aliquot sample was rapidly transferred into a folded capillary cell with two caps. Because the processing time is too short for CO_2 to reach equilibrium at gas/ solution interface, the CO_2 concentration in the capillary cell including that both dissolved in the liquid phase and adsorbed on the surface of metal oxide NPs is roughly constant. N2-saturated electrolyte solution was used to disperse Fe_3O_4 NPs, and the atmo-