Advanced Powder Technology 26 (2015) 1676–1686

Contents lists available at ScienceDirect

Advanced Powder Technology

journal homepage: www.elsevier.com/locate/apt

Original Research Paper

Understanding ligand–nanoparticle interactions for silica, ceria, and titania nanopowders

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ARTICLE INFO

Article history:
Received 5 July 2015
Received in revised form 1 September 2015
Accepted 8 October 2015
Available online 24 October 2015

Keywords:
Nanoparticle
Ligand
Colloid
Stability
Aggregation

ABSTRACT

We performed a systematic study on titania, ceria, and silica nanopowders, to investigate their interactions with ligands and the corresponding colloidal stability in aqueous solutions. Electrospray–differential mobility analysis (ES–DMA) was employed for characterization of particle size distributions (PSDs), including the peak diameter ($d^*_{\mathrm{p,m}}$) and the full width at half maximum (FWHM) of nanoparticle suspensions. Transmission electron microscopy and zeta potential analysis were employed orthogonally to provide information of particle imagery and surface charge, respectively. Bovine serum albumin, sodium dodecyl sulfate, and cetyltrimethylammonium bromide were chosen as representative ligands. Results show that we were able to successfully characterize the ligand–nanoparticle interaction including the aggregation, de-aggregation, and the surface dissolution of nanoparticle using ES–DMA. Based on the measured $d^*_{\mathrm{p,m}}$, FWHM, and the number concentrations over various experimental conditions, we observed that the colloidal stability was strongly dependent of the environmental pH, isoelectric point (IEP) of nanoparticle, and the acid dissociation constant ($\mathrm{p}K_\mathrm{a}$) of ligand. Fast aggregation was found when the absolute zeta potential of nanoparticles was below 18 mV and/or Ω (defined as $|(\mathrm{IEP} + \mathrm{p}K_\mathrm{a})/2 - \mathrm{pH}|$) < 2. Our work demonstrates a prototype study for establishing the capability of characterizing ligand–nanoparticle interactions and developing a correlation to the corresponding colloidal stability in a variety of aqueous environments (e.g., formation chemistry, natural water system).

1. Introduction

Nanomaterials are highly attractive to current industry and emerging technology [1–13]. Among the nanomaterials available in the market, ceramic nanopowders, especially silica, ceria, and titania, have been employed extensively as important components in nanomaterials-enabled products [7–9,14–17]. For examples, silica and ceria nanopowders can be used as abrasive particles in a variety of slurry products for chemical mechanical planarization in the manufacture of electronic industry [7–9]. The specific nano-scale dimension can induce strong particle–wafer contact for the delivery of the mechanical force and the formulants involved in the contact. This contact can accelerate the removal rate and increase the selectivity in surface planarization. Titania nanopowders are commonly used in the formulation chemistry of sun cream-related products or surface coating materials, due to their superior properties in photocatalysis. Moreover, these ceramic nanopowders can also be used to alter the properties of the foods [1,5]. By choosing a suitable formulation chemistry (e.g., surfactant-type ligands), these nanopowders are able to be dispersed and formed nanoparticle suspensions to achieve the desired performance in a variety of industrial applications [5,11–13,16,18].

Although the recent advancements in nanotechnology led to improvements in the performance of materials in many aspects, the wide-spread usage or frequent contacts with these nanopowders in the form of particle suspensions can result in negative consequences in the environmental health and safety. For example, previous studies have shown that nanoparticles with sizes less than 100 nm may be able to cross the biological barrier, in contact with the cells, disrupt normal activity and lead to malfunction and diseases [1,5,19–21]. The mechanism of nanoparticle-induced hazards can be even more complicated when involved in ligands

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http://dx.doi.org/10.1016/j.apt.2015.10.005

presented in the media. In order to continuously support industrial development, a necessity to be included in the rational design is the strategy of assessing and minimizing the potential hazards. Hence a better understanding of ligand–nanoparticle interaction is of critical importance.

However, a challenge is about the capability in the characterization of the key materials properties for nanoparticles. Uncertainties in the measured properties could lead to confusions in data interpretation for the corresponding impact of nanoparticle in environmental health and safety. These general crucial concerns, could adversely affect the eventual implementation of promising nanoparticles and their related products. Recent studies have shown that physical dimension (size, state of agglomeration), composition, surface properties (including molecular conjugation), and colloidal stability are critical to the performance of nanoparticles and their impact in EHS [1,2,5,22]. To correctly evaluate the material properties and the corresponding colloidal stability, it is necessary to establish a suitable characterization approach for nanoparticle in the form of suspension over various environments.

In this work, we choose three types of nanopowders, silica (SiO_2-NP), titania (TiO_2-NP), and ceria (CeO_2-NP), as our model systems, and we study the effect of acidity on colloidal stability of these nanoparticle suspensions. Bovine serum albumin (BSA), sodium dodecyl sulfate (SDS), and cetyltrimethylammonium bromide (CTAB) were chosen as representative ligands due to high interest in these ligands in current technology [7–9,11,12,16,17,23,24]. BSA is an amphoteric protein molecule (the isoelectric point, IEP, ≈5) and has shown to be the most widely used serum protein due to its wide availability and structural/functional similarity to human serum albumin [25]. CTAB is a cationic quaternary surfactant that can be used as an antiseptic agent against bacteria. The acid dissociation constant in logarithmic form, pK_a, is ≈10.5 for CTAB. SDS is an anionic surfactant (pK_a, ≈1.9) typically used in cleaning/hygiene products. In addition, SDS can unravel proteins for the subsequent analysis of gel electrophoresis. In addition to the functionalities described above, all of the three ligands can be used for stabilizing nanoparticles in aqueous solutions. Our strategy is to use electrospray–differential mobility analysis (ES–DMA) and characterize particle size distributions (PSDs) of CeO_2-NPs, SiO_2-NPs, and TiO_2-NPs in aqueous solution. Based on the observed results in PSDs, we can correctly probe the surface reactivity to ligands (BSA, CTAB and SDS) and the corresponding phenomena of nanoparticles in environments (i.e., aggregation, de-aggregation, surface dissolution). Transmission electron microscopy (TEM), zeta potential analysis, and X-ray diffractometry (XRD) are used orthogonally to provide information of morphology, surface potential, and crystalline state, respectively. Our objective is to develop a methodology to characterize the key material properties of nanoparticles and to establish a correlation of ligand–nanoparticle interactions to colloidal stability.

2. Experimental

2.1. Materials

The nanoparticle suspensions were prepared by dispersing titanium dioxide powders (Degussa P25, Sigma–Aldrich, St. Louis, MO, USA), silicon dioxide powders (HDK® N20, Wacker, Munchen, Germany), and in-house synthesized CeO_2 powders [26] directly in de-ionized (DI) water. The samples of TiO_2-NP were sonicated for 6 h using an ultrasonic processor (UP-500, E-Chrom Tech., Taipei, Taiwan, R.O.C) at a power of 20% of maxima (500 W); the samples of SiO_2-NP and CeO_2-NP were dispersed directly using an ultrasonic bath (LEO-801S, YSC Inc., Hsinchu, Taiwan, R.O.C.). The particle dispersions were shown to be homogeneous and were not found further de-aggregation by increasing the sonication time through the analysis of particle size distributions. To avoid the lot-to-lot variation, we chose to use the same batch of nanoparticle dispersion for further comparisons. Bovine serum albumin (BSA, >98%, Sigma–Aldrich), sodium dodecyl sulfate (SDS, 95%, Sigma–Aldrich) and cetyltrimethylammonium bromide (CTAB, 98%, Alfa Aesar, Ward Hill, MA, USA) were used without further filtration. Nitric acid (1st grade, Union Chemical Works Ltd., Taiwan, ROC), acetic acid (>99.7%, Macron Fine Chemicals™, Avantor Performance Materials, Center Valley, PA, U.S.A), and ammonium hydroxide (>98.5%, Sigma–Aldrich) were used to adjust the acidity of the samples. Biological grade 18.2 MΩ cm DI water (Millipore, Billerica, MA, USA) was used to prepare solutions and nanoparticle suspensions. The mass fraction of nanoparticles in the samples was determined by measuring the concentrations of Ti, Si, and Ce in solution phase using inductively coupled plasma mass spectrometry. Results show that the mass concentrations of particles in solution were ≈37.6 ppm for the SiO_2-NP samples, ≈66.7 ppm for the TiO_2-NP samples, and ≈17.2 ppm for the CeO_2-NP samples. BSA was employed as an amphoteric surfactant, and CTAB and SDS were used as representative anionic and cationic surfactant molecules, respectively.

2.2. Electrospray–differential mobility analysis (ES–DMA)

The ES–DMA was used to obtain a number-based particle size distribution [27–31]. Briefly, the electrospray aerosol generator (model 3480, TSI Inc., Shoreview, MN, USA) was used to aerosolize particles by continuously sampling a particle dispersion through a fused silica capillary (40 μm inner diameter) using a differential pressure of 3.7 psi. The aerosolized particles (1.2 L/min) were delivered to an electrostatic classifier (Model 3081, TSI Inc.), where the particles were classified based on their electric mobility under an applied DC electric field, with a sheath flow of dry and filtered air carrying nanoparticles downstream (10.0 L/min). As the electric field was varied, the nanoparticles with the specific mobility size, $d_{p,m}$, were counted by a condensation particle counter (CPC, Model 3775, TSI Inc.). The step size used was 2 nm and the time interval between each step size was 10 s. For the characterization of colloidal stability, the number density was directly recorded by CPC without further correction in the selected size and also the size-dependent charge efficiency [27,28,32]. Mass concentrations of nanoparticles were constant in the samples of dispersions over the reaction time.

2.3. Transmission electron microscopy (TEM)

The morphology of nanoparticles was imaged using a TEM (model: JEM-1200EX II, JEOL, Tokyo, Japan) operated at 80 kV. To investigate the primary size and the morphology of individual nanoparticles, positively-charged aerosolized particles were delivered to a home-made electrostatic precipitator and deposited onto a copper grid with carbon film operated at a sample flow rate of ≈1.5 L/min and −(2–5) kV/cm electric field. Due to the electrostatic repulsion, the deposition-induced aggregation was negligible during sample collection [27,28,33,34]. The drop-cast method was also employed to prepare samples used for the study of surface dissolution of nanoparticles.

2.4. X-ray diffraction (XRD)

The XRD patterns of ceramic nanopowders (TiO_2-NPs, CeO_2-NPs, and SiO_2-NPs) were recorded using a X-ray powder diffractometer (Ultima IV, Rigaku Cooperation, Japan), with Cu Kα radiation (λ = 1.5406 Å) at 40 kV, 20 mA, and a scanning rate