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Original Research Paper

Low-energy bead-milling dispersions of rod-type titania nanoparticles and their optical properties

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ABSTRACT

The low-energy dispersion of nanomaterials in the bead-milling process is examined. The effect of milling parameters including bead size, rotation speed, and milling time on the dispersibility of fragile rod-type titanium dioxide nanoparticles is investigated. From experimental data obtained for the morphological, optical, and crystalline properties of dispersed nanoparticles, an unbroken primary particle dispersion in colloidal suspension was obtained only by conducting the bead-milling process using the optimum milling parameters. Deviation from the optimum conditions (i.e., higher rotation speed and larger bead size) causes re-agglomeration phenomena, produces smaller and ellipsoidal particles, and worsens crystallinity and physicochemical properties, especially the refractive index, of the dispersed nanoparticles. We also found that decreases in refractive index induced by the milling process are related to collisions forming broken particles and the amorphous phase on the surface of the particles. In addition, the present low-energy dispersion method is prospective for industrial applications, confirming almost no impurity (from breakage of the beads) was apparent in the final product.

1. Introduction

Recently, the dispersion of nanomaterials has attracted tremendous attention because only well-dispersed and undamaged single nanoparticles show great potential for use in electronic, chemical, mechanical, and biological applications [1,2]. Well-dispersed nanoparticle suspensions are important because they are able to be reformed and reassembled into either larger particles [3–6] or films [5,7,8] with controllable structures. Various well-dispersed nanoparticles are now commercially available, such as metals, metal oxides, metal nitrides, metal carbides, and polymers [9].

Many methods for dispersing nanomaterials have been utilized including ultrasonic-assisted dispersion, jet, ball, bead, and roll milling, and homogenization. However, only partial information about the effects of operating conditions, dispersion media, surface-modification agents, and type of collision and energy involved in current dispersion methods on the dispersion process is available.

Previously, we studied the dispersion behavior of various nanomaterials such as titanium oxide, aluminum oxide, zinc oxide, boron nitride, titanium nitride, iron oxide, carbon black, and nickel metal in bead milling [1,10–14]. Bead milling is effective for dispersing nanomaterials without chemical reaction or changing material properties. However, the influences of the processing parameters of bead milling on the optical properties and crystallinity of the dispersed nanomaterials have not yet been studied in detail.

Here, we investigated the effects of bead-milling dispersion parameters including bead size, rotation speed, and milling time on the dispersibility of nanoparticles and examined the morphological, optical, and crystalline properties of the dispersed nanoparticles. Additionally, to minimize the impact energies during the dispersion process, we conducted bead milling using beads with diameters of several tens of micrometers, whereas current milling processes use beads that are hundreds of micrometers in diameter [15–22]. The use of smaller beads helps to prevent the fragmentation of nanoparticles and maintain their properties (e.g., crystallinity). Rod-type titanium dioxide (TiO_2) was used as a model dispersed nanomaterial. TiO_2 was selected because it is widely used, nontoxic, and inexpensive, but most commercially available

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TiO_2 materials are in bulk or aggregated forms [3]. A rod-type material was chosen to examine the ability of our present bead-milling process to disperse a fragile material. To show the effectiveness of our present method for industrial applications, we also added an investigation of the purity of the beads-milling product, especially from the breakage of bead, while information about purity is typically disregarded in the current dispersion papers.

2. Dispersion behavior of agglomerated nanoparticles in the bead-milling process

Fig. 1 shows illustration of the particle dispersion during the bead-milling process based on the type of energy used in the dispersion process. We used two types of dispersions: high energy and low energy. In this classification of energy, low energy defines the condition of bead-milling process that provides the break of agglomerated particles in the agglomerate position only.

In the case of high-energy milling process (the first route), the properties of final dispersed materials sometimes changed. High-energy dispersion process allows the radical break up of particles. The break up position can be in both agglomerate and main body of crystal positions. As a result, dispersed slurry contains multisized particles. Further, this condition is incompatible for the case of fragile materials. In addition, milling time is also important. Too long milling process leads the re-agglomeration phenomena.

To be effective for dispersing material with less properties damage, the second route can be an alternative. Since the nanoparticles typically softly agglomerate, optimization process that is able to break the agglomerated particles in the agglomerate position only is crucial. Indeed, when applying the low-energy dispersion process, the final slurry contains single sized of dispersed nanoparticles with properties that are similar to their original characteristic.

Based on the current development, to get low-energy dispersion process in the realistic bead-milling process, several operating parameters should be considered, including milling time, temperature, bead and particle sizes, rotating speed, physicochemical properties and composition of dispersed media, and agglomerated particles. In our previous works [13,14], the low energy in bead-milling dispersion can be obtained when conducting the milling process with a specific condition. This condition can be achieved when the process was conducted with rotational speed and bead size of 10 m/s and 30 μm, respectively. Deviation from this condition results re-agglomeration phenomena, produces smaller and broken particles, and worsens crystallinity and physicochemical properties of the dispersed nanoparticles. Therefore, in this study, influences of less milling time, lower rotational speed, and smaller bead size were investigated, whereas other operating parameters will be discussed in our future study.

3. Experimental method

Commercial rod-type TiO_2 nanoparticles (MT-01, rutile phase; Tayca Co. Ltd., Japan; surface modified with stearic acid and alumina) as a nanoparticle source were dispersed in toluene (Kanto Chemical Co. Ltd., Japan) using Crodafos (oleth-5-phosphate and dioleyl; Croda, Japan). The composition of raw materials was fixed at a mass ratio of toluene/TiO_2/Crodafos of 90/5/5. This suspension is referred to as the TiO_2 slurry.

The TiO_2 slurry was then added to the bead-milling apparatus. A schematic diagram of the bead-milling apparatus is shown in Fig. 2 and detailed apparatus information is reported in our previous reports [1,10–12]. In brief, the apparatus was a bead-milling vessel with a volume of 0.15 L equipped with a pump to supply the nanoparticle slurry, a mixer tank, and a centrifuge to separate the beads and TiO_2 slurry. The inner diameter and height of the bead-milling vessel are 50 and 150 mm, respectively. Regarding the configuration in the bead-milling vessel, we used a rotor with a diameter of 44 mm equipped with 11 of rotor pin. The bead filling ratio is 65% of the total vessel volume. Prior to adding the TiO_2 slurry, beads (zirconia beads; Nikkato Corp., Osaka, Japan) were added to the bead-milling system. In this study, milling time, bead size, and rotation speed were varied. During the bead-milling process,

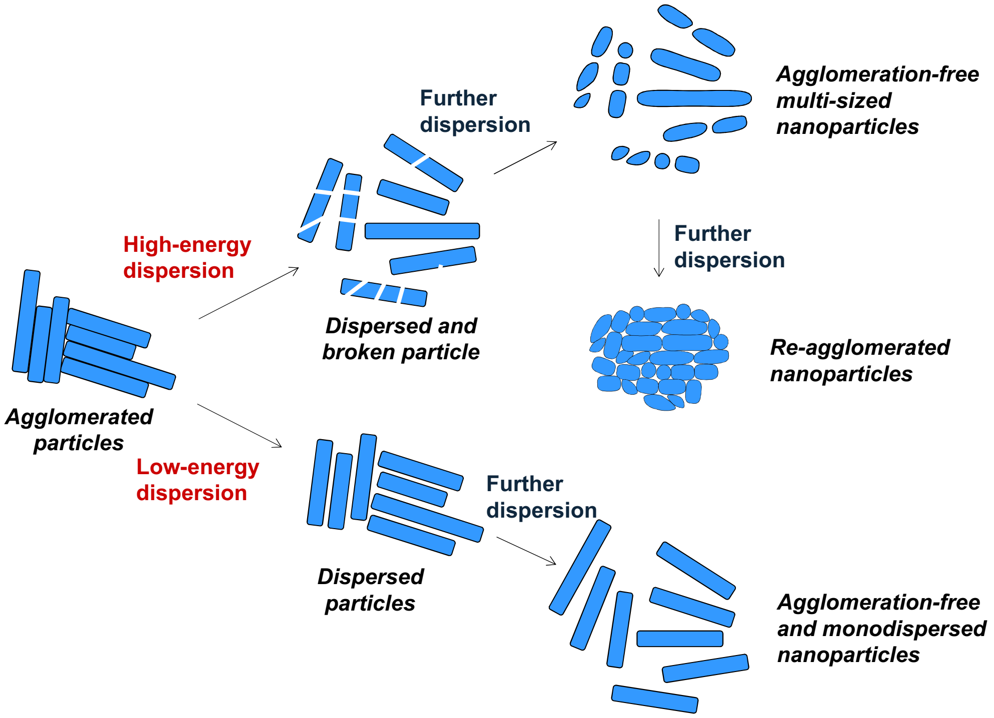

Fig. 1. Schematic illustration of the particle dispersion process considering the effect of dispersion energy.

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