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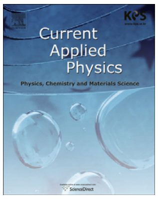

Surface coating of Al nanoparticles by using a wet ball milling method: A facile synthesis and characterization of colloidal stability

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ABSTRACT

A facile surface coating of aluminum (Al) nanoparticles with various dispersants by using a wet ball milling method is reported. Various mixtures of Al nanoparticles ($d = 30–130$ nm) and dispersants in solvent were ball milled. The excellent surface coating was observed with coating thickness ranging from 10 to 13 nm. The resulting good colloidal stability confirmed by both visual inspection of colloidal precipitation and Turbiscan backscattering was attributed to a stable dispersant organic layer formed on Al nanoparticle surfaces after ball milling as observed in HRTEM images. This method can be extended to the synthesis of a variety of any other metallic nano-colloidal solutions.

1. Introduction

Surface coating of nanoparticles is very important in both science and technology [1–4]. They should be well coated for protection, solubility, and functionalization. The stable nano-colloids can be applied to a variety of areas such as electronic devices, biomedicines, pharmaceutics, cosmetics, foods, paints, pigments, inks, ferrofluids, and so on [3]. The colloidal stability depends on dispersants, solvent, pH, temperature, and particle size [5].

Among nano-colloids, metallic nano-colloids are very important because of their magnetic, electric, and optical properties. They can be applied to MRI contrast agents [6–8], hyperthermia [6–8], and magnetic storages [9,10] by using their magnetic properties. They can be also applied to electrodes in multilayer ceramic capacitors (MLCC) by using their electric properties [11,12], and inks, paints, and pigments by using their optical properties [13,14]. For these applications, both excellent surface coatings for good colloidal stability and large scale productions are necessary. In this regard, the wet ball milling method [5,15] seems to be suitable for this purpose as investigated in this work.

In the wet ball milling method, a mixture of nanoparticles, dispersant, and solvent is ball milled. The mechanism for surface coating of nanoparticles with dispersant is as follows. The nanoparticles collide with balls during ball milling. Surface atoms or ions then become activated due to collision with balls. These activated surface elements form chemical bonds with functional groups of dispersant. The final products are dispersant-coated nanoparticles, *i.e.*, nano-colloids. The ball milling can be even used for organic reactions in which activation energy for reaction is obtained from ball milling [16]. It should be aware that the dispersants may be degraded during ball milling process. Thus, proper dispersants, ball size, solvent, and milling time are important [17,18].

In this work, we applied the wet ball milling method to coat aluminum (Al) nanoparticles with various dispersants. We used terpineol as a solvent and Hypermer KD-2, polyethylene glycol diacrylate 400, and ethoxylated trimethylolpropane triacrylate as dispersants (see Table 1 for chemical structures). Terpineol is a general solvent used for dispersion of surface coated nano-colloids and stable during ball milling. The three dispersants are also commonly used as dispersants and also highly soluble in terpineol. As shown in Table 1, both polyethylene glycol diacrylate 400 and ethoxylated trimethylolpropane triacrylate have C=O groups and Hypermer KD-2 have NH_2 groups. These functional groups are used for conjugation to surface Al^{3+} ions on surface oxide passivated Al nanoparticles. Dispersants with carboxyl groups can be also used as dispersant as used by Graule group [19]. The surface coating layer thicknesses as well as particle diameters were estimated by using a high resolution transmission electron microscope (HRTEM). The

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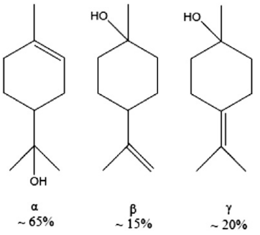
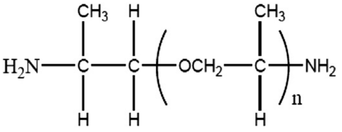
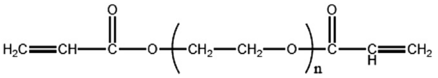
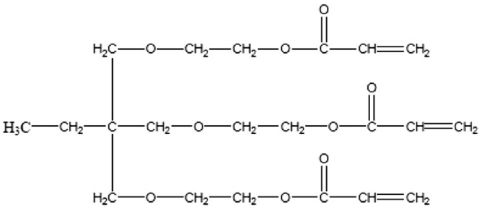
Table 1
Chemical structures of solvent and dispersants.

Solvent/Dispersant	Chemical structure
Terpineol	
Hypermer KD-2	 $H_2N{-}\overset{CH_3}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}\left(OCH_2{-}\overset{CH_3}{\underset{H}{C}}\right)_n{-}NH_2$
Polyethylene glycol diacrylate 400	 $H_2C{=}CH{-}\overset{O}{\overset{\|}{C}}{-}O{-}\left(CH_2{-}CH_2{-}O\right)_n{-}\overset{O}{\overset{\|}{C}}{-}\underset{H}{C}{=}CH_2$
Ethoxylated trimethylolpropane triacrylate	

colloidal stabilities of Al nano-colloidal solutions were evaluated by using both visual inspection of colloidal precipitation and Turbiscan backscattering.

2. Experimental

2.1. Materials

The Al nanoparticles were synthesized by plasma arc-discharge method [20]. In this method, heated plasma (H_2 + Ar) was electrically directed into target Al rod which was then locally melt, from which the evaporated metal vapor grew into Al nanoparticles. The surface oxide passivation of Al nanoparticles naturally occurs when the synthesized Al nanoparticles are exposed to air. Terpineol (α-form: 65%, β-form: 10%, γ-form: 20%) as an organic solvent was purchased from Sigma–Aldrich. Hypermer KD-2, polyethylene glycol diacrylate 400, and ethoxylated trimethylolpropane triacrylate as dispersants were purchased from Uniqema (UK) and Sartomer (USA), respectively [21]. Benzene (>99%) used for HRTEM measurement was purchased from Sigma–Aldrich. All chemicals were used as received without further purification.

2.2. Characterization of Al nanoparticles

The particle diameter (d) of Al nanoparticles was estimated by using a HRTEM (JEOL, JEM-2200FS). The Al nanoparticles were dispersed in benzene. A copper grid covered with an amorphous carbon membrane was placed onto a filter paper and then, a sample solution was dropped over the copper grid by using a micropipette (Eppendorf, 2–20 μL). The elemental mapping by using an electron energy loss spectroscopy (EELS) of HRTEM was used to reveal surface oxide layer of Al nanoparticles. The surface area of Al nanoparticles was estimated by using a Surface Area & Pore Size Analyzer (BET) (Quantachrome, Autosorb-iQ & Quadrasorb SI). In order to measure this, the Al nanoparticles (0.2621 g) were first degassed at 300 °C for 2 h 30 min in vacuum. The N_2 was used as absorbing gas. An X-ray diffraction (XRD) spectrometer (Philips, X'PERT PRO MRD) with an unfiltered CuKα ($\lambda = 1.54184$ Å) radiation was used to determine the crystal structure of Al nanoparticles. The scan step and range in 2θ were 0.033° and 15–100°, respectively.

2.3. Surface coating of Al nanoparticles

A ball milling instrument (Dongseo Science Co., Ltd., South Korea, model: DS – Bm5L) was used to coat Al nanoparticles with

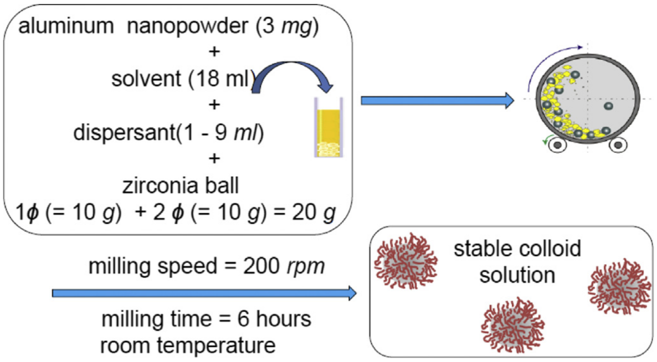


Fig. 1. A schematic diagram of a wet ball milling experiment.