



# Direct scanning electron microscopy-based observation of dispersed core–shell-type nanoparticles in a wet state

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## Abstract

A new sample holder for observing non-dried samples by SEM is presented, and it is employed to investigate the effect of heating on core–shell-type ceria/polymer hybrid nanoparticles to 200 °C in air. Through this, heating is shown to reduce the shell thickness of the nanoparticles. Furthermore, despite this reduction in shell thickness, the nanoparticles maintain a good dispersibility in an aqueous solution. Some sub-micrometer sized agglomerated particles are formed, but only in those instances where the shell thickness is insufficient. This new technique is therefore confirmed as an effective means of assessing the dispersibility of nanoparticles.

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## 1. Introduction

In industrial applications, nanoparticles are rarely used in the form of a powder, but rather, are used as a sol or dispersion [1]. However, this creates problems because nanoparticles in dispersion more readily agglomerate with decreasing particle size, and thus, it is often not possible to fully exploit the unique properties of nanoparticles.

Izu et al. have previously reported that a core–shell-type ceria/polymer hybrid nanoparticle exhibits good dispersibility in water or alcohol when a lyophilic polymer (polyvinyl pyrrolidone: PVP) is used for the shell [2–5]. The thickness of the shell was about 10 nm, when the size of a core-shell nanoparticle was 110–120 nm [3,5]. Moreover, it has been demonstrated that the refractive index of a resin film can be increased by the addition of core–shell ceria/polymer nanoparticles [6]. Since this increase in refractive index is directly proportional to the volume of ceria, the volume ratio of the shell should ideally be reduced.

However, any reduction in the shell volume is expected to reduce the dispersibility of the nanoparticles, and thus a simple method to evaluate the dispersibility of nanoparticles is needed.

To date, dynamic light scattering (DLS) has been the preferred method [7–9] to evaluate the dispersibility of nanoparticles, wherein the particle size is determined from the Brownian motion of particles in a liquid [9]. Since agglomerated nanoparticles are viewed as if they were a singular particle, a determination of particle size by DLS does provide a useful means of evaluating the dispersibility. However, for the size to be determined the refractive index and viscosity of the dispersion needs to be known, and thus, particle size is largely dependent on the accuracy of these calculations. For example, if the particle size changes in response to a change in the dispersion medium, it is very difficult to draw any definite conclusions. This is because the genuine agglomeration of particles is not readily differentiated from basic errors in the measurement of the viscosity and refractive index of the dispersion.

Observation by scanning electron microscopy (SEM) provides an easy way to characterize a sample, and provides a

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range of valuable information regarding its physical and chemical characteristics. However, the need to dry samples prior to observation by SEM has so far limited its applicability in determining the dispersibility of nanoparticles in a wet state. This changed with the development by Ogura of a new atmospheric sample holder to observe wet samples directly by SEM [10,11], which can be applied to nanoparticles dispersed in a liquid.

By taking advantage of this new technology, this study evaluates the effect of the reduction in the ceria/polymer-nanoparticle shell thickness through thermal decomposition, on their dispersibility in water.

## 2. Experimental

A water dispersion of core-shell-type ceria/polymer hybrid nanoparticles was supplied by Hokko Chemical Industry Co., Ltd. The shell was made from PVP and the thickness was about 6 nm. The size of the nanoparticles was approximately 70 nm, with 1 g of nanoparticles per 10 mL of dispersion. This dispersion is hereafter referred to as Dispersion A.

Nanoparticles with reduced shell thickness were obtained by the following process: First, a water dispersion of nanoparticles (Dispersion A) was dried, and then heat treated at 200 °C for 4 h in air to reduce the shell volume; this temperature was selected because it is insufficient to cause sintering of the ceria particles. The resulting powder was then added into water and ultrasonically dispersed. This dispersion contained an equivalent 1 g of nanoparticles per 10 mL of the solution, and is hereafter referred to as Dispersion B.

Both dispersion types were set in a sample holder designed for the observation of wet samples by SEM, a schematic of which is provided in Fig. 1. Samples were prepared by first placing 3  $\mu$ L of solution dropwise onto the upper silicon nitride (SiN) film (thickness of 50 nm). After 1 min, the sample holder and sample drop were placed into a 5 mL centrifugal tube, and the sample was removed using a centrifuge (FlexiFuge Centrifuge, Argos Technologies, USA) at 6000 rpm for 10 s.

Those nanoparticles remaining attached to the sample holder were sealed by a second SiN holder using double-sided tape.

The sample holder was then set in a field emission scanning electron microscope (FE-SEM; JSM-7000F, JEOL, Japan) and images were captured by a secondary electron detector under the following conditions: a magnification of 10,000–50,000, image size of 1280  $\times$  1024 pixels, scanning time of 40 s, working distance of 3–4 mm, electron beam (EB) acceleration voltage of 3–3.5 kV and an EB current of 10–30 pA. Since only transmitted secondary electrons were detected, the nanoparticles were revealed as a black contrast.

Dried powders of Dispersions A and B, denoted Dried Powders A and B, respectively, were characterized by thermogravimetric (TG) analysis (TG-DTA2010SA-II, Bruker Corporation) and Fourier transform infrared (FTIR) spectroscopy (NICOLET NEXUS 470 FT-IR, Thermo Electron Corporation).

## 3. Results and discussion

If the 7.9 wt% of adsorbed water in Dried Powder B is taken into account, then its TG data reveals a 4.0 wt% weight loss during heating to 900 °C that can be attributed to the weight ratio loss of shell. In comparison, the weight ratio of the shell in Dried Powder A was 14.4 wt%, clearly showing that Dried Powder B has greatly reduced shell volume (Table 1).

Fig. 2 shows SEM images of nanoparticles in Dispersions A and B. In Fig. 2 (a), the white space between the 70 nm sized nanoparticles clearly demonstrates that they are well dispersed in water. Conversely, Fig. 2 (b) and (c) reveals sub-micron agglomerated particles, as well as many dispersed particles. The presence of dispersed particles shows that even a thin shell is effective in ensuring good dispersibility; the agglomeration of particles likely occurred due to the shell thickness being insufficient. In Fig. 2 (a), the poorly defined contour of nanoparticles makes observations at magnifications higher than 50,000  $\times$  difficult, even though the FE-SEM used in this study typically allows magnifications of twice this when a normal sample holder is used. This clearly imposes a degree of limitation on the use of this sample holder, although it does allow the dispersibility of core-shell nanoparticles to be directly observed by SEM with sufficient detail to determine their dispersibility.

Fig. 3 shows FTIR spectra of the dried powders, which are similar except for the clear absorption peaks observed in the range of 1200–1800  $\text{cm}^{-1}$  for Dried Powder A; this is attributed to the difference in shell volume and state. Since no absorption peak is observed in this range in the spectrum of

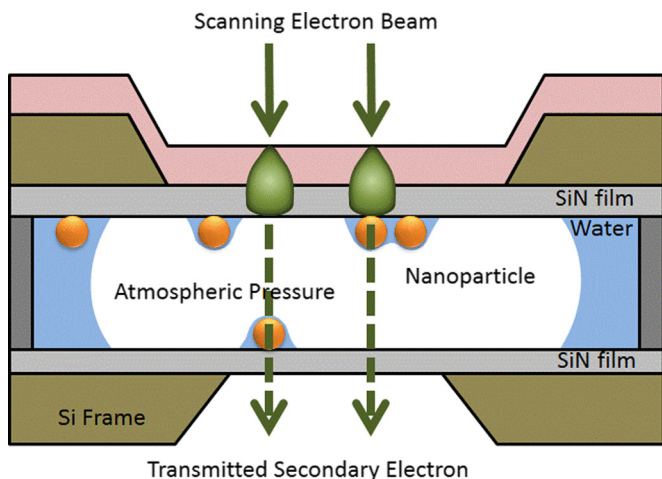


Fig. 1. Schematic drawing of a new sample holder to observe wet samples.

Table 1  
Weight loss of dried powders A and B during heating to 900 °C.

Sample	Total weight loss ( $W_t$ )	Adsorbed water ( $W_w$ )	Weight loss due to shell combustion ( $W_s = W_t - W_w$ )
Dried powder A (wt%)	20.0	5.6	14.4
Dried powder B (wt%)	11.9	7.9	4.0

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