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Distribution of density in spherical colloidal particles by transmission electron microscopy

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ABSTRACT

The variation in the distribution of density in colloidal spherical particles was evaluated by transmission electron microscopy (TEM), without utilizing a high-resolution mode, and quantified by image processing. The method eliminates the dependency of the image contrast on sample crystallinity. The advantage of such approach is manifested by the short time sample preparation, fast instrument tune-up, rapid image acquisition and analysis, all of which shorten the processing time. Colloid silver spheres and gold nanoparticles were examined and compared to amorphous silica and acrylate–methacrylate polymer spheres. The latter can be considered as ideal homogeneous model samples. Image files having **.dm3* extension, obtained from TEM, were processed with *ImageJ* software, and later analyzed with script written in *Microsoft Visual C++*. It is shown that the radial distribution of density of highly crystalline gold nanoparticles resembles the used models, while in larger polycrystalline silver spheres it differs significantly from the "ideal" case. Deviations from linearity for gold and silver were interpreted in terms of finite polydispersity and internal inhomogeneities. The described method made it possible to estimate rapidly and accurately the number of subunits needed to achieve properties of an equivalent sphere, without considering the crystalline nature of such particles.

1. Introduction

It is well known that many properties of finely dispersed matter (optical, magnetic, adsorptive, etc.) depend not only on chemical composition, but also on the size, shape, and internal structure of individual particles. It is important in many applications for solids to consist of entities as uniform as possible. While many methods are available for the preparation of well-defined nanometer to micrometer size particles of different morphologies [1–3], their size distribution may vary somewhat, as well as the internal structure or some other properties. For example, the internal density of spheres may change from the center to the periphery, which could affect their optical, electrical, and thermo-mechanical characteristics. Therefore, it is desirable to have methods to quantify such properties within individual particles, without resorting to complicated techniques, such as high-resolution TEM.

This study describes an analytical procedure that allows to evaluate density variation due to internal inhomogeneity, of perfect spherical shape, and particle size by a transmission electron microscopy (TEM) technique. Multiple radial distributions of density of each individual metallic sphere (silver and gold) were constructed and compared to those, obtained for internally homogeneous spheres of silica and the polymer.

The method is based on relationship [4]:

$$\log\left(\frac{I_0}{I(x)}\right) = \mu\rho d, \tag{1}$$

where I_0 is the incident intensity $I(x)$ is the transmitted intensity at the distance x from the center of a particle, μ is a quantity that involves experimental parameters, such as objective aperture and exposure conditions, ρ is the material density, and d is the thickness of the sample at distance x from the center. The plot of $\log(I_0/I(x))$ as a function of d for an ideal sphere should give a straight line. Indeed, the studied model systems produced such a linear relationship, while deviations from linearity for gold and silver particles could be interpreted in terms of finite polydispersity and internal inhomogeneities. Thus, the method yields not only the bulk density data, but also qualitative indications on some physical properties of the dispersed matter.

2. Experimental

2.1. Materials

Silica particles were chosen due to their near perfect sphericity and optimum contrast gradient when using bright field TEM (BFTEM). A dispersion of such particles, which were prepared by

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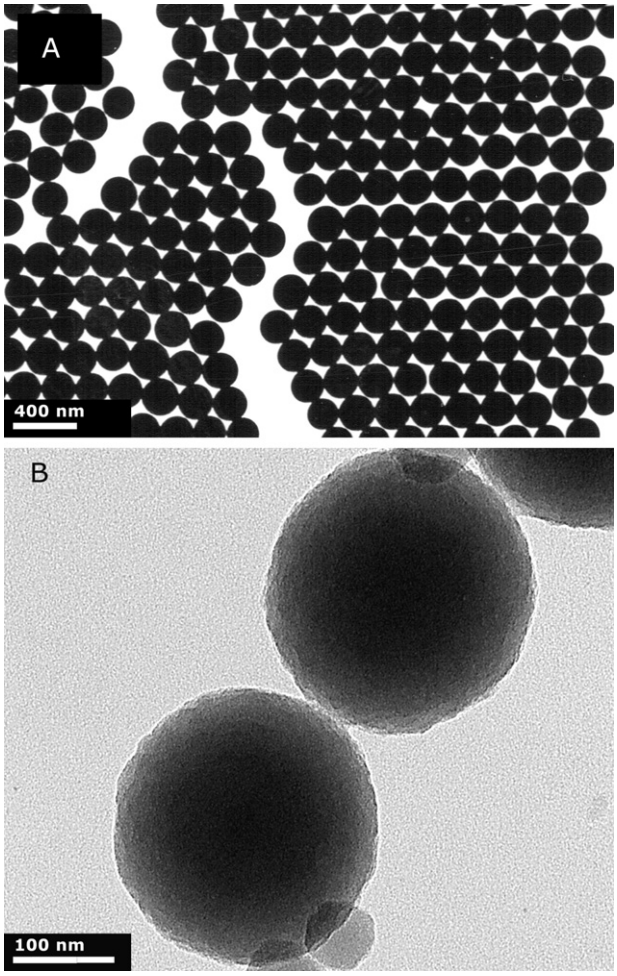

Fig. 1. (A) Example of a dispersion of silica particles prepared by hydrolysis of TEOS [5,6], (b) TEM of two silica particles used in this study.

hydrolysis of tetraethyl-orthosilicate (TEOS) as originally described by Stöber et al. [5] is illustrated in Fig. 1(A) [6]. Two such particles of ~200 nm were evaluated in the analysis (Fig. 1(B)). The application of the model to larger spherical particles of lower specific gravity was verified with acrylate–methacrylate polymers of ~3 μm in diameter (Fig. 2) supplied by CONPART (Oslo, Norway). The uniform gold nanoparticles (Fig. 3) were obtained by chemical precipitation in homogeneous solution to be described elsewhere. Polycrystalline spherical silver particles (Fig. 4), consisting of nanosize subunits were prepared by reduction of a silver-polyamine complex with *iso*-ascorbic acid as reported in Ref. [7]. Essential properties of the materials are summarized in Table 1.

2.2. Characterization methods

For the TEM measurements particles were centrifuged onto carbon coated copper grids (TED PELLA INC.) placed at the bottom of the tubes. The excess solvent was then removed and the grids were kept under vacuum overnight. Data were acquired by bright field

Table 1
Physical properties of particles.

Material	Specific gravity (kg m^{-3} 10^3)	Size (nm)
Gold	19.3 (Ref. [8])	~20
Silver	10.5 (Ref. [8])	50–100
Silica	2.2 (Ref. [8])	~200
Acrylate–methacrylate	1.08 (Ref. [9])	~3000

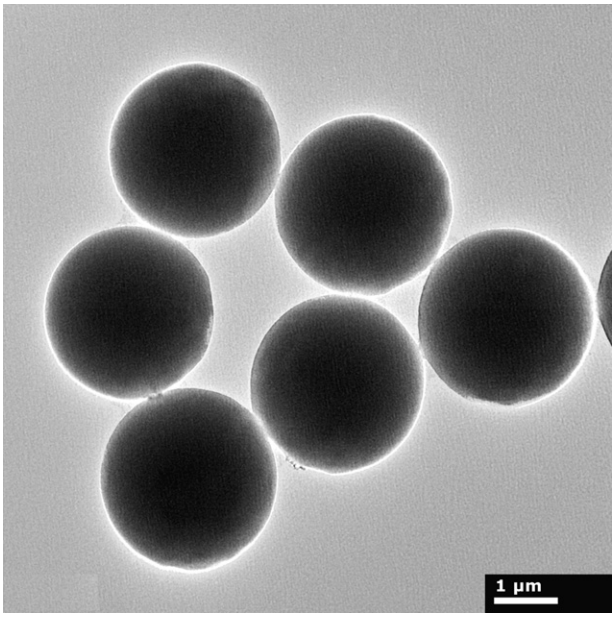

Fig. 2. TEM of acrylate–methacrylate polymer particles.

TEM and elemental mapping in scanning transmission electron microscope (STEM) mode with a JEOL-2010 TEM instrument. Digital images, obtained with the *Digital Micrograph* software (GATAN INC.) were saved in **.dm3* format, which allowed them to store the relevant information needed in this study, such as exposure conditions, the incident and transmitted electron beam intensities, as well as the size of the pixels in units of length (e.g. nanometers).

2.3. Data processing and interpretation

Digital images, acquired in bright field TEM mode, were evaluated using the *ImageJ* (image processing software [10,11]) as follows: a straight line was drawn from the approximate center of a particle towards the periphery (Fig. 5, single line). To avoid artifacts caused by angular variations of the intensities, a moderate thickness

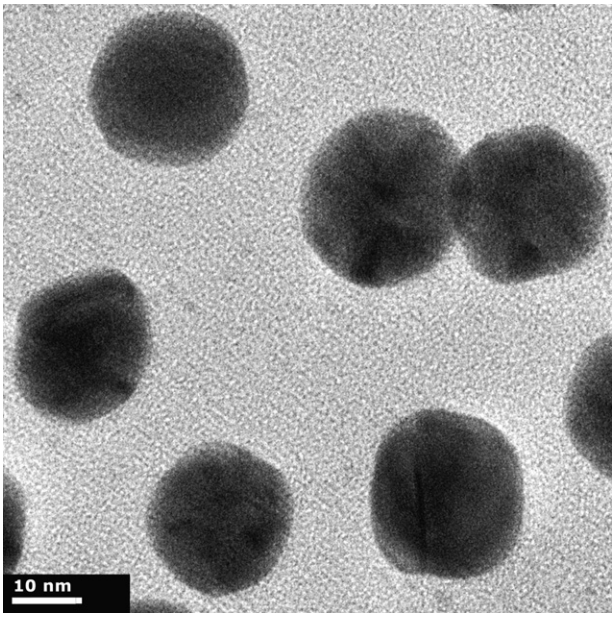

Fig. 3. TEM of gold particles prepared by chemical precipitation in homogeneous solution.