Chemical Physics Letters 654 (2016) 72–75

Contents lists available at ScienceDirect

Chemical Physics Letters

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

Research paper

Refractive index measurement of nanoparticles by immersion refractometry based on a surface plasmon resonance sensor

Hiroshi Kano [a], Ayumu Iseda [a], Katja Ohenoja [b], Ilpo Niskanen [c,d,*]

[a] Department of Information and Electronic Engineering, Muroran Institute of Technology, Mizumoto 27-1, Muroran, Hokkaido 050-8585, Japan
[b] Faculty of Technology, Fibre and Particle Engineering Group, University of Oulu, P.O. Box 4500, FI-90014 Oulu, Finland
[c] Faculty of Technology, University of Oulu, P.O. Box 4500, FI-900014 Oulu, Finland
[d] National Institute of Industrial Science and Technology, Namiki 1-2, Tsukuba, Ibaraki 305-8564, Japan

ARTICLE INFO

Article history:
Received 28 January 2016
In final form 7 May 2016
Available online 9 May 2016

Keywords:
Nanoparticles
Refractive index
Surface plasmon resonance technique

ABSTRACT

Accurate determination of the refractive index of nanoparticles has important ramifications for applications, such as pharmaceuticals, cosmetics, paints, textiles, and inks. We describe a new method to determine the refractive index of nanoparticles by immersion refractometry with a surface plasmon resonance sensor. With this method, the refractive index of the nanoparticles is perfectly matched with that of the surrounding liquid. We demonstrate this method for calcium fluoride nanoparticles that have an average diameter of 100 nm; the results achieve an accuracy of better than 0.002 refractive index units.

1. Introduction

Nanoparticles are one of the most-researched materials today due to their range of potential applications in biomedical, optical, and electronic fields. The refractive index of nanoparticles is one of the most important physical parameters used to inspect the quality of particle-based solids. Materials technology strives to tune the effective refractive index of nanoparticles to manipulate their matrix properties at a molecular level [1]. Tuning the optical, magnetic, and electrical properties of refractive index can be tailored nanoparticles for specific applications, thus increasing their effectiveness. It is difficult to precisely measure the refractive index of nanoparticles with current techniques [2]. In general, the refractive index is not only related to the chemical composition, crystal structure, and symmetry of each particle but is also affected by the temperature, wavelength of incident light and internal stresses in the sample [3].

Several techniques have been developed to measure the refractive index of nanoparticles. Total internal reflection has been used to determine the refractive index of ZnO, TiO_2, and ZrO_2 nanoparticles; this technique is based on measuring the critical angle of total internal reflection [4]. The refractive index is measured with the experimental uncertainty of 1%. The critical-angle method has long been applied in the Abbe refractometer; the advantages include easy experimental implementation and a simple calibration [5]. The critical-angle method is precise to about ±0.002 refractive index units, RIU. Turbid liquids contain a high concentration of solid particles that scatter light toward the detector, combining with the specular reflection to cause an error [6]. Ellipsometry has been used to measure the refractive index of gold and TiO_2 nanoparticles; it is based on the change in the polarization state of light reflected from the surface of a sample [7,8]. Interferometry has been used to determine the refractive index of CdSe nanoparticles [9]. Interferometry and ellipsometry are accurate techniques (0.0001–0.00001 RIU), but they are expensive and require samples with very smooth surfaces [10]. Optical methods and electron microscopy have been used to determine the size distribution and complex refractive index of magnetite (Fe_3O_4) nanoparticles [11]. Immersion matching has been used to measure the refractive indices of various types of nanoparticles [12,13]. The principle of the immersion method is to match the refractive index of solid particles with that of the immersion liquid. In the event of a perfect match between the index of the non-absorbing pigments and the immersion liquid, the transmittance will be 100% and the scattering intensity will approach zero. The advantages of immersion matching are that the technique is independent of the shape or size of a particle, and the measurement is easy and relatively fast to perform [14]. The refractive index of an immersion liquid is generally in the range of 1.4–1.8 [15]. As to the accuracy of the immersion methods, various authors assign it an error of 0.001–0.005 as usually performed. Dynamic holography techniques have been used to measure the refractive index of

* Corresponding author at: Faculty of Technology, University of Oulu, P.O. Box 4500, FI-900014 Oulu, Finland.
E-mail address: ilpo.niskanen@oulu.fi (I. Niskanen).

http://dx.doi.org/10.1016/j.cplett.2016.05.013
0009-2614/

carbon nanoparticles [16]. In-line holographic microscopy of micrometer-scale techniques have been measured refractive index of silica particles with a resolution of 0.002 RIU [17]. Nanoparticle tracking analysis (NTA) is a relatively new technique for determining the refractive index of suspended nanoparticles based on the rate of their Brownian motion [18,19] which an uncertainty in the range is 0.021–0.046 RIU. NTA currently works best for particles having a diameter of approximately 10–1000 nm. The lower detection limit depends on the refractive index of the nanoparticles; characterization is only possible for nanoparticles composed of materials with a high refractive index, such as gold or silver. The upper detection limit is due to the limited Brownian motion of large nanoparticles. The rate of particle diffusion is related to the viscosity and temperature of the liquid [20,21]. Surface plasmon resonance (SPR) sensors can also perform refractive index measurements [22]. In this technique, surface plasmons (SPs), the quanta of collective electron oscillations excited on a metallic surface, are used as a measurement probe because the propagating constant of the SPs strongly depends on the refractive index on the metallic surface. In the most typical setup, p-polarized incident light is given to a metallic thin film through a prism coupler. The light having a proper incident angle resonates with the SPs that consume light energy. Therefore, the resonance angle found in angular dependency of reflectance tells the refractive index on the metal surface. The electric field produced by the SPs shows an evanescent decaying property and remarkable field enhancement against incident light. These properties provide surface sensitive and high-sensitive measurements. The theoretical resolution in the refractive index measurement with a typical setup reaches 5×10^{-7} RIU. The high sensitivity contributes to detection of an adsorbed monomolecular layer on the metallic surface [23]. A variation of the SPR sensor enables a microscopic measurement while maintaining the high resolution in the refractive index measurement [24,25]. In this case, an excitation beam is tightly focused onto a metallic thin film coated on a glass substrate by using an oil immersion objective lens with high numerical aperture; interference of excited SPs propagating in many directions localize the SPs in the optical diffraction limit region. In the measurement of nanoparticle, the localized SPs are useful for probing a region with high particle density. Furthermore, the localized-SPR sensor can be combined with the immersion technique while retaining the advantages described above, viz., refractive index measurements that are independent of the shape and size of particles. In this case, we examine a condition showing perfect index matching between the nanoparticles and the immersion liquid by using localized-SPR sensor.

The aim of this study is to get the refractive index of a nanoparticle by immersion liquid method based on a localized-SPR sensor. The high sensitivity of the localized-SPR sensor enhances index mismatch between the sample and the immersion liquid, resulting in higher precision.

2. Materials and methods

We examined this technique by measuring the refractive index of prepared nanoparticles. To produce the nanoparticles, CaF_2 powder (Merck, 97%) was purchased; it contained trace amounts of Fe, Mg, Na, and SiO_4, according to the product description. The median particle size (on a volumetric basis) was 7.0 μm, measured by a Beckman Coulter LS 13 320 laser diffraction analytical device. Nanogrinding was carried out for the CaF_2 powder via a two-step process with a stirred media mill (90 AHM hydro mill, Hosokawa Alpine). The operation of the mill has been previously described in detail [26]. After the first grinding (370 min with 560 μm Zirconia (YSZ) beads), the median particle size was 110 nm and the width of the particle size distribution $W_{PSD} = ((d_{90} - d_{10})/d_{50})$ was 1.2. Grinding proceeded with smaller beads (320 μm for 150 min), resulting in a median particle size of 104 nm and $W_{PSD} = 1.06$. Further grinding broadened the particle size distribution, indicating that the first two steps had achieved the grinding limit [27,28]. Samples processed by the first two steps were used in this study. The Field Emission Scanning Electron Microscope (FESEM) image taken with a Zeiss Ultra Plus is presented in Fig. 1, along with the particle size distribution of a ground CaF_2 suspension measured by laser diffraction.

Fig. 2 shows a schematic of the localized-SPR sensor. The beam width of linearly polarized light with a wavelength of 632.8 nm was enlarged by a beam expander; the polarization was converted from linear to radial by using a radial polarization converter (ARCoptix, Switzerland) to obtain the optimal localization of SPs [25]. The position of the converter is imaged to the entrance pupil of an oil immersion objective lens with a numerical aperture of 1.65 (Olympus, Japan). The light converged from the objective lens and illuminated a coverslip coated with a metallic thin film. The reflected light from the coverslip was relayed to an image sensor located at an optically conjugate plane of the exit pupil of the objective lens. The image sensor recorded the spatial frequency distribution of the reflected light.

A typical measurement recorded by the image sensor is shown in Fig. 3. An absorption ring appeared in the image; its radius is used to calculate the propagating constant of the surface plasmons. The absorption pattern is fit by computational processing to quantify the radius and coordinates of the ring. The radius that corresponds to the real part of the propagating constant of excited SPs can be approximately expressed by the following equation [22,25,29]:

$$\rho_{sp} = Re(k_{sp}) \cong Re\left(k_0 \sqrt{\frac{n_m^2 n_s^2}{n_m^2 + n_s^2}}\right) \quad (1)$$

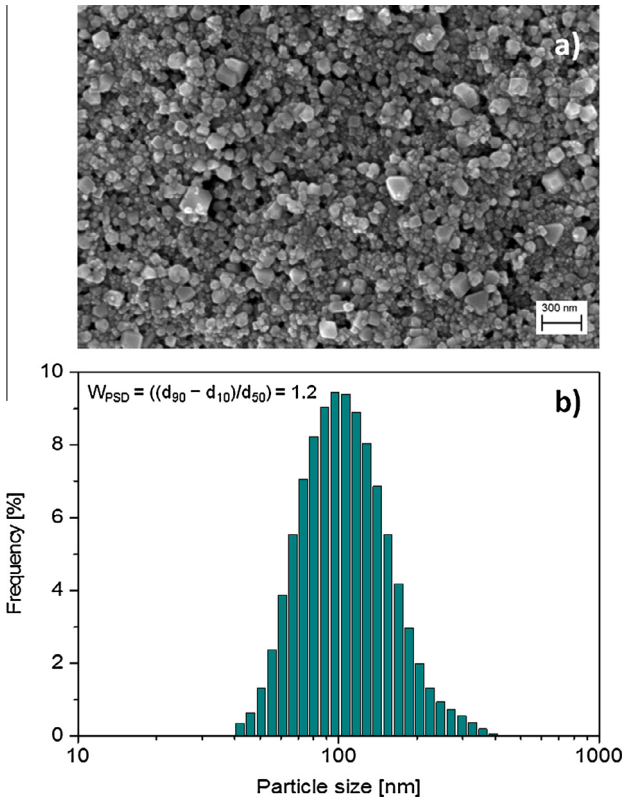

Fig. 1. (a) FESEM image and (b) particle size distribution of ground CaF_2 nanoparticles. The scale bar in the FESEM image represents 300 nm.