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Modeling TiO_2's refractive index function from bulk to nanoparticles

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ABSTRACT

In recent decades, the use of nanomaterials has become very common. Different nanomaterials are being used in over 1600 consumer products. Nanomaterials have been defined as having at least one dimension in the range of 1 – 100 nm. Such materials often have unique properties. Despite some warnings of applying bulk optical constants for nano size materials, stated already in 1980s, bulk constants are still commonly used in the light scattering measurements of nano size particles. Titanium dioxide is one of the materials that is manufactured and used as an engineered nanomaterial in increasing quantities. Due to the aforementioned facts, it is quite crucial for successful research and production of nanoparticles to find out the dependence of the refractive index function (RIF) of the material on its crystal size. We have earlier performed several ab initio computations for obtaining the dependence of the RIF of TiO_2 on the crystal or on the cluster size, for particles of size up to ca. 2 nm. Extending the calculations to greater sizes has turned out to be infeasible due to the unbearable increase in computational time. However, in this study we show how the crystal-size-dependent-RIF (CS-RIF), for both rutile and anatase can be modeled from measured extinction or turbidity spectra of samples with varying crystal and particle sizes. For computing the turbidity spectrum, we constructed a model including primary crystals whose distributions were parameterized by mean and standard deviation, and also including aggregates consisting of mean sized primary particles, parameterized just by mean aggregate size. Mainly because of the long computing times Mie calculation was used in the computation of extinction spectra. However, in practical process applications, the obtained RIF will be used together with the T-matrix method. We constructed the RIFs used in the model using generalized oscillator model (GOM) as expanded to crystal size dependence. The unknown parameters of the model were solved using nonlinear least squares estimation. When the crystal size becomes smaller than the bulk size the shape of the estimated CS-RIFs reveal two distinct regions for both rutile and anatase. In the first region, starting apparently already from ca. 200 nm, the height of both the real part and the imaginary part of CS-RIF decreases on crystal diameter. However, the band gap remains constant. In the second region, starting when the crystal diameter is decreased to ca. 3 nm, a blue shift starts to increase the band

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gap. The band gap dependence on crystal size is quite consistent with the existing experimental values. Consequently, it is of great importance to use CS-RIF in light scattering measurements for nanoparticle size determination. Neglecting this, the smaller particles in the size distribution will have too small values, already for sub-micrometer particles, naturally distorting also the mean value. To our knowledge, this is the first time ever that a CS-RIF from bulk to 1 nm size is determined for any material.

1. Introduction

Bohren and Huffman [1] reminded already in 1983 in their classical book *Absorption and Scattering of Light by Small Particles* that bulk optical constants, without modification, may not always apply to small particles. Somewhat later Huffman gave a more advanced review of this matter, in which he stated among other things: "The optical constants appropriate to bulk matter have been applied to small particles in many areas of applied science, although there is obviously a lower size limit below which this procedure is invalid. It is abundantly clear that the optical properties of solids are qualitatively different from the optical properties of their constituent atoms and molecules when isolated" [2].

As well known, these optical constants are required in the light-scattering computations, e.g., they are needed in the research and production of pigmentary particles or nanoparticles [3]. In the computations, the complex refractive index function (RIF) or the complex dielectric function (the square of RIF) of the measured crystal material for all wavelengths used in the measurement is needed. Suitable methods are, e.g., the Mie theory for spherical, and the T-matrix method for spheroidal particles. In recent decades, the use of nanomaterials has become very common [4–7].

According to three recent extensive reviews [5–7]: the rapidly advancing field of nanotechnology offers potential benefits to almost all industries and products. According to the Woodrow Wilson International Center for Scholars' Project on Emerging Nanotechnology, nanomaterials are already in 2013 being used in over 1600 consumer products [8]. Nanomaterials have been defined as having at least one dimension in the range of approximately $1-100$ nm. Such materials often have unique or novel properties that arise from their small size [7]. Metal oxides, such as titanium dioxide (TiO_2), belong to the multitude of materials that are manufactured and used as engineered nanomaterials in increasing quantities [5]. As compared to pigmentary TiO_2, nano-TiO_2 is much more reactive, and also a UV light attenuator. Therefore, it can be applied as a catalyst and as a UV light attenuator contrary to a visible light attenuator (i.e., a pigment). Applications that use nano-TiO_2 to attenuate UV light include consumer products, such as sunscreens or similar cosmetics, various plastic-based products and containers, and clothing. Applications that use nano-TiO_2 as a catalyst include various consumer products such as household cleaning products, household self-cleaning coatings, household air filtration devices, electronics (e.g., computer keyboard and mouse), and hair styling devices. Commercial applications also include cleaning products, self-cleaning coatings, air filtration devices, and environmental remediation of pollutants. Emerging applications include solar cells that use nano-TiO_2 for its electron transfer properties [6].

In spite of the above cited remark of Bohren and Huffman [1] in 1983 of the limits of bulk optical constants, commonly only RIs of bulk materials are used in the nano size material computations. Even a recent review [9] claims that the Mie theory would not be suitable for nanoparticle computations. Yet, no considerations of the suitability of the RIs of bulk materials used in the computations are given.

There are, however, special cases in which the nanoparticle RIFs are modeled based on the measured results. They are mostly related to thin films: Real and imaginary parts of the dielectric functions of thin films consisting of isolated aluminum (5.0 nm) and silver (7.8 nm) particles on oxide-covered Si substrates, are measured by spectroscopic ellipsometry (SE) [10]. The Generalized Critical Point Model and the Generalized Oscillator Model (GOM) have both been used for simulations of the dielectric functions of polycrystalline nanosize silicon materials [11–13]. In addition, RIF's have been extracted successfully from turbidity spectra of very thin TiO_2 films (<100 nm) by using so called Forouhi−Bloomer model [14–16]. RI of silver particles (<21.0 nm) suspended as colloid in photosensitive glasses was determined from absorption measurements by using Mie calculation [17]. None of these does, however, consist of the full particle size dependence on the material's RIF from bulk to nanosize. Neither do they include the very small particle size region in which semiconductor particles can have different absorption properties. The phenomenon is commonly known as the quantum-size effect or size quantization [18].

In our previous publications [18,19], we expressed the importance of sub-micrometer-size titanium dioxide pigment particles in many applications and described their production control by a recently developed light-scattering-based method, the turbidity spectrum method (TSM) [3,20,21]. In TSM, the particle size distribution (PSD) is determined from a turbidity spectrum measured from a diluted water solution by means of the T-matrix. The method is now optimized for sub-micrometer size particles. As it was then pointed out [18,19], we are now expanding TSM to nanosize materials. Due to the above facts, we need to know how the RIF depends on the crystal size.

Computational complexity limits the particle size in ab initio computations to ca. 2 nm [19]. Consequently, we explored other options. In these, reported in this study, we succeeded to solve the RIF directly from turbidity spectra from TSM-measurements using nonlinear least squares estimation. This type of modeling has earlier been applied using the Kramers−Kronig (KK) relation (see, e.g., Ossenkopf et. al. [22]). When the particles are small, spherical,