Journal of Quantitative Spectroscopy & Radiative Transfer 126 (2013) 160–168

Contents lists available at SciVerse ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

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

Sizing highly-ordered buckyball-shaped aggregates of colloidal nanoparticles by light extinction spectroscopy

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ARTICLE INFO

Article history:
Received 5 June 2012
Received in revised form
13 August 2012
Accepted 14 August 2012
Available online 24 August 2012

Keywords:
Aggregates
Aerosol
Light extinction spectrometry
Scattering models
T-matrix
Inversion

ABSTRACT

We produced self-assembled, densely-packed and highly-ordered aggregates of silica nanoparticles arranged in a rather regular hexagonal–pentagonal surface lattice. To investigate the formation of these aggregates, produced by means of a spray drying method, we developed a light extinction setup and all related models. It is shown that with a geodesic dome model, to describe their morphology, and a *T*-matrix method to calculate their extinction cross sections, the size distribution and concentration of these flowing aggregates may be recovered from the inversion of transmission spectra.

1. Introduction

The optical, electrical or mechanical properties of nanoparticles are determined by their material properties, certain quantum effects and their unmatched specific surface (i.e., their size and shape). Because of the potential for interesting new properties and applications based on new nanoparticle morphologies, many efforts are devoted to the manufacture of nanoparticles with specific and well-controlled shapes (nanotubes, nanowires, liposomes, etc.). We recently succeeded in producing, by means of a spray drying method, large and highly ordered aggregates of silica (SiO_2) nanoparticles of a new kind. Fig. 1 shows some typical (a) scanning and (b) transmission electron microscopy (SEM, TEM) images of these aggregates. On their surfaces, the nanoparticles tend to self-organize into a pentagonal–hexagonal lattice (with, however, some defects), showing some similarities to that observed for fullerene molecules (also known as buckyballs, e.g., [1]). There are, however, two major differences with respect to fullerene molecules: silica nanoparticles (in close contact) replace distant atoms and the internal structure of these "silica nanoparticle buckyballs (SNBs)" is quite densely packed. Shell-structured (e.g., liposomes) or densely-packed aggregates of spheres have been widely studied in the literature (e.g., [2–5]), but none of them is as regular, as dense or as large as the self-assembly aggregates that we have observed. Understanding and controlling the formation mechanisms of SNBs require being able to perform extensive parametric studies.

This paper focuses on work aimed at developing a light extinction spectrometer (LES) and the related models for the in-situ and real-time characterization of the particle size distribution (PSD) and concentration of these complex

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http://dx.doi.org/10.1016/j.jqsrt.2012.08.018

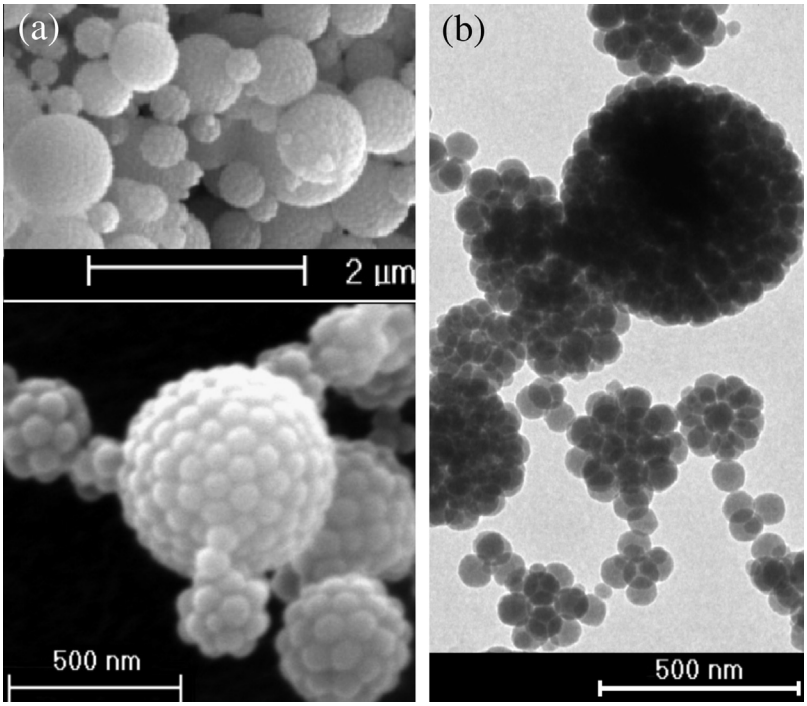

Fig. 1. (a) Scanning and (b) transmission electron microscopy images exemplifying the self-organisation of the highly-ordered buckyball-shaped aggregates of silica nanoparticles (SNBs).

aggregates. The paper is organized as follows. Although it is unusual, for the sake of clarity, Section 2 directly describes the setups used to produce and analyze the SNBs. Section 3 details the work done to build aggregates similar to experimental ones, which is a prerequisite for the calculation of their light scattering properties. Section 4 briefly reviews the basic principle and requirements of LES, before presenting the light scattering calculations and inversion methods used to analyze light extinction spectra. In Section 5, we compare experimental results obtained with these different approaches, while Section 6 is a conclusion.

2. Experimental setup and correction

The spray drying and optical setups are depicted in Fig. 2. A Laskin nozzle aerosol generator (ATM220, TOPAS GmbH)(1) is used to spray colloidal silica suspensions (Klebosol®) (2) with dry and nanofiltered air at different pressures (1–6 bar) (3). These suspensions, supplied by AZ Electronic Materials France SAS, are anionic colloidal suspensions containing, in terms of mass, 29% of SiO_2 particles and 0.2% Na_2O as a stabilizer, the rest being pure water. The pH and zeta potential of these suspensions are measured at 8.5 and -56 mV, respectively. When a sample of these suspensions is evaporated on a flat surface [6], the nanoparticles self-organize in the form of a hexagonal lattice. Lattice defects are mostly attributed to the suspensions polydispersity with, for the mean diameter and standard deviation of the three suspensions considered in our study: K30R50 (81 ± 16 nm), K30R25 (67 ± 7 nm) and K30R12 (31 ± 6 nm). The aerosol of

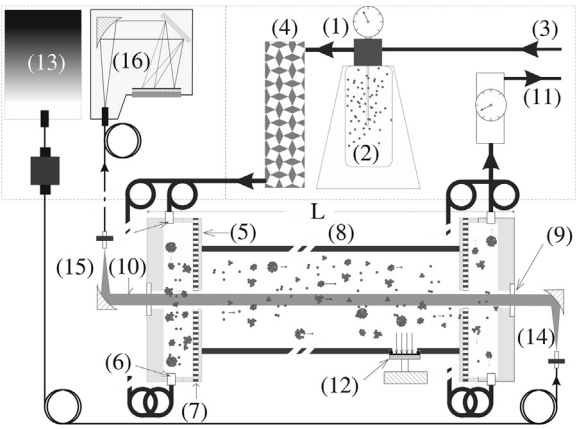

Fig. 2. Sketch of the spray drying and optical setups.

microdroplets of suspension is directed to a diffusive drier unit filled with silica gel grains (4). The role of this drier is to absorb the water vapor released during the slow evaporation process at atmospheric pressure. In our opinion, this is the key mechanism responsible for the formation of SNBs. In fact, due to electric double layer repulsion forces, the silica nanoparticles tend to maximize their inter-distances. However, during the evaporation process, the water/air interface increases the containment and the nanoparticles gradually approach each other. Finally, capillary forces, and afterwards, van der Waals forces, stick the nanoparticles together as Coulomb repulsive forces vanish [2]. The aerosol of dry aggregates is then directed to a mixing chamber (5), equipped with