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Photonic crystal microspheres

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ABSTRACT

Spherical samples of photonic crystals formed by colloidal SiO_2 nanoparticles were synthesized. Synthesis of microspheres from 160 nm, 200 nm and 430 nm diameter colloidal nanoparticles was performed over a wide size range, from 5 μm to 50 μm. The mechanism of formation of void microparticles exceeding 50 μm is discussed. The spectral measurements verified the association of the spectra with the peaks of selective reflection from the cubic lattice planes. The microparticle morphology is characterized by scanning electron microscopy (SEM).

1. Introduction

Particles with a specified pore system, specific structure and morphology are attractive to researchers owing to their potential application in pharmacology [1], biological and chemical sensors [2], micro- and nanolenses [3], catalysis [4], in photonic crystal sensors [5], optical emission modulators [6] and electronic printing [7].

Numerous papers are devoted to synthesis of spherical and nearly spherical particles [4,8–11], yet, the degree of the structural order in those works was not sufficiently high. The approaches applied included spray-drying [12–14,1], the microfluidic technique [15], emulsion [16–18], supramolecular templating [9]. The spray-drying method was most frequently used for synthesis of mesostructured particles using different surfactants [19,11,12]. Spherical microparticles with photonic crystal properties were synthesized by electrospraying [14] and the microfluidic technique [15]. Latex particles doped with silicon dioxide nanoparticles were used in the first synthesis method. The obtained photonic spheres demonstrated a specific optical property: they exhibited reflection peaks related to the photonic forbidden zone and independent of the angle of light incidence. In the second work [15] the silicon dioxide submicron particles were dispersed into ETPTA (ethoxylated trimethylolpropane triacrylate) polymer with a photoinitiator and emulsified in water with addition of Pluronic F108 block copolymer. In the composite microparticle (SiO_2-ETPTA) the silicon dioxide particles form a layered structure of concentric spherical shells starting from the external layers. The formation mechanism of spherical microparticles upon droplet evaporation is well known, see, for instance, [20,14]. Liquid evaporation from the drop involves self-assembly of colloidal SiO_2 particles with participation of capillary forces that ensure close packing of the colloidal particles and form a spherically symmetric configuration bound by van der Waals forces.

We demonstrate spherical microparticles from 5 to 50 μm in size formed by monodisperse colloidal SiO_2 particles by way of their close packing into an fcc lattice. To this end, colloidal SiO_2 particles 160 nm, 200 nm, and 430 nm in size were synthesized. The microparticles were synthesized by spray-drying of aqueous suspension of colloidal SiO_2 particles without use of surfactants which distinguishes our work from the previous ones devoted to production of polymer microparticles using organic templates, polymerization processes and organic liquid media. Liquid evaporation from the drop involves capillary contraction of colloidal particles which forms a spherically symmetric configuration bound by van der Waals forces.

The suspension was sprayed using an ultrasound activator. The spectra of selective reflection from different domains were measured with an optical microscope. First measurements were made of local microdiffraction from individual microspheres including microreflexes at large angles to the (1 1 1) fcc plane. The microparticle morphology was characterized by scanning electron microscopy (SEM).

2. Experimental

The colloidal SiO_2 particles were synthesized [21] by a multistage method combining two known sequential techniques of

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tetraethoxysilane hydrolysis: the heterogeneous technique in the presence of amino acids [22,23] and the traditional Stöber method [24]. When synthesizing the colloidal SiO_2 particles, we managed to achieve a very narrow particle size distribution with a standard deviation from the mean value of 1.0–1.5% for the best samples. Spontaneous crystallization of colloidal particles into an fcc lattice on their self-assembly during evaporation of the solvent is critically dependent on particle size homogeneity. With a standard deviation of 5% and above colloidal particles do not form a defectless close packing [25]. The high homogeneity of our colloidal particles plays a decisive role in their packing during droplet evaporation since the whole process of spherical microparticle formation occurs in time of the order of 1 s. The concentration of colloidal particles in the drop is also critical. The experiments were performed with concentrations of colloidal particles of 18 vol%. (160 nm), 13 vol%. (200 nm) and 16 vol%. (430 nm) in aqueous suspension. Spray-drying was carried out at room temperature and 60% humidity. The fall time of the drop was about 1 s, the drop path length to the substrate about 2 m. The optical studies were made using a Leitz microscope in reflected light. The reflection spectra were measured in "backward" geometry upon illumination by white light using an Avantes-2048 CCD spectrometer. The spectra were measured from different regions of the spheres. When measurements were performed from the central part of the sphere nearly perpendicular to the incident light, the region from which the spectra were measured was about 10 μm in size. Upon shift from the central to the lateral part of the sphere the illuminated area on the sample increased (in the employed "backward" geometry). When measurements were performed on the edge of the sample, some part of the light missed the sphere. All this hampered measurements of the absolute reflection intensity. Moreover, the intensity of the reflection bands even in the central part of the sphere could vary from sample to sample. This may be related to the domain structure of the spherical samples which was observed with SEM. Thus, in this work we discuss the spectral positions and width of the reflection bands rather than the absolute intensities. The sample morphology was examined with a Zeiss Supra 50VP FESEM equipped with an EDX spectrometer.

3. Results and discussion

Fig. 1 shows SEM images of the microparticles formed from colloidal SiO_2 particles 430 nm (Fig. 1a–d), 200 nm (Fig. 1e) and 160 nm in diameter (Fig. 1f). The sizes of the microparticles shown in Fig. 1 are: 50 μm (a), 30 μm (b), 25 μm (c), 5 μm (d), 34 μm (e), 28 μm (f). The images of the microparticles (Fig. 1a–f) demonstrate a nearly perfect spherical form and show areas of ordered close-packed colloidal particles separated by boundaries. The microparticle morphology depends on drop size, concentration of colloidal particles and the evaporation rate [26].

Humidity affects the rate of water evaporation from the drop. Increasing humidity involves a reduction of the evaporation rate and an increase of the internal drop pressure that may lead to swelling and/or disintegration of particles. Regarding the correlation between microparticle quality and colloidal particle concentration in suspension, two concentration values responsible for radical changes in particle morphology should be distinguished: 16 vol%., the percolation limit below which void particles may frequently occur [26]; 50 vol%, the concentration that initiates a liquid–solid phase transition in the colloidal system [15]. In the optimal concentration range, 16–33 vol%., the quality of microparticles is independent of concentration (but may depend on other parameters, for instance, the evaporation rate). The microsphere size is a function of drop size, given the same concentration in the suspension.

SEM analysis of the morphological features of the microparticles revealed that the particles sized more 50 μm are void (Fig. 2) when they are formed from colloidal SiO_2 particles 160 nm and 200 nm in diameter. We observed no void microparticles formed from 430 nm colloidal particles. Yet, in the case of 430 nm particles large microparticles (exceeding 50 μm) have a flat form down to flat discs, which points to their deposition upon incomplete evaporation of water from the microparticle. The reasons of the formation of void microparticles can be understood following the percolation theory and model approximations of the process of solid particle formation in aerosols [26,27]. If the volume fraction of the colloidal particles exceeds or is equal to the percolation

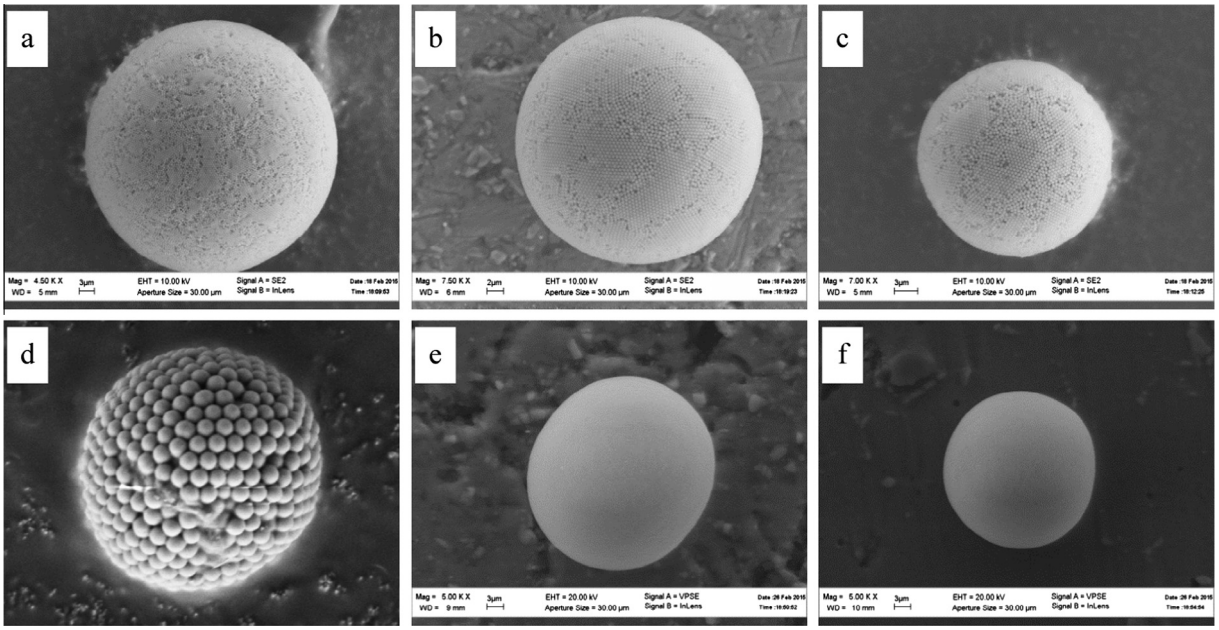

Fig. 1. SEM images of microparticles formed from colloidal SiO_2 particles 430 nm (a–d), 200 nm (e) and 160 nm (f) in diameter.