Towards ceramic 3DOM-materials as novel high-temperature reflective coatings and filters for thermophotovoltaics

R Kubrin1,4, H S Lee2, A Petrov2, R Janssen1, G A Schneider1, J Bachmann3, K Nielsch1 and M Eich2

1 Institute of Advanced Ceramics, Hamburg University of Technology (TUHH), Denickestrasse 15, 21073 Hamburg, Germany
2 Institute of Optical and Electronic Materials, Hamburg University of Technology (TUHH), Eissendorfer Strasse 38, 21073 Hamburg, Germany
3 Institute of Applied Physics, University of Hamburg, Jungiusstrasse 11, 20355 Hamburg, Germany

E-mail: roman.kubrin@tu-harburg.de

Abstract. Studies on evaporation-induced vertical convective self-assembly as well as horizontal self-assembly are presented including inversion of the opals and deposition of heterostructures. Opaline coatings were deposited on microscope slides from monodisperse particles of polystyrene and silicon dioxide with the particle sizes in the range from 400 to 1100 nm. Well defined photonic stopgaps were observed for both direct and inverted structures. We show that the horizontal deposition method facilitates self-assembly of large silica particles, so that the limitation of the conventional vertical convective self-assembly can be overcome. Successful stacking of the self-assembled polystyrene templates with unequal particle size is demonstrated.

1. Introduction
Periodically structured porosity can provide ceramic coatings with important additional functionality of a photonic crystal. Three-dimensionally ordered macroporous (3DOM)-materials with the topology of an inverted opal (i.e., solids with spherical pores of uniform size arranged in a face-centered cubic lattice) can effectively reflect light in a certain wavelength range, which is determined by the refractive index of the material, the angle of incidence and the size of the pores. The width of the so-obtained photonic stopgap can be enlarged by stacking several inverse opals either made of different materials [1] or possessing unequal lattice constants in the subsequent layers, analogously to direct hetero-opals [2]. Theoretically, multilayered 3DOM-coatings could be used as broadband reflectors of thermal radiation and facilitate new types of thermal barrier coatings and filters for application in thermophotovoltaics. However, there are several technological issues that have to be solved before the performance of such structures in a high temperature environment can be tested in a laboratory. 3DOM-materials are usually produced by self-assembly of opaline templates from monodisperse particles of silica or various polymers followed by infiltration with ceramics (e.g., by atomic layer deposition (ALD) [3] or sol-gel technique) and inversion of the structure by calcination or etching away the

4 To whom any correspondence should be addressed.
template. Existing processing techniques are prone to generation of cracks and other structural defects in the coatings. Particularly challenging is the self-assembly of the templates from heavy macrocolloidal particles (≥ 1 µm) and deposition of the second and further layers of the inverse opals (i.e., production of 3DOM-heterostructures).

Herein, we present the first results of experiments aimed at development of a manufacturing route of the multistacked ceramic photonic crystals, which could effectively reflect the infrared radiation in a wavelength range of 1-6 µm thus covering a major part of the blackbody radiation at a temperature of about 1500 K.

2. Experimental

The polystyrene (PS) and silica monodisperse particles were purchased as concentrated suspensions in water (Microparticles GmbH, Berlin, Germany), and were diluted with deionized water to a desired concentration or re-dispersed in ethanol (p.a.) by centrifugation or sedimentation, removal of the supernatant liquid and ultrasonic homogenization in the new medium. Standard microscope slides cleaned by soaking for several days in a solution of a detergent (Mucasol), brushing, rinsing in deionized water and drying by a nitrogen gun were used as substrates for 3DOM-structures.

For deposition of the opaline templates from the PS-particles (400 – 1000 nm), a vertical convective self-assembly (VSA, figure 1) technique was utilized [4]. The substrate was put nearly vertically into a beaker with suspension, which slowly evaporated. In a typical experiment, concentration of colloidal particles was in the range of 0.5-2 mg/ml. VSA from water-based suspensions was performed in an oven at a constant temperature between 50 and 70°C for several days. VSA from suspensions in ethanol was carried out at room temperature in a fume hood.

Direct opals from silica particles (1.11 µm in diameter) were deposited by horizontal self-assembly (HSA, figure 2) also referred to as inward-growing self-assembly [5]. Usually, a small volume (30-120 µl) of highly concentrated suspension (50-200 mg/ml) was put onto the substrate placed horizontally by a micropipette and, if required, spread over the desired area with a pipette tip. Then it was left to dry out for several hours at room temperature in the fume hood.

The polystyrene templates were infiltrated with titanium dioxide by atomic layer deposition [3] in a home-made ALD reactor working in a stop-mode (40 s exposure time followed by 70 s pump and purge time). TiO₂ was chosen due to its high refractive index. Titanium isopropoxide and water were used as sources of titanium and oxygen, respectively. Duration of the process was varied in a range of 300-900 cycles. The temperature inside of the ALD chamber was kept at 95°C. Infiltrated samples were used for the deposition of the second opal layer or inverted by calcination at 500°C for 30 min.

The average thickness of the coatings was derived from the weight difference of the substrates before and after self-assembly and known sample area. Structure of the templates and 3DOM-coatings was investigated by means of scanning electron microscopy (LEO 1530). Optical transmission was studied with a Perkin-Elmer UV/VIS/NIR spectrometer Lambda 19. Additionally, optical properties of 3DOM-coatings were simulated with the frequency-domain finite integration technique (FIT) implemented in a software package “Microwave Studio” provided by CST (Darmstadt, Germany).

Figure 1. Schematic arrangement of the vertical convective self-assembly (VSA) experiment. Figure 2. Horizontal (inward-growing) self-assembly (HSA).
3. Results and discussion

3.1. FIT simulation
FIT-calculations for idealized yttrium-stabilized zirconia (YSZ) inverse opals showed that the position ($\lambda_{SG}$) and width of the stopgap in the transmission spectra linearly depend on the pore size. A coating consisting of 10 3DOM stacks (each one 10 layers of pores thick) with the constant porosity of 74% and the pore size increasing stepwise from 500 nm ($\lambda_{SG} = 1.18 \mu m$, FWHM = 250 nm) to 2600 nm ($\lambda_{SG} = 5.8 \mu m$, FWHM = 1190 nm) would reflect about 90% of the normally incident radiation in the wavelength range 1-6 µm. The total thickness of such coating would amount to less than 120 µm.

3.2. Vertical self-assembly (VSA) of polystyrene templates
VSA method is known for its simplicity and superior quality of the opaline coatings. Coating density obtained in VSA is mainly determined by weight concentration of colloidal particles in the suspension, tilt of the substrate and rate of evaporation of the liquid (i.e., it also depends on the ambient temperature and relative humidity). The concentration of particles in the suspension changes in the progress of self-assembly and deposited coatings get thicker towards the end of the sample. For the optimized conditions, the initial concentration of PS-particles of 1 mg/ml resulted in the average coating thickness of approximately 10 µm (for samples with the standard length of 20-30 mm). Figure 3 demonstrates the final result of the infiltration by titania and removal of the VSA-templates. A well defined stopgap can be observed in the spectrum of transmittance of the 3DOM-structure.

The main disadvantage of VSA is that it can only be used with relatively stable colloids. Opals of PS-particles with sizes of up to 1.0 µm could be successfully deposited. It is, however, impossible to deposit silica particles of similar size with this technique.

3.3. Horizontal self-assembly (HSA) of templates from macrocolloidal silica particles
For the large silica particles, which sediment too fast in suspensions, the opaline templates could be deposited by HSA. When a droplet of suspension is left to dry out on a horizontal surface, the suspended particles are carried to the edges of the droplet by the solvent flux caused by evaporation. The meniscus moves to the centre of the droplet so that the opals nucleate on the edge and start to grow inwards. HSA can facilitate self-assembly of macrocolloidal particles, if the lateral drying of the suspension prevails over the normal drying, i.e., if the meniscus moves sufficiently fast over the substrate. Coatings grown from the water-based suspensions of silica particles (1.11 µm in diameter) were strongly disordered and crystalline arrangement was observed only at the edges of the coated area. On the other hand, for particles dispersed in ethanol, most of the deposited area of the samples was iridescent. The opaline structure was observed with the electron microscope and traces of a stopband in the transmittance spectrum were observed in these coatings.

Figure 3. SEM of a titania inverse opal (left) and its transmittance spectrum with an optical photograph in the inset (right). Scale bars in SEMs correspond to 1µm, pore size is 476 nm.
infrared (IR) range could be found (figure 4). The low suppression in the stopgap should be attributed to a large number of structural defects due to the inherently ununiform orientation of domains of the colloidal crystals and a relatively low refractive index of silica particles (<1.5). It can be expected that inversion of such structure with a high-index material will result in a 3DOM-coating with the desired photonic properties. The structural quality could be improved by promoting crystallization in a single preferred orientation, e.g., by a method similar to meniscus dragging as described by Prevo et al. [6].

3.4. Deposition of heterostructures using VSA technique
In order to produce 3DOM-multistacks, one could manufacture a direct hetero-opal and infiltrate the whole structure at once. However, the PS-opals are hydrophobic and cannot be used as substrates for self-assembly in water-based suspensions. It was attempted to carry out repetitive VSA-depositions in ethanol or a mixture of ethanol and water. Unfortunately, the so-obtained second layers of direct opals were significantly less ordered and often peeled off from the previous layer. Additionally, the ALD infiltration of thick templates was inefficient. It came out that the heterostructures could be produced, when each single layer of the template was infiltrated before depositing the next one (figure 5).

4. Conclusions
The concept of photonic broadband reflectors of thermal radiation was suggested. High-quality titania 3DOM-coatings were successfully obtained. For deposition of heterostructures, each opaline layer had to be infiltrated separately in order to facilitate the self-assembly of the next layers. Feasibility of the self-assembly of macrocolloidal particles by horizontal self-assembly method was demonstrated.

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