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Mechanical stability enhancement by pore size and connectivity control in colloidal crystals by layer-by-layer growth of oxide

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Control of the pore size and connectivity of micro-sphere colloidal crystal lattices has been achieved by a layer-by-layer growth of silica using atmospheric pressure room temperature chemical vapour deposition of silica, a method which largely increases the mechanical stability of the lattice without disrupting its long range order.

Colloidal crystals have attracted the attention of researchers in numerous fields such as ceramics,[1] photonics,[2] chemical sensing[3] and membranes.[4] The pore size and the connectivity of these lattices are important parameters that largely affect their mechanical and optical properties as well as the diffusion of fluids through them. The approach generally employed to increase the connectivity of colloidal crystals, is based on the sintering of the particles from which they are made. In order to do so, lattices are subjected to thermal annealing at temperatures between 700 and 1100 °C. This treatment induces the softening of the silica and the occurrence of viscous mass flow processes, which, eventually, will provide mass continuity to the structure and decrease the pore size, which can be gradually varied with the sintering temperature.[5] A contraction of the center-to-center distance between the particles is also observed.

Here we present an alternative method to control the pore size and, at the same time, increase the connectivity and mechanical stability of colloidal crystals. Chemical vapour deposition of silicon tetrachloride, followed by reaction with water hydrogen bonded to the micro-sphere surface, is performed at room temperature and atmospheric pressure in a layer-by-layer process to coat the micro-sphere lattice with a continuous layer of silica. We show evidence of the accurate control of the coating thickness and, therefore, pore size achievable by this procedure.

Samples employed in this study were prepared as follows. Firstly, monodispersed suspensions of colloidal silica particles of diameter between 200 and 400 nm were prepared following the Stöber method.[6] After that, the particles were crystallized by convection induced self-assembly using a glass slide or a silicon wafer as substrates, as described in the literature.[7] Colloidal lattices prepared in such a way present interesting photonic crystal properties and applications.[7,8] However, they cannot be sintered without strongly disturbing the order of the lattice. In addition, in some cases, the low thermal stability of the substrate does not even allow thermal annealing of the colloidal lattice. For these reasons, these structures are particularly interesting for checking the applicability of the method presented herein.

The silica deposition is performed at atmospheric pressure and room temperature using a chemical vapour deposition (CVD) process. $SiCl_4$(l) is placed in a bubbler through which a N_2(g) stream is flown. This flow transports the reactive species to the reactor where the colloidal crystals are located. A porous glass septum placed between the bubbler and the reactor favours the homogeneity of the reactive gas in the sample compartment. Here, we take advantage of the highly hydroxylated surface of the silica particles. Due to this, a layer of water, hydrogen bonded to the silanol groups, covers each particle in the lattice, as thermogravimetric measurements indicate.[9] This water reacts with the $SiCl_4$(g) flow to form silica. The nucleophilic attack of the $SiCl_4$ by H_2O results in the formation of silicic acid $Si(OH)_4$ and HCl, the latter of which, in turn, may act as a catalyst of the polycondensation of ≡Si–OH bonds to form water and siloxane bonds.[10] Eventually, this gives rise to the formation of a continuous silica layer that coats each micro-sphere and extends through the whole lattice, therefore providing mass continuity to the structure. The pore volume of the structure is determined by the thickness of the coating, which can be controlled by successive deposition of water and $SiCl_4$ vapours, as depicted in Fig. 1.

Scanning electron microscopy (SEM) was used to study the structural modifications induced by the CVD process. Micrographs shown in Fig. 2 clearly demonstrate that a high connectivity of the lattice is achieved without disturbing the long range order of the lattice. The analysis of cleaved edges of the colloidal crystals allowed the homogeneity of the infiltration and the degree of micro-sphere overlapping resulting from the silica coating to be checked. A closer look at the structure reveals the dramatic changes in pore size resulting from the layer-by-layer growth of silica. It is worth pointing out that in order to obtain similar degrees of necking between neighbouring particles by sintering, temperatures higher than 1000 °C must be employed.[11] An accurate control of the final coating thickness can be attained by the cyclic repetition of the above-mentioned CVD procedure or by controlling the amount of water present on the micro-sphere surfaces.

Young modulus, or stiffness, and hardness of the same sample after different numbers of $SiCl_4$ CVD treatments were estimated using depth-sensing nanoindentation. Results are

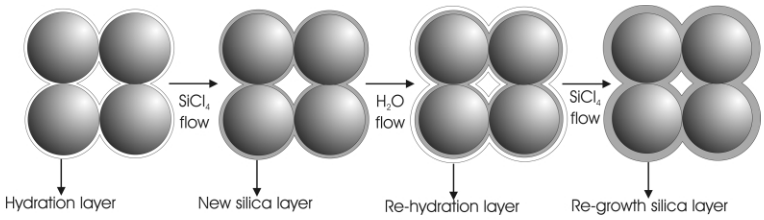

Fig. 1 Diagram of the atmospheric pressure room temperature silica chemical vapour layer-by-layer deposition process of silicon tetrachloride vapour onto a colloidal crystal showing explicitly the control over the dimensions of the pores and the connectivity of the lattice.

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plotted in Fig. 3, in which it can be seen that the stiffness increases from 1.5 GPa in the as-grown film up to 15 GPa after 4 CVD treatments, while the hardness changes from 0.01 GPa to 0.8 GPa. Typical values of these parameters for dense silica glass are 70 and 5.5 GPa, respectively. CVD necking has a dramatic effect on the mechanical properties of the colloidal crystal.

A measure of the fine tuning of pore size achievable by the method herein presented can be obtained by analysing the evolution of the optical properties of the colloidal crystals. It is well known that the 3D ordering of sub-micrometer size colloids gives rise to diffraction of visible and near infrared light at wavelengths determined by the refractive index of the particles and the geometry of the arrangement. These optical properties are extremely sensitive to disorder or lack of homogeneity. Therefore, the uniformity of the silica coating should reflect in the quality of the optical spectra of the silica-infiltrated crystals. In Fig. 4 we show three spectra corresponding to a planarized crystal prior and after different degrees of silica infiltration by CVD. The spectral maximum detected corresponds to the diffraction coming from the (111) colloidal crystal planes of the sample, while the side fringes are a consequence of the finite crystal size of the sample. As we grow silica on the micro-spheres, a clear red-shift of the main peak is observed, which can be explained by the formula:[12]

$$\lambda_{(111)} = 2d_{(111)}\langle\varepsilon\rangle^{1/2} \qquad (1)$$

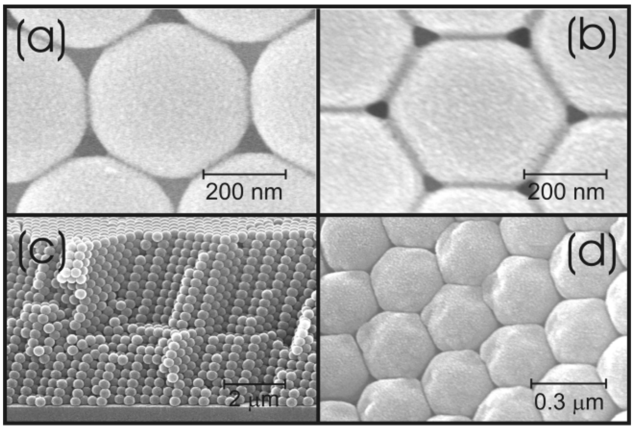

Fig. 2 SEM characterization of planarized colloidal crystals made of silica micro-spheres after being infiltrated with silica using the coating process described in the text. (a) and (b) show details of the external surface prior to and after a few silica coating cycles, respectively. (c) Cleaved edge showing that the treatment does not disturb the long range order of the planar structure. (d) Detail of a cleaved edge corresponding to an internal {111} plane of the structure. The closing of the external pores occurs when the coating thickness reaches the value 1.155*D*, where *D* is the diameter of the spheres. However, at this value the internal pores of the structure remain open although not interconnected any more.

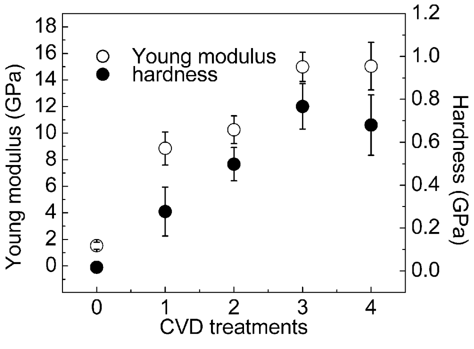

Fig. 3 Young modulus (open circle) and hardness (solid circles) of a planarized colloidal crystal *versus* the number of CVD cycles, as obtained by depth-sensing nanoindentation.

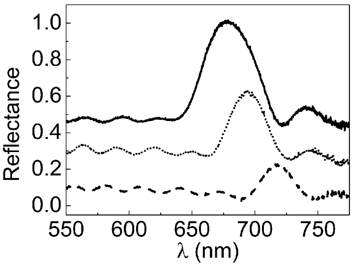

Fig. 4 Optical reflectance spectra of a planarized colloidal crystal prior to silica infiltration (solid line) and after two different silica infiltration treatments (dotted and dashed line). From the optical analysis we can estimate that 30 and 70% of the pore volume is infiltrated, respectively.

where $d_{(111)}$ is the interplanar distance along the [111] direction and $\langle\varepsilon\rangle$ is the volume averaged dielectric constant of the composite:

$$\langle\varepsilon\rangle = ff_{\mathrm{SiO_2}}\varepsilon_{\mathrm{s}} + (1 - ff_{\mathrm{SiO_2}})\varepsilon_{\mathrm{b}} \qquad (2)$$

where $ff_{\mathrm{SiO_2}}$ is the filling fraction of silica, and ε_{s} and ε_{b} the dielectric constant of the micro-spheres and the background, respectively. Thus we are gradually increasing the average refractive index in the structure as we increase the filling fraction of silica and close the air pores, keeping the lattice constant of the system unaltered. Formulas (1) and (2) combined explains the red shift in the position of the reflectance maximum detected and allows us to estimate the infiltrated pore volume (see Fig. 4). In addition, the fine structure, that is, the secondary minima resulting from finite crystal size effects, remains after the CVD infiltration. The good optical quality of the infiltrated samples are proof of the uniformity of the silica coating achieved by the CVD process proposed herein.

In conclusion, we report here a new method to control the pore size and enhance the connectivity of silica colloidal crystals. A chemical vapour deposition process performed at room temperature allows the growth of a continuous silica layer of controlled thickness interconnecting all the micro-spheres while maintaining unaltered the order and unit cell dimensions of the lattice. This method represents an alternative way to increase the mechanical stability of a colloidal crystal when sintering is not possible. Also, it is not limited to silica CVD on silica micro-spheres and can be extended to micro-spheres and CVD precursors of other compositions.

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