=Supporting Information Available=

Rapidly Infrared-assisted cooperative self-assembled highly ordered multiscale porous materials

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Comparison of qualities of mono-CCs and MIOs made by the PCIHVD method

In our recently reported two-parameter method — PCIHVD method[6a] based on the relation between the boiling point of solvent and vapor pressure, the solvent evaporation rate can be largely changed by adjusting both the growth temperature and the vapor pressure simultaneously while maintaining an enhanced convective body flow under the near-boiling critical condition. It was confirmed from experimental and theoretical aspects that the optimal growth condition for self-assembling mono-CCs in which the temperature, vapor pressure and growth rate are 35 , 39.0mmHg and 0.71cm/hr (0.12mm/min) respectively, can be precisely obtained and high-quality CCs can be rapidly fabricated with the PCIHVD method.

For the sake of comparison, cooperative self assembly (CSA) of binary colloidal particles with large size ratios is carried out with the PCIHVD method. In our experiments, 7nm silica nanoparticles and polystyrene (PS) colloidal spheres from 400nm to above 1μm are cooperative self-assembled by the PCIHVD method under the same growth condition used above. After removing the PS spheres by calcinations of the samples at $450^{\circ}C$,[5a,b] silica inverse opals (IOs) are formed from the original composite CCs. It is found that the CSA encounters great difficulties with the PCIHVD method which becomes more and more inapplicable along with the increasing of colloidal sphere size. For small PS spheres, the quality of the IOs is extraordinarily poor, as shown in the SEM image of silica IOs made from 596nm PS spheres. These porous materials are almost amorphous, in which the domains are confined by the transverse and longitudinal cracks spaced 50-100μm and the air spheres are completely randomly packed in every domains. Cracks emerge every 30-50μm. This is in sharp contrast with the perfect crystal structure and the lack of defect in the mono-CCs made from the same PS spheres by the PCIHVD method (see the SEM image shown in Fig.S1a which is the same as fig.S3c in ref.6a). For PS spheres beyond 600nm, the cooperative self assembly even can not be accomplished for any growth conditions. Almost all colloidal particles accumulate on the bottom of the growth vial.
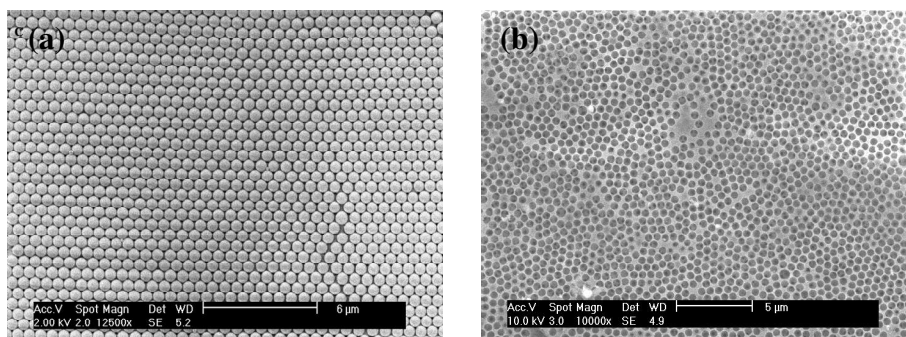
Figure S1 Representative SEM images for (a)[6a] mono-CCs made from 596nm PS spheres at the optimal growth condition by the PCIHVD method and (b) mono-IOs made through CSA of 596nm PS spheres and silica nanoparticles at the same growth condition and following calcinations.

Experimental setup for the IACSA method

The schematic of experiment setup for IA-PCIHVD method is illustrated in Fig.S2. The growth chamber is sealed with a glass cover which is connected to the pressure controlling system (a vacuum pump connected to the growth chamber with a soft suction pipe). The characteristic infrared (CIR) light is set up right above the growth vial irradiating the growing interface. The pressure in the growth chamber can be modulated with a needle valve. The emission spectrum peak of the CIR light just coincides with the symmetric and asymmetric O-H stretching vibration band of liquid water[8]. The O-H stretching vibration in water molecules near the growing interface can be significantly strengthened due to extensively absorbing and resonating with the CIR light. So the evaporation of water can be significantly accelerated without changing the bulk growing environment.
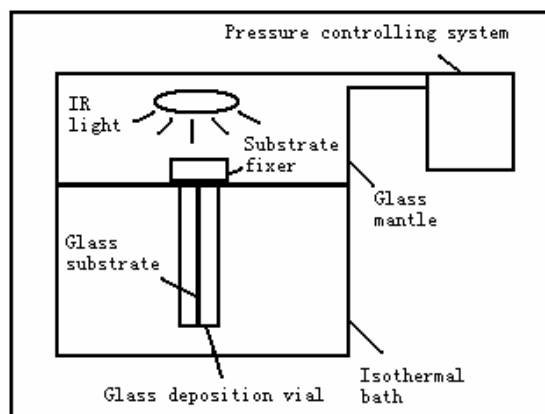
Figure S2 Schematic of the experimental setup for the IACSA method.

Growth parameters for fabricating BCCs and TCCs with the IACSA method:

By the IACSA method, bimodal colloidal crystals (BCCs) are fabricated using mixed suspensions of silica nanoparticles and PS microspheres with diameter from 200nm to 1.5µm, and trimodal colloidal

crystals (TCCs) with two different surface patterns are fabricated from mixed suspensions of silica nanoparticles, 200nm and 1μm PS microspheres under different concentration ratios of the multiple colloids. Here, the temperature and air pressure are set to 35.0°C and 39.0mmHg, respectively, which is a critical near-boiling condition for liquid water. Other parameters in the optimal conditions (CIR intensity I, growth rate R, concentration ratio φ of multiple colloids in the mixed dispersion) for preparing BCCs and TCCs using PS spheres of different sizes with this method are listed in Table S1.

Table S1 Growth parameters for fabricating BCCs and TCCs with PS colloidal spheres of different sizes and silica nanoparticles by uing the IACSA method.

	BCCs (200nm)	BCCs (451nm)	BCCs (596nm)	BCCs (1μm)	BCCs (1.35μm)	TCCsa	TCCsb
$\varphi_{S/L}$ (C_S/C_L)	0	0	0	0	0	0.12	0.14
$\varphi_{N/L}$ (C_N/C_L)	0.42	0.42	0.42	0.42	0.42	0.27	0.27
I +/-0.2 (w/cm^2)	5.03	6.52	7.51	10.28	12.55	10.28	10.28
R (mm/min)	0.4	0.48	0.53	0.68	0.8	0.68	0.68

In this table, C represents concentration, L, S and N represent large, small colloidal spheres and nanoparticles respectively, and a, b represent the two surface patterns of the TCCs shown in fig.3a, b, respectively. After calcinations, highly ordered mono-inverse opals (MIOs) and binary inverse opals (BIOs) are formed from the original BCCs and TCCs.

Spectra Analysis:

The transmittance spectrum of the inverse opal films prepared here are measured with normal incident light perpendicular to the (111) surface of the fcc lattice. In this case, the positions of PBGs can be approximated by Bragg's law:[3a] $\lambda_{max} = 2 d_{111} n_{eff}$, where λ_{max} is the peak position of the PBGs, d_{111} is the interlayer spacing in (111) direction which is in direct proportion to the diameter of the large PS

sphere, n_{eff} is the effective refractive index of the medium, which can be given by [5c] $n_{eff}^2 = \sum_i n_i^2 \phi_i$,

where n_i and ϕ_i are the refractive index and volume fraction of each component i in the crystal material.

In our OPMs, the air spheres are shrunk to 2-5% smaller than the origin PS spheres from which they formed. For MIOs, the air spheres are organized in close packed arrays. So, the volume fraction of air spheres and silica nanoparticles are assumed to be 74% and 26%, respectively. The PBG center of the MIO prepared using 451nm PS spheres is measured at 771nm. Assuming the refractive index of air to be 1, the refractive index of silica framework can be derived as 1.26 from Bragg's law, which is lower than that of silica bulk material $(1.43)^{[5c]}$ mainly due to the micro porous structure of the silica-air matrix. Considering that the silica nanoparticles are in random closed packing[5] and the refractive index of silica bulk material is $1.43^{[5c]}$, the n_{eff} of the silica matrix can be calculated as 1.33 which is higher than the approximate value derived from the transmittance spectrum due to the novel properties of nanoparticles different from their bulk materials. According to the Bragg's law and assuming n_{eff} of the silica media as 1.26, the PBG positions of MIOs prepared from 596nm 1μm and 1.35μm PS spheres are given as 1018nm, 1705nm and 2307nm respectively by scaling with the diameters of air spheres. Obviously, the measured PBG positions accord with the calculated values, which further confirm our approximation of the n_{eff} of the silica media and the shrinkage of structural lattice. Silica BIOs with the two surface patterns are considered to have the same hierarchical structure with crystal stoichiometries of LS_{21-23}. So, the volume fraction of small spheres can be calculated as 83-84% in these BIOs structure. Consequently, according to the Bragg's law, the PBG peak position of the BIOs can be calculated to be 1656-1670nm which is correspondent with the measured value of 1664nm in the transmittance spectrum of the BIOs. This confirms the hierarchical structures of the BIOs obtained in the experiments.