Supporting Information

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SI Text

SI 1

Photonic Band-Structure Calculations. Plane-wave photonic band-structure calculations were performed for the inverse NaCl structure, showing that the relative gap width (Fig. S1*A*) is significantly larger than for an inverse fcc structure. In Fig. S2*B*, the gap widths are shown for varying sphere size ratio S/L. The fcc structure corresponds with a size ratio of S/L = 0. Because the NaCl structure only consists of layers stacked in an fcc-like fashion, it is crucial to avoid the hcp-like stacking of NiAs when growing these binary colloidal crystals for photonic applications.

Photonic band diagrams were calculated by using the MPB package, version 1.4.2 [Johnson et al. (2001) Block-iterative frequency-domain methods for Maxwell's equations in a planewave basis. *Optics Express* 8:173–190]. In addition, an MPB patch file by Mischa Megens (e-mail: mischa.megens@philips.com) was installed to calculate the effective dielectric constant by averaging over Wigner–Seitz cells rather than over the parallelepipeds spanned by the lattice vectors. This patch also ensures proper weighting of the dielectric constant at the edges of the unit cell and thus avoids double-counting.

SI 2

Drying the Binary Colloidal Structures. As we were initially motivated by the photonic band-structure calculations presented in *SI 1*, we also studied the feasibility of postprocessing of our binary colloidal crystals. After all, the calculations showed that there is only a photonic band gap for inverse NaCl structures, in which the spheres have a lower dielectric contrast than the background medium. A successful method for contrast inversion in dry colloidal crystals is infiltration with a high-index material by chemical vapor deposition or atomic layer deposition, after which the spheres are removed by using a heat treatment or a wet-chemical etch. To determine whether the index contrast in our samples could be similarly inverted, we dried out a crystal with a NaCl structure which had been grown from a binary dispersion of silica colloids in a water/glycerol mixture. Subsequently, the crystal was removed from its original substrate and imaged from the bottom side, against the direction of gravity, by using SEM (Phenom, FEI). Two typical SEM images are shown above. As is apparent from the figures above, the fcc structure is retained without serious cracking, which means that most smaller spheres will also have remained on their lattice positions because of their confinement. This makes inverting the binary structure with chemical vapor deposition as feasible as with single-sphere fcc crystals of silica.

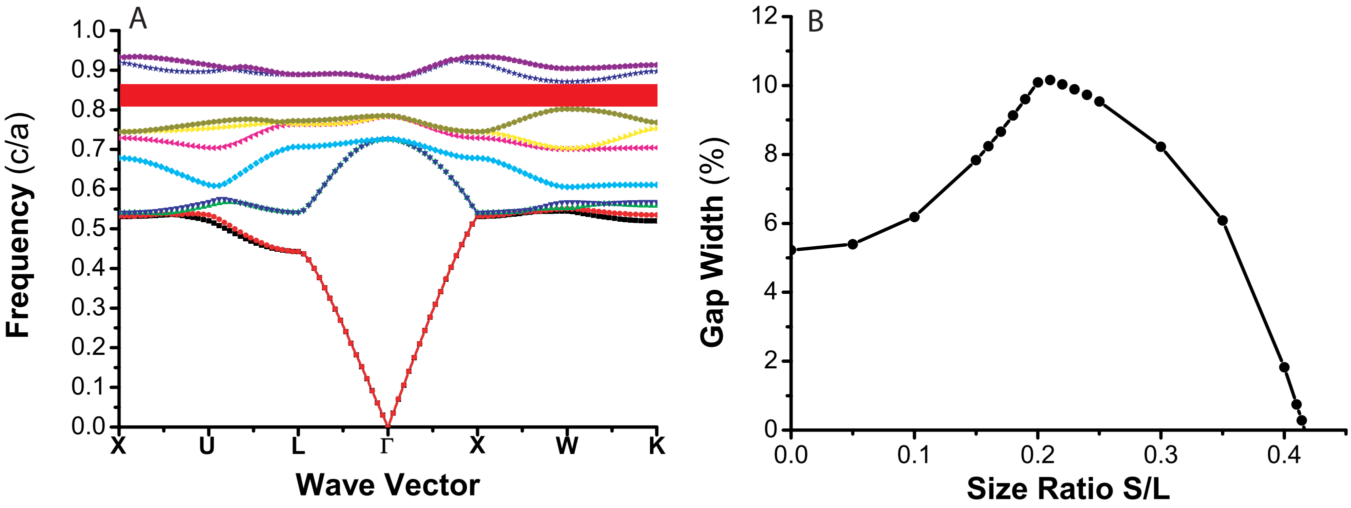

Fig. S1. Photonic band-structure calculations for an inverse NaCl crystal. (*A*) Photonic band-structure diagram of an inverse binary NaCl structure of air spheres (dielectric constant, $\epsilon=1$) in silicon ($\epsilon=12$) with a size ratio between the two types of spheres of 0.3. The large spheres are touching. Calculated with the MIT Photonic Bands software by using 32 x 32 x 32 grid points to discretize the real-space unit cell. The photonic band gap between bands 8 and 9, with a width of approximately 8.2%, is indicated by the red rectangle. (*B*) Graph containing relative width of the photonic band gap between band 8 and band 9 versus the size ratio of the small spheres versus the large spheres. The size ratio is varied, whereas the position of the center of the small sphere in the unit cell is fixed in the center of the octahedral hole of the fcc lattice of the large spheres. The lines are a guide to the eye.

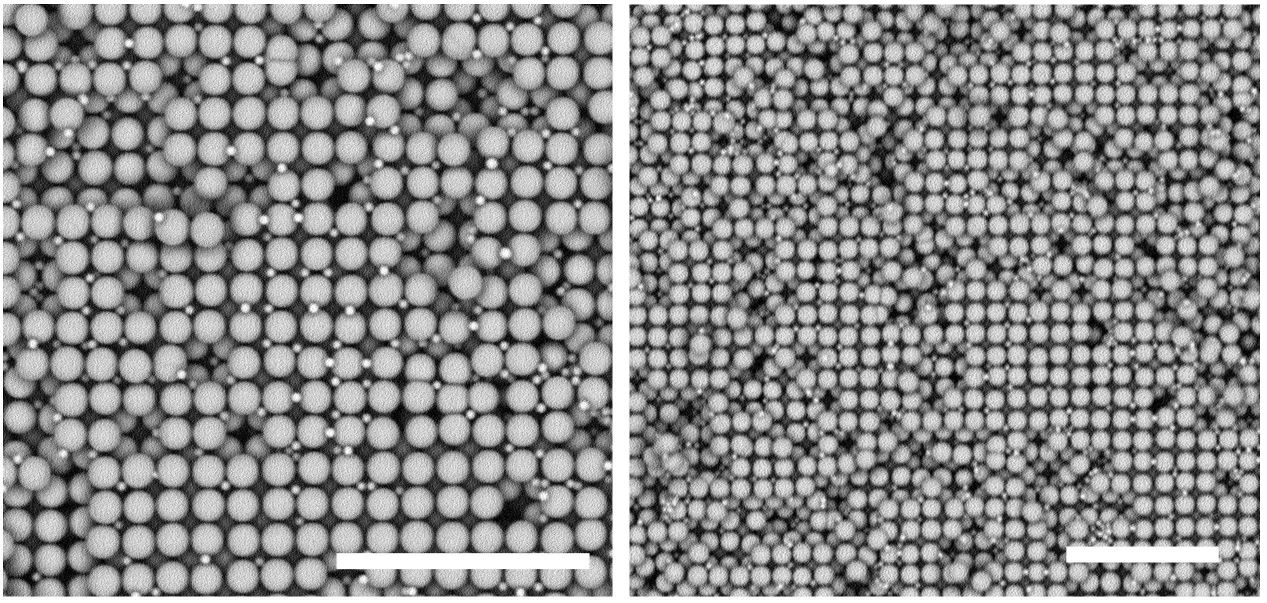

Fig. S2. SEM images of the bottom (100)-layers of a dried binary colloidal crystal with a NaCl structure grown by sedimentation on a square template. Because the SEM images were taken of the bottom layers of the crystal, the fraction of small particles is quite low. Furthermore, some small (and large) particles were lost in the process of removing the crystals from the substrate. (Scale bars: 10 μm.)