Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Debye Ring Diffraction Elucidation of 2D Photonic Crystal Self-Assembly and Ordering at the Air-Water Interface

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Supporting Information

Contents

1. **Representative SEM Images of 2DPC for 409, 570, and 915 nm Particles for all salt concentrations**

a. **915 nm Diameter 2DPC**

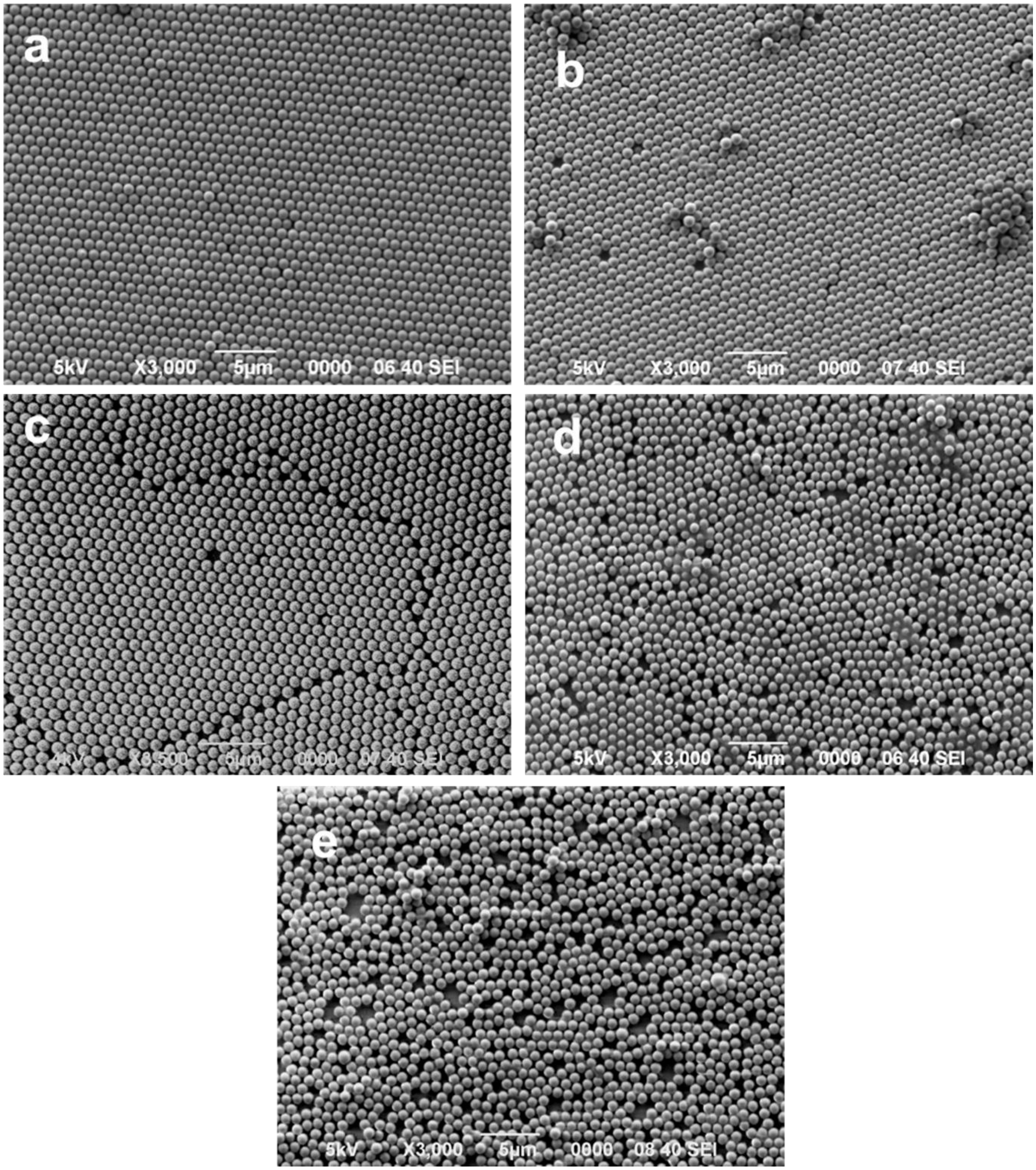

Fig. SI 1- SEM micrographs of 2DPC fabricated by self-assembly of 915 nm diameter charged polystyrene particles at the air-water interface of electrolyte solutions containing NaCl. A. Pure Water B. 0.001 M NaCl C. 0.01 M NaCl D. 0.1 M NaCl E. 1 M NaCl

b. 570 nm Diameter 2DPC

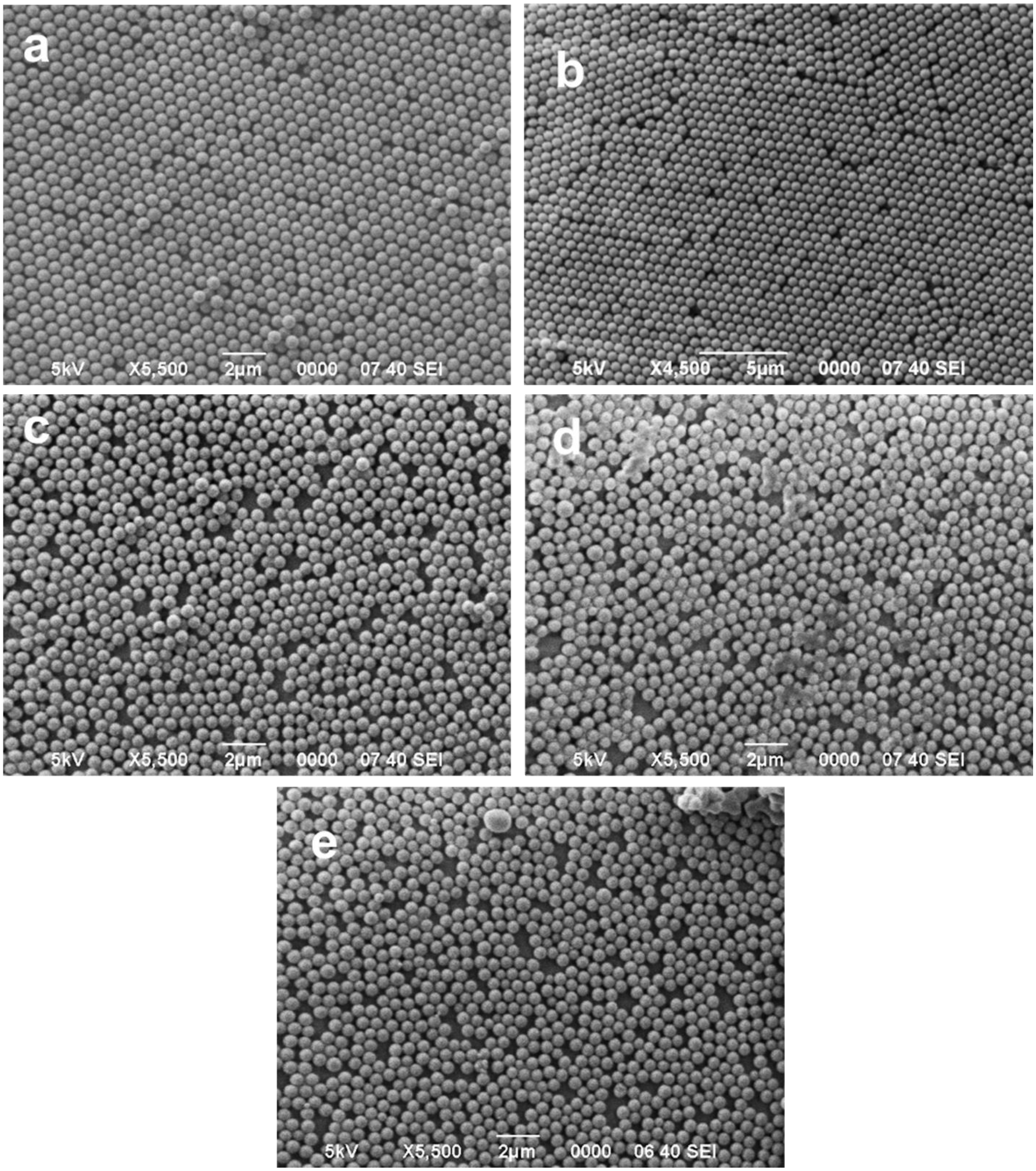

Fig. SI 2- SEM micrographs of 2DPC fabricated by self-assembly of 570 nm diameter charged polystyrene particles at the air-water interface of electrolyte solutions containing NaCl. A. Pure Water B. 0.001 M NaCl C. 0.01 M NaCl D. 0.1 M NaCl E. 1 M NaCl

c. 409 nm Diameter 2DPC

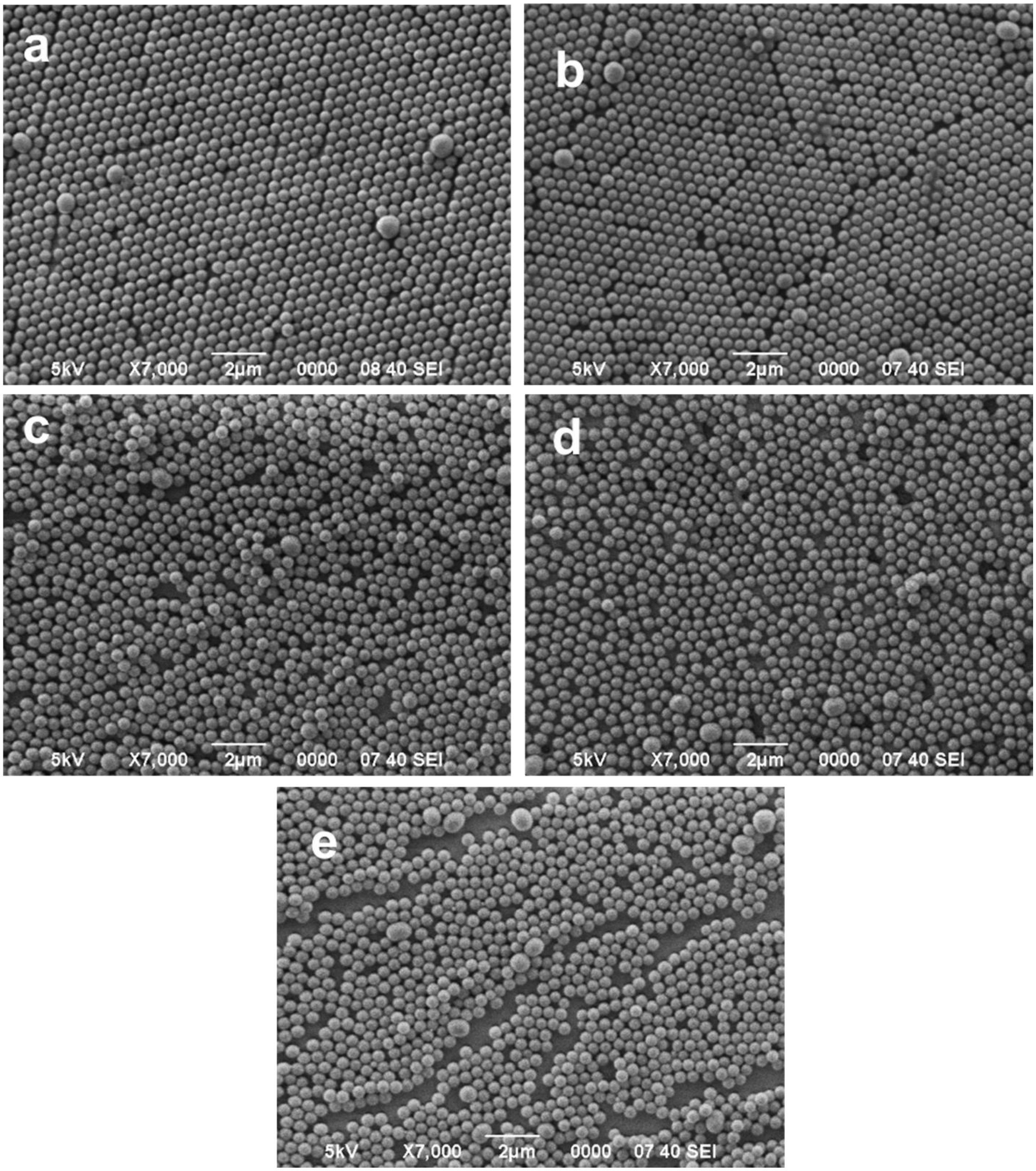

Fig. SI 3- SEM micrographs of 2DPC fabricated by self-assembly of 409 nm diameter charged polystyrene particles at the air-water interface of electrolyte solutions containing NaCl. A. Pure Water B. 0.001 M NaCl C. 0.01 M NaCl D. 0.1 M NaCl E. 1 M NaCl

2. 2DPC Order Analysis

First, each image was transformed into a black and white binary image using the GNU Image Manipulation Program (GIMP) using a difference between Gaussians edge-detection filter. The particles in each image were then found using the circle Hough transform algorithm included in the MATLAB scripting package (MathWorks). The centers of the detected particles were passed into a function to calculate the pair correlation function (Eq. 1). The program counts the number of particles, dn, in the area of the shell, da having an inner diameter, r, and outer diameter, r + dr.

$$(1) \qquad g(r) = \frac{1}{\langle p \rangle} \frac{dn(r, r+dr)}{da(r, r+dr)}$$

This was done for increasing shell radii, r = 0 to 14, increasing by, dr = $0.016R_0$, where R_o is the particle radius[1]. A plot of g(r) with respect to the normalized distance $R/2R_o$ from 15 SEM images was produced for each particle size and salt concentration. The function utilized is appended as arrayOrdering.m and automated with the appended 2DOrderingProc.m

The g(r) plots were further analyzed utilizing a discrete Fast Fourier Transform (FFT). The FFTs of the average g(r) spectra were taken using the FFTW library included in the MATLAB software. The Full Width Half Maximum (FWHM) bandwidth of the first peak of the FFT of g(r)-1 can be used to quantify 2DPC ordering[1-3]. The width of the first peak is directly related to the decay in g(r). As the 2DPC long range order decreases, the width the first FFT peak increases. The dimensionless ordering parameter (κ/κ_o) is the ratio of the FWHM of the FFT peak for a fabricated 2DPC, κ and the FWHM of the FFT peak for a perfect array[1]. κ was averaged over all 15 data sets for each salt concentration and particle size with the appended KAve.m

A Gaussian baseline was observed in the FFTs of 2DPCs of poor ordering. A Gaussian peak in the g(r) spectrum appears as a Gaussian peak in the FFT of g(r)-1[4]. The baseline was nearly eliminated by removing the first Gaussian peak in the g(r) spectrum. Removal of the first Gaussian peak in g(r) does not affect the rate of decay in g(r) peaks, the source of the line width, therefore the FFT bandwidth is not effected.[4]

a. g(r) plots generated from 15 SEM micrographs of 2DPC for each particle diameter fabricated on water and NaCl solutions

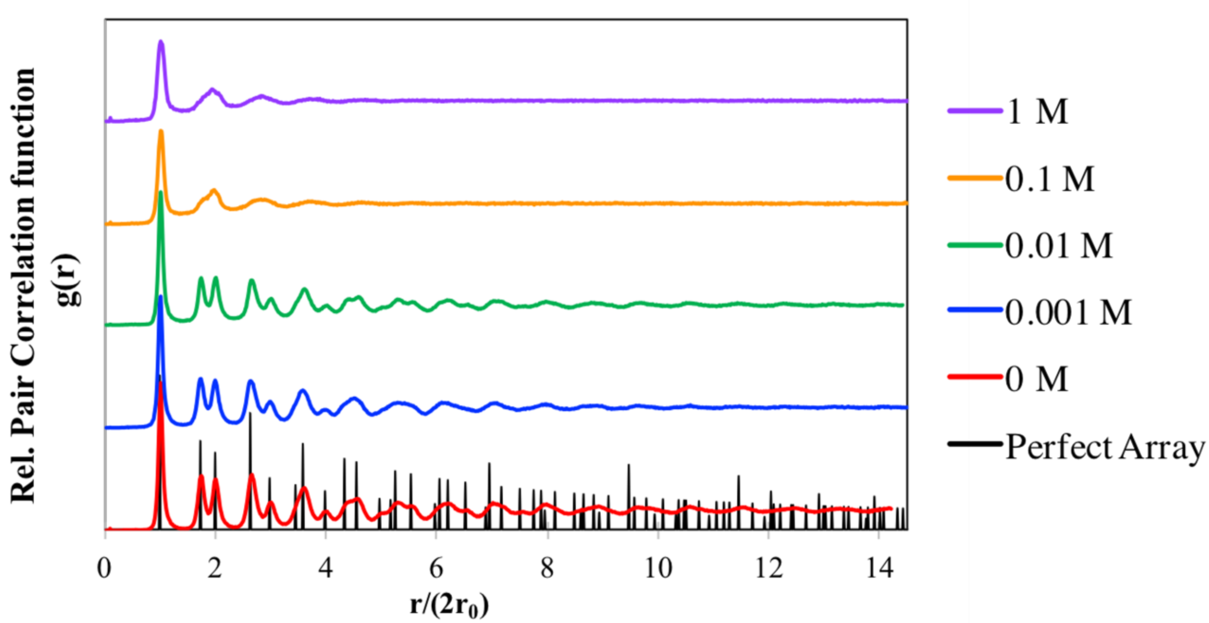

Figure SI 4- 2D Pair Correlation function for a perfect close-packed 2D array of circles with 409 nm diameters and 2DPC of 409 nm particles fabricated on pure water and on 0.001, 0.01, 0.1, and 1M NaCl solutions

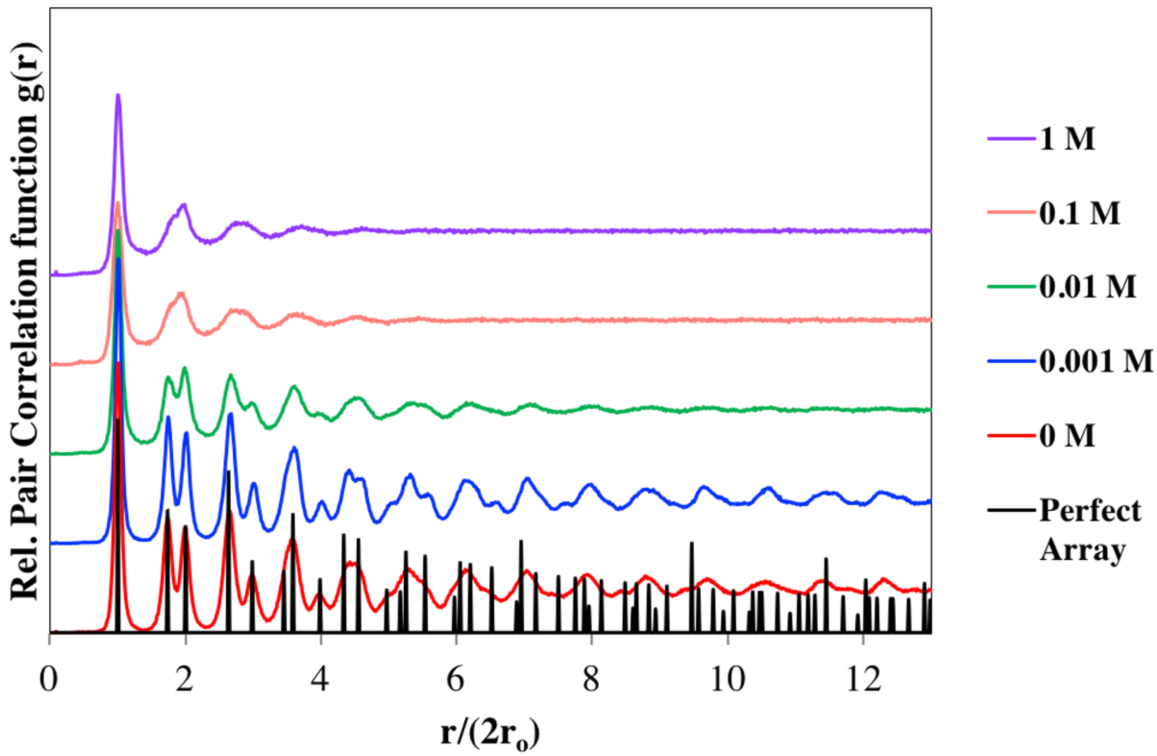

Figure SI 5- 2D Pair Correlation function for a perfect close-packed 2D array of circles with 570 nm diameters and 2DPC of 570 nm particles fabricated on pure water and on 0.001, 0.01, 0.1, and 1M NaCl solutions

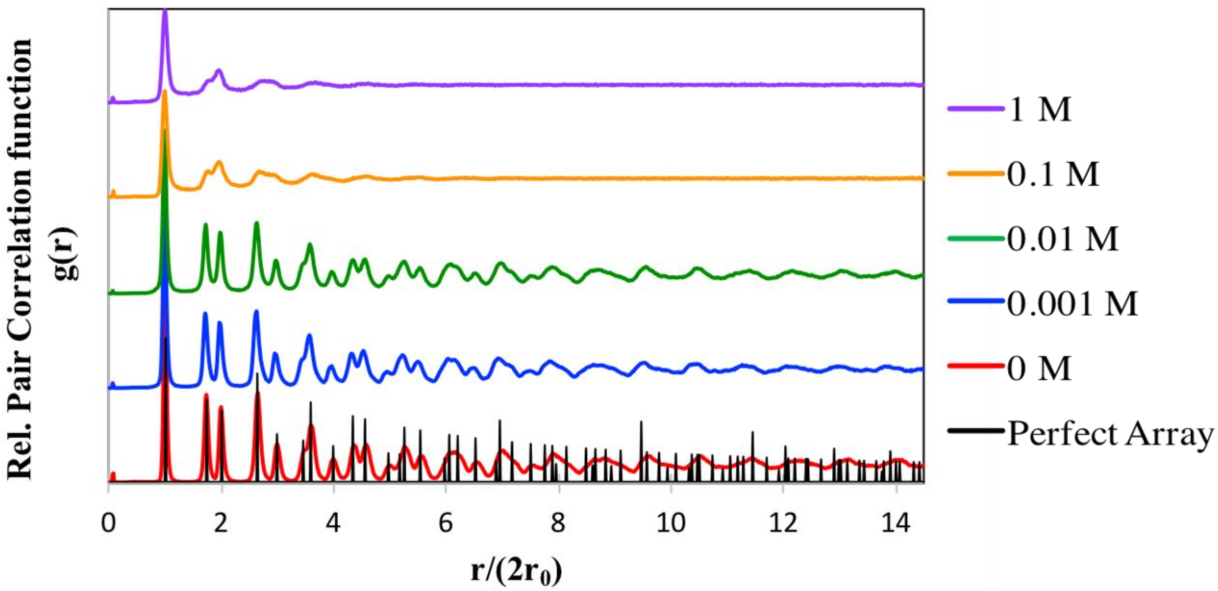

Figure SI 6- 2D Pair Correlation function for a perfect close-packed 2D array of circles with 915 nm diameters and 2DPC of 915 nm particles fabricated on pure water and on 0.001, 0.01, 0.1, and 1M NaCl solutions

b. Fast Fourier Tranforms (FFT) of (g(r)-1) of 2DPC for each particle diameter fabricated on water and NaCl solutions

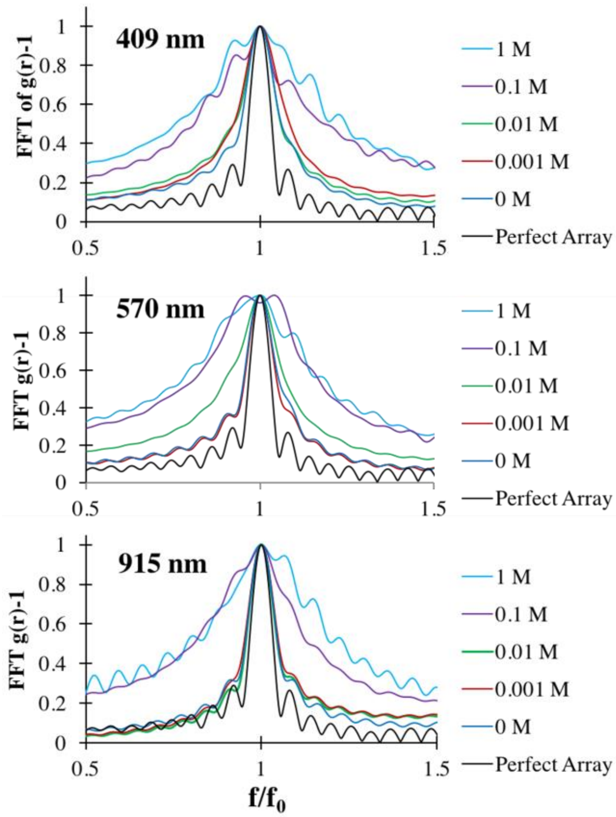

Fig. SI 7- The first peak of the FFT of g(r)-1 plots for 2DPC arrays of 413nm (top), 570nm (middle), and 915nm (bottom).

Supporting Information References

1. Zhang, J.-T.; Wang, L.; Lamont, D. N.; Velankar, S. S.; Asher, S. A., Fabrication of Large-Area Two-Dimensional Colloidal Crystals. *Angew. Chem. Int. Ed.* **2012,** *51* (25), 6117-6120.

2. Bohn, J. J.; Ben-Moshe, M.; Tikhonov, A.; Qu, D.; Lamont, D. N.; Asher, S. A., Charge stabilized crystalline colloidal arrays as templates for fabrication of non-close-packed inverted photonic crystals. *J. Colloid Interface Sci.* **2010,** *344* (2), 298-307.

3. Rengarajan, R.; Mittleman, D.; Rich, C.; Colvin, V., Effect of disorder on the optical properties of colloidal crystals. *Physical Review E* **2005,** *71* (1), 016615.

4. Bracewell, R. N., *The Fourier transform and its applications*. McGraw Hill: Boston, 2000; Vol. 3rd.