Electronic Supplementary Information (ESI)

Colloidal Assembly Manipulated by Light-responsive Ag_3PO_4 Nanoparticles

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1. Supporting Videos

The play speed for videos S1 to S3 is 10 frames/s, and the real time between adjacent frames is 2 s.

Video S1. Formation of crystallites under UV irradiation. The intensity of UV is 10 μW/cm^2, ϕ_{PS} = 0.469, C_{Ag3PO4} = 100 μg/mL.

Video S2. Formation of chains under UV irradiation. The intensity of UV is 20 mW/cm^2, ϕ_{PS} = 0.212, C_{Ag3PO4}= 100 μg/mL.

Video S3. Formation of gels under UV irradiation. The intensity of UV is 20 mW/cm^2, ϕ_{PS} = 0.368, C_{Ag3PO4} = 100 μg/mL.

2. Supporting Figures

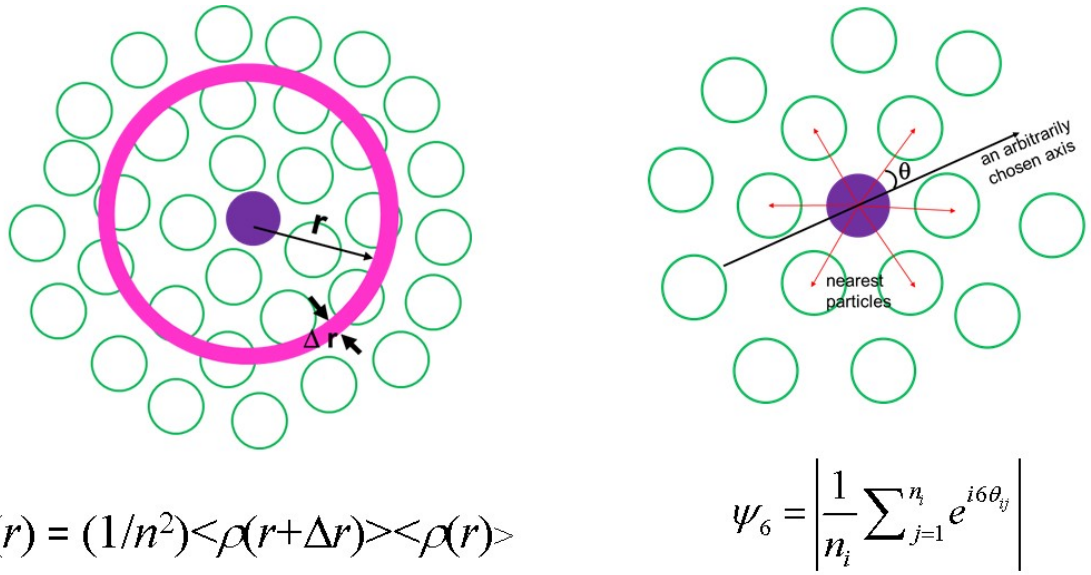

Fig. S1 Schematic demonstration of *g*(r) and ψ_6.

The radial distribution function, *g(*r) characterizes the static structure of a particulate system[1]. It represents the probability for a given particle to find other particles within a certain range. $g(r) = (1/n^2)<\rho(r+\Delta r)><\rho(r)>$, where *n* represents the number density of the PS microspheres, and $\rho = \sum_{i=1}^{N(t)} \delta(r - r_i(t))$ represents the distribution of particles in the field of view. The orientational order parameter, ψ_6 is calculated to quantify the six-folded order of particles, which has been widely used to characterize the crystalline ordering of spheres in two dimensions [2]. $\psi_6 = \left| \frac{1}{n_i} \sum_{j=1}^{n_i} e^{i6\theta_{ij}} \right|$, where n_i is the number of nearest particles of particle i, θ_{ij} is the angle between the vector from particle i to its *j*th nearest neighbor and an arbitrarily chosen axis. Particles with ψ_6 = 1 denotes that they have perfect six-folded order.

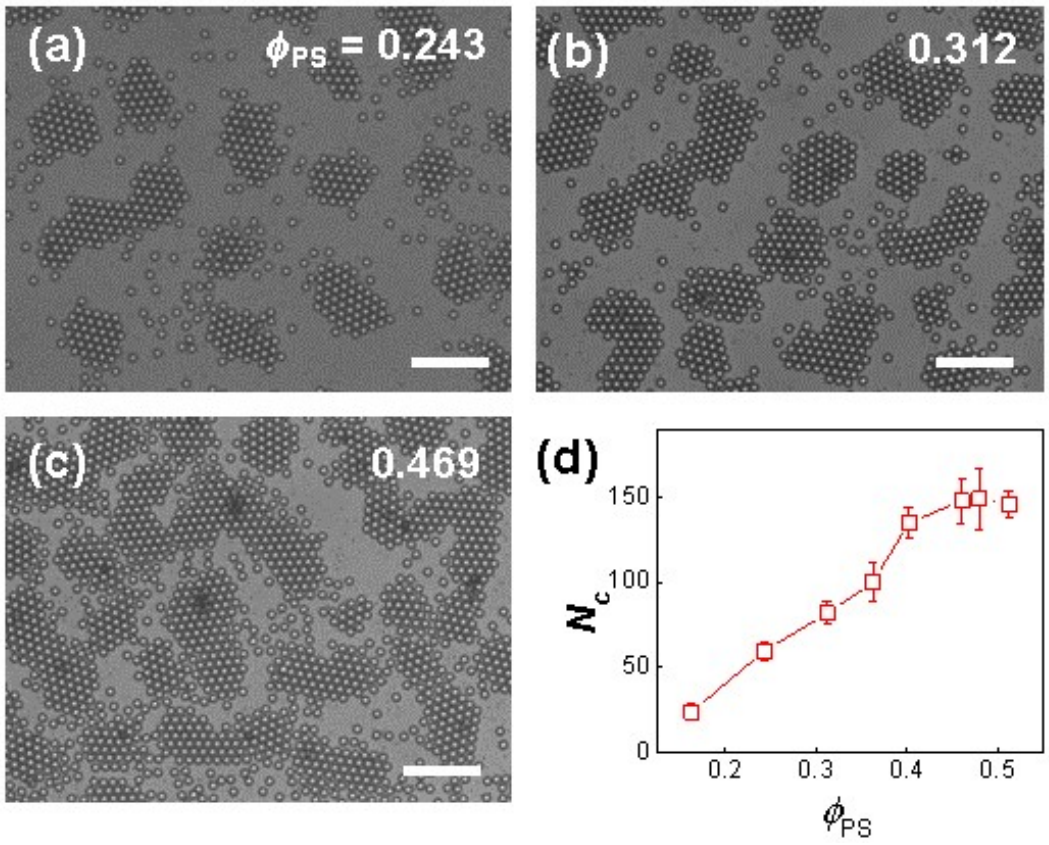

Fig. S2 The size of the crystalline cluster increases with the packing density of the PS microspheres. (a-b) Bright-field microscope images of the assemblies at different packing densities of PS microspheres under a weak UV intensity (10 μW/cm^2) with same concentration of Ag_3PO_4 nanoparticles (C_{Ag3PO4} = 100 μg/mL). Scale bar: 30 μm. The packing density of PS microspheres is indicated on the images and defined as $\phi_{PS} = N\pi r^2/S$, where N is the number of PS microspheres, r is the radius of PS microspheres, and S is the area of the field of view. (d) The averaged size, N_c (average number of particles in clusters) of the assembled crystallites as a function of ϕ_{PS}. The size is characterized by the number of the particles in a crystallite.

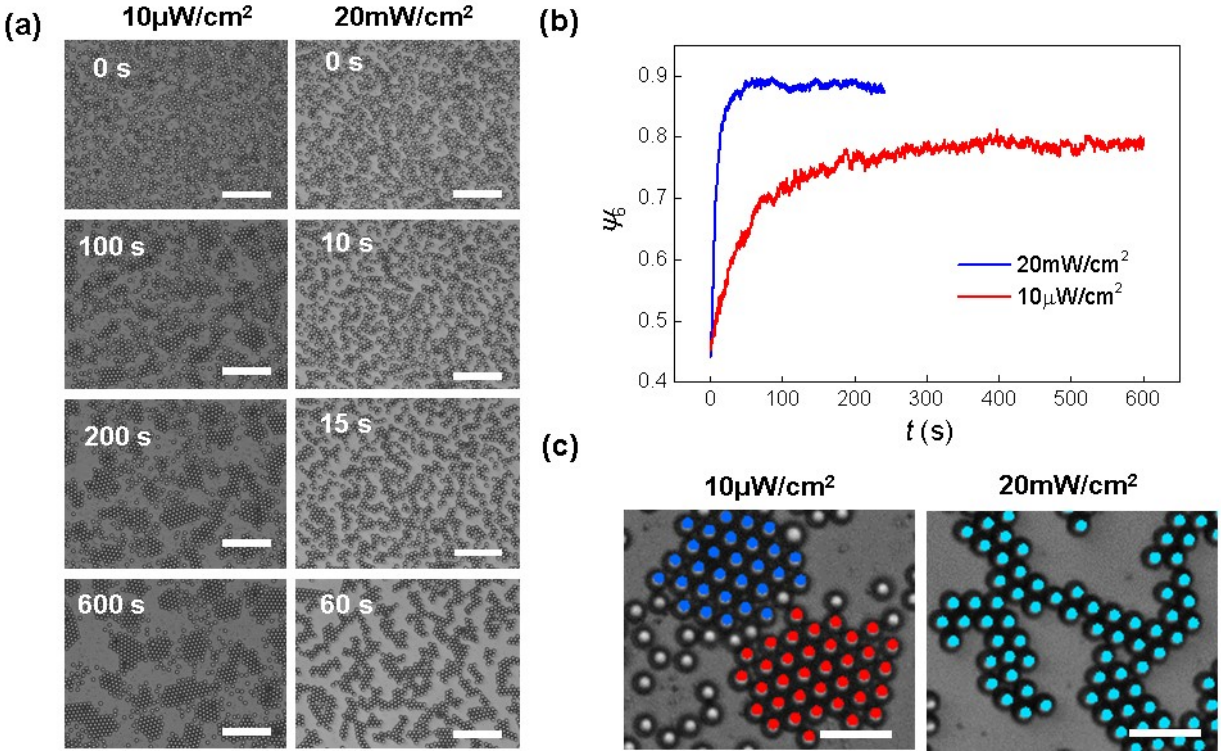

Fig. S3 Assembly of PS microspheres under different light intensity. (a) Image sequences showing the assembly process of PS microspheres under a lower (10 μW/cm^2) and a higher (20 mW/cm^2) light intensity. Scale bar: 40 μm. (b) Growth of orientational order parameter, ψ_6 of the whole microsphere system as a function of time under different light intensities. (c) Enlarged view of the assembled crystallites. Here particles with the same color belong to the same cluster. Scale bar: 10 μm.

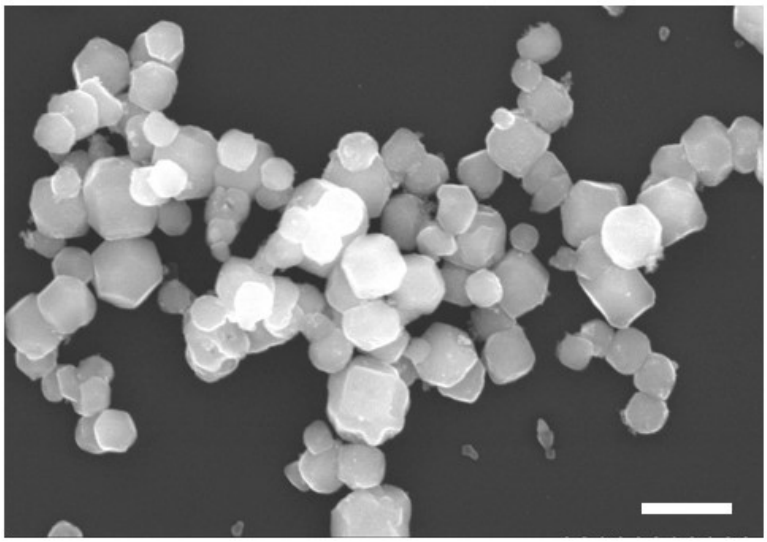

Fig. S4 SEM image of the as-prepared Ag_3PO_4. Scale bar: 500 nm.

3. Materials and Methods

3.1 Materials

All the reagents were analytical grade and used without further purification. Silver nitrate ($AgNO_3$), sodium hydroxide (NaOH), ammonium sulfate ($(NH4)_2SO_4$), dipotassium phosphate (K_2HPO_4) and ethanol were purchased from Aladdin Reagent (Shanghai) Co., Ltd, polystyrene microspheres (3 μm in diameter) were obtained from Thermo Fisher Scientific. All solutions were prepared with deionized water with resistivity ≥ 18.2 MΩ cm^{-1}.

3.2 Synthesis of Ag_3PO_4 nanoparticles

The synthesis of Ag_3PO_4 nanoparticles was carried out follow the method reported in literature with some modifications[3]. The detailed process was as followed. 4 mL of 0.05M $AgNO_3$ was added to a flask, and then 1.8 mL of 0.2M NaOH and 1 mL of 0.2M $(NH_4)_2SO_4$ were added and mixed thoroughly to form a homogeneous solution. Next, the solution was stirred vigorously to ensure Ag^+ were fully reacted into $[Ag(NH_3)_2]^+$ .Then, 4 mL of 0.1M K_2HPO_4 was added to the solution, after that the solution turned yellow due to the generation of Ag_3PO_4 nanoparticles. The whole synthesis was operated in dark environment and lasted for 20 min. The resulted particle suspension solution was centrifuged at 6000 rpm for 5 min, and the solid sediment was washed with water for 3 times. Large agglomerates of Ag_3PO_4 in Ag_3PO_4 precipitate can be separated and removed by multiple sedimentations. Finally, Ag_3PO_4 particles were kept in 99.8% ethanol for later use.

3.3 Preparation of Microscopy Samples

For microscopy samples, the mixture of Ag_3PO_4 nanoparticles and PS microspheres were dispersed in 0.1% H_2O_2 solutions and the dispersion was added in a simple round sample cell made of a glass slide and a plastic ring fixed together with epoxy glue. The concentration of Ag_3PO_4 nanoparticles in the mixture was changed from 10 μg/mL to 150 μg/mL. After the mixture suspension was added, the cell was sealed using an epoxy adhesive to prevent contamination and solvent evaporation. The Ag_3PO_4 and PS microspheres sediment on the bottom of the cell due to the gravity.

3.4 Microscopy Observation and Image Acquisition

The assembly of PS microspheres were observed and recorded at 10 frames per second by a Basler ACE camera fitted on an Olympus IX73 microscope using a 40X objective. The packing density of PS microspheres and ultraviolet intensity were varied to study the influence of the packing density and light intensity on the assembled structures. The particles in the micrographs were identified by image analysis using ImageJ (NIH) to obtain the particles' positional coordinates. The positional data were further analyzed using in-house computer programs written in IDL (RSI) to analyze the assembled structures.

References

1. Z. Zhang, N. Xu, D. T. N. Chen, P. Yunker, A. M. Alsayed, K. B. Aptowicz, P. Habdas, A. J. Liu, S. R. Nagel and A. G. Yodh, *Nature*, 2009, **459**, 230-233.
2. Y. Chen, X. Tan, H. Wang, Z. Zhang, J. M. Kosterlitz and X. S. Ling, *Phys. Rev. Lett.*, 2021, **127**, 018004.
3. Y. Bi, S. Ouyang, N. Umezawa, J. Cao and J. Ye, *J. Am. Chem. Soc.*, 2011, **133**, 6490-6492.