

## Supporting Information

### Templated Self-Organization of Polymer-Tethered Gold Nanoparticles into Freestanding Superlattices at Liquid-Air Interface

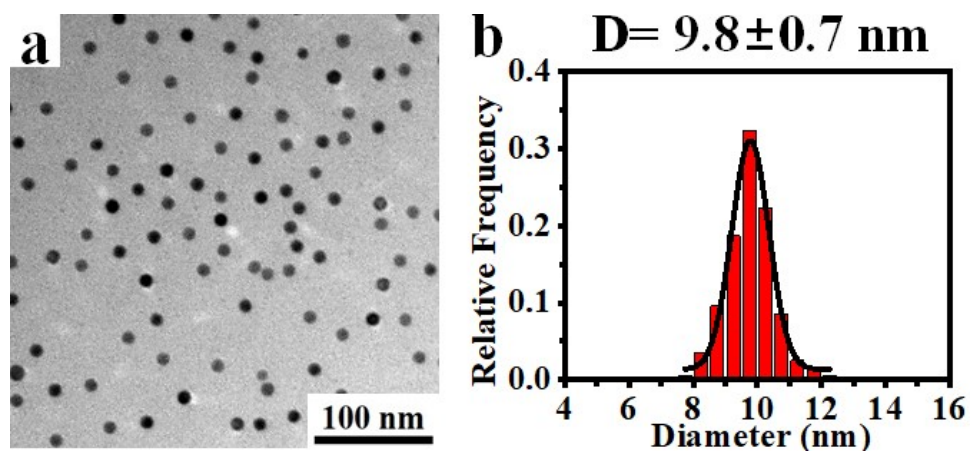
Ye Gao,<sup>1</sup> Lingli Wan,<sup>1</sup> Yuqing Song,<sup>1</sup> Shan Gao,<sup>1</sup> Nan Yan,<sup>1,\*</sup> Fan Wu,<sup>3,\*</sup> Yanqiu Du<sup>2,\*</sup>

<sup>1</sup>College of Chemistry, Research Institute for Scientific and Technological Innovation,  
Changchun Normal University, Changchun Normal University, Changchun 130032,  
China

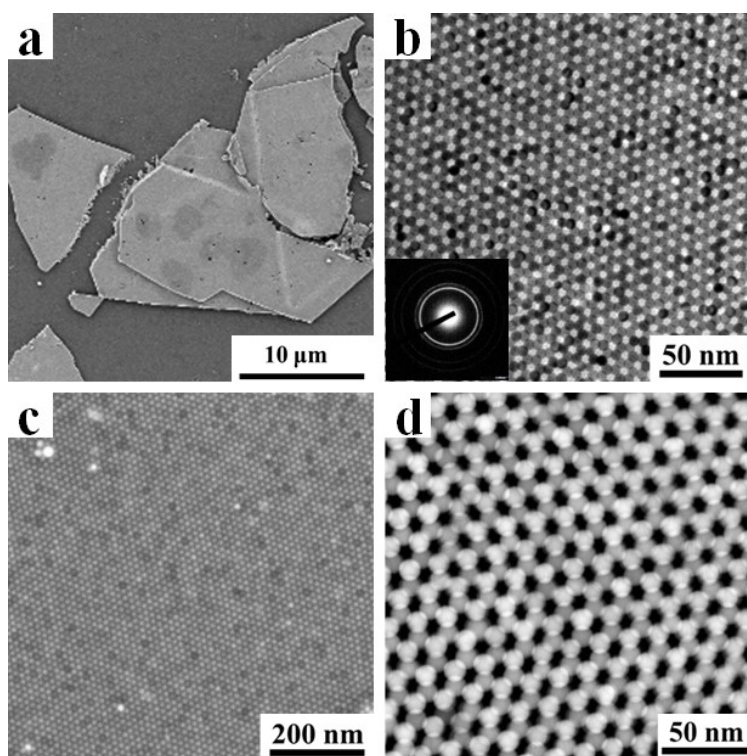
<sup>2</sup>College of Materials and Textile Engineering, Jiaying University, Jiaying 314001,  
China

<sup>3</sup>State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of  
Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

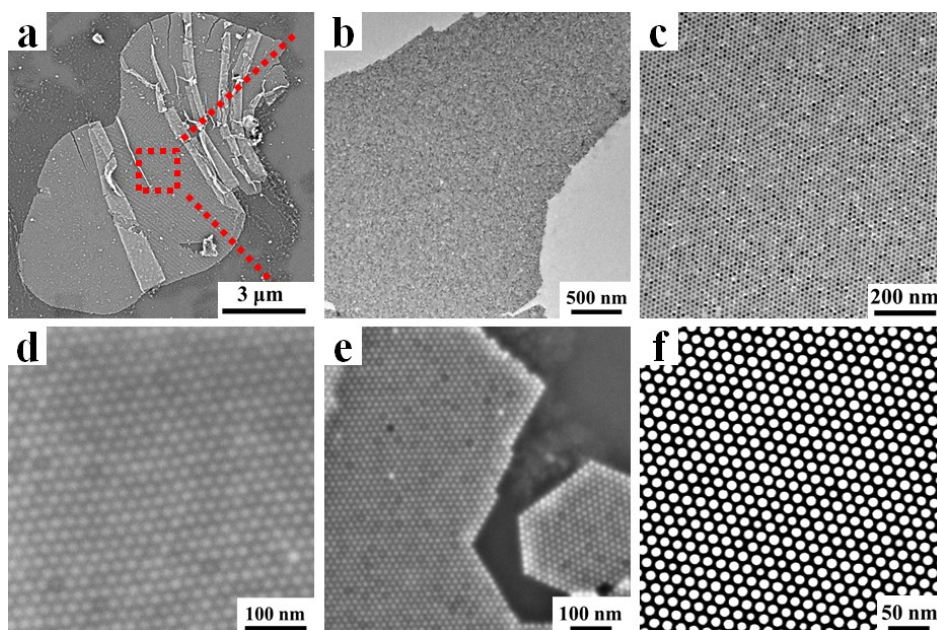
E-mail: yannan@ccsfu.edu.cn; fwu@ciac.ac.cn; yqdu@zjxu.edu.cn



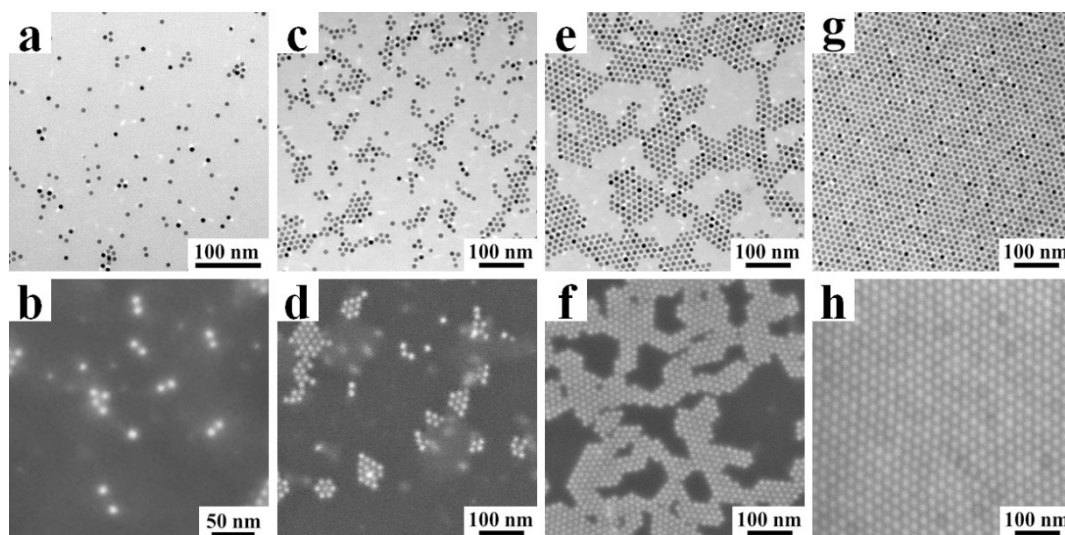
**Fig. S1.** (a) TEM image of the synthesized AuNPs@PS<sub>2k</sub> building blocks before interfacial self-assembly. (b) Relative frequency distribution histogram of the diameter of synthesized AuNPs generated from statistics of more than 100 nanoparticles.



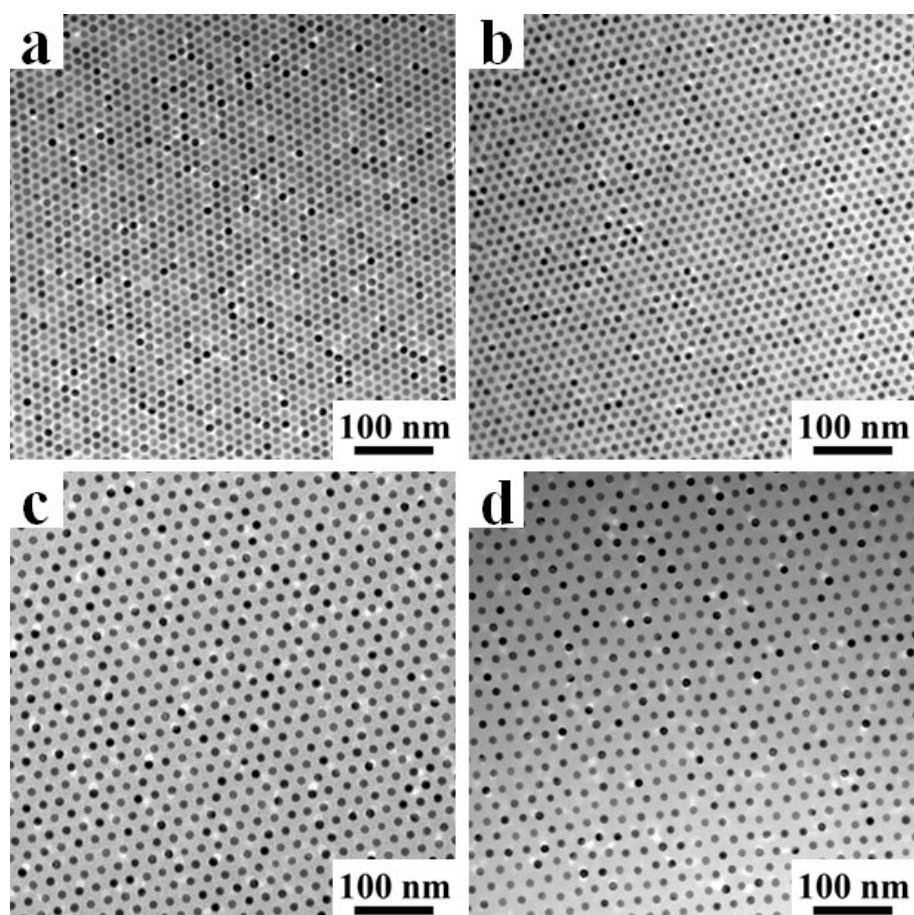
**Fig. S2.** (a-c) SEM and TEM images of the 3D freestanding multilayer AuNPs@PS<sub>2k</sub> superlattices under different magnifications. The inset in (b) is the selected area electron diffraction pattern of the superlattice. (d) STEM image of the multilayer superstructure.



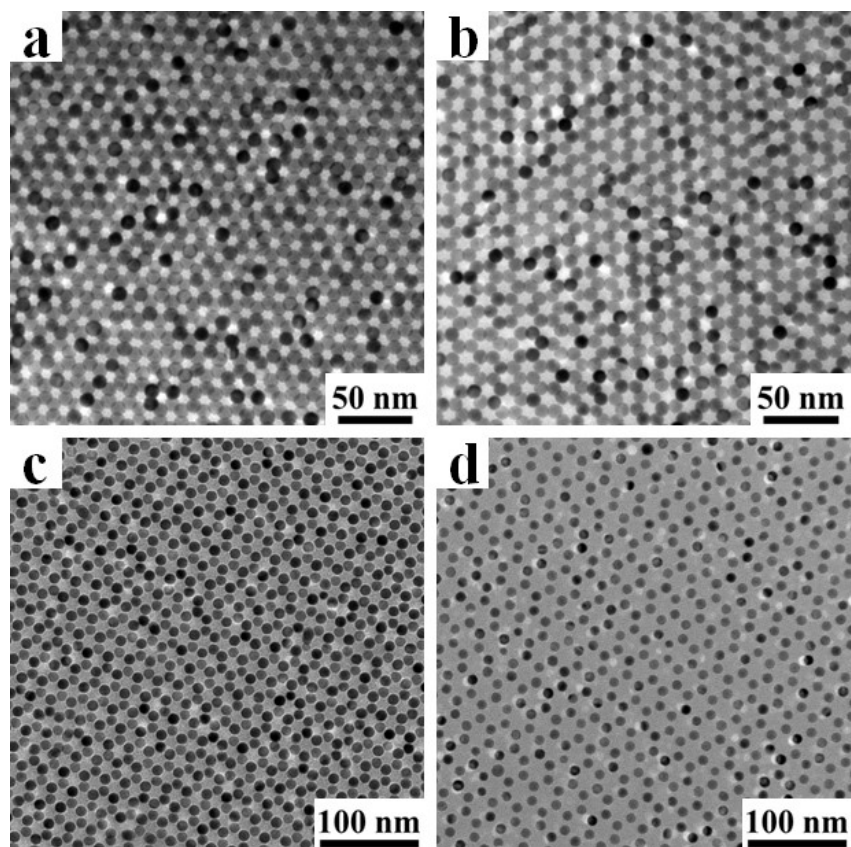
**Fig. S3.** (a) SEM and (b) TEM images showing the monolayer superlattice membranes self-assembled from AuNPs@PS<sub>2k</sub> building blocks at the DEG-air interface. (c) TEM image illustrating the highly-ordered arrangement of AuNPs in the superlattice membrane over a large scale. (d) and (e) are magnified SEM images of the surface and edge position of the superlattices. (f) STEM image of the AuNP superlattice.



**Fig. S4.** TEM and SEM images of the distribution and arrangement of AuNPs@PS<sub>2k</sub> building blocks at the liquid-air interface with varying concentrations. (a, b) 0.001 mg/mL; (c, d) 0.01 mg/mL; (e, f) 0.1 mg/mL; (g, h) 0.5 mg/mL.



**Fig. S5.** TEM images of the 2D monolayer superlattices assembled from varied AuNPs@PS building blocks with different  $M_n$  of PS ligands. (a) AuNPs@PS<sub>2k</sub>; (b) AuNPs@PS<sub>5k</sub>; (c) AuNPs@PS<sub>12k</sub>; (d) AuNPs@PS<sub>22k</sub>.



**Fig. S6.** TEM images of the 3D multilayer superlattices with tunable internal pattern assembled from varied AuNPs@PS building blocks with different  $M_n$  of PS ligands. (a) AuNPs@PS<sub>2k</sub>; (b) AuNPs@PS<sub>5k</sub>; (c) AuNPs@PS<sub>12k</sub>; (d) AuNPs@PS<sub>22k</sub>.