Supporting Information

Entropy-Driven Assembly of Nanoparticles within Emulsion-Evaporative Block Copolymer Particles: Crusted, Seeded, and Alternate-Layered Onions

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■ Supporting Figures and Table

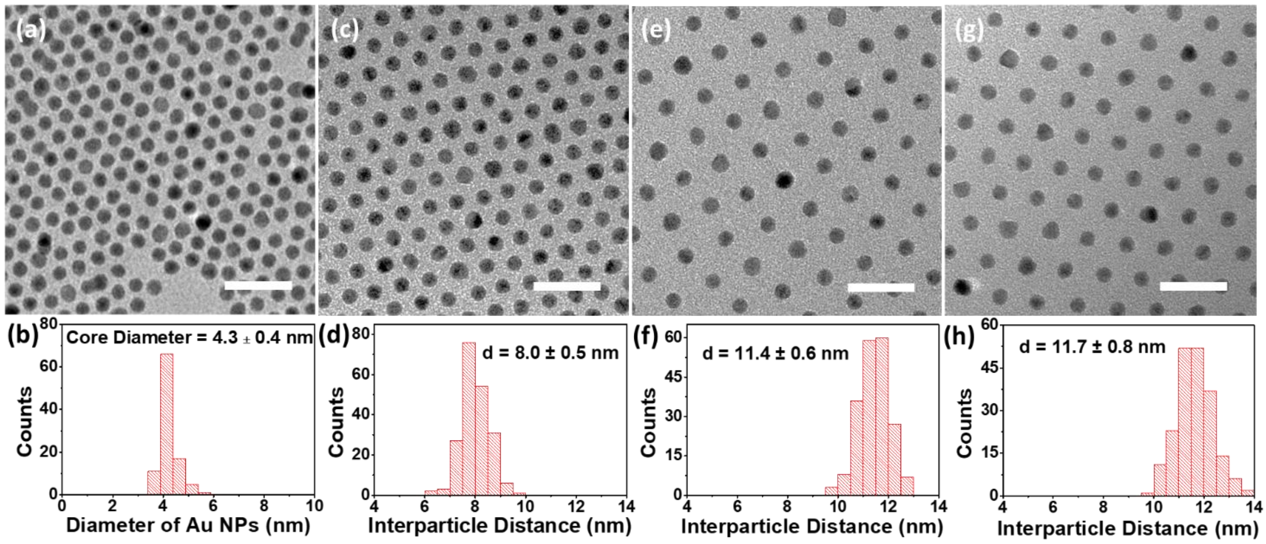


Figure S1. Characterization of Au@PS with different M_n of PS ligands. TEM images and histograms of (a, b) as-synthesized Au NPs, (c, d) 4Au@2kPS, (e, f) 4Au@4kPS, and (g, h) 4Au@6kPS. Scale bars are 20 nm. The average core diameter of the Au NPs was 4.3 ± 0.4 nm, and the interparticle distance (*d*) was 8.0 ± 0.5, 11.4 ± 0.6, and 11.7 ± 0.8 nm for 4Au@2kPS, 4Au@4kPS, and 4Au@6kPS, respectively.

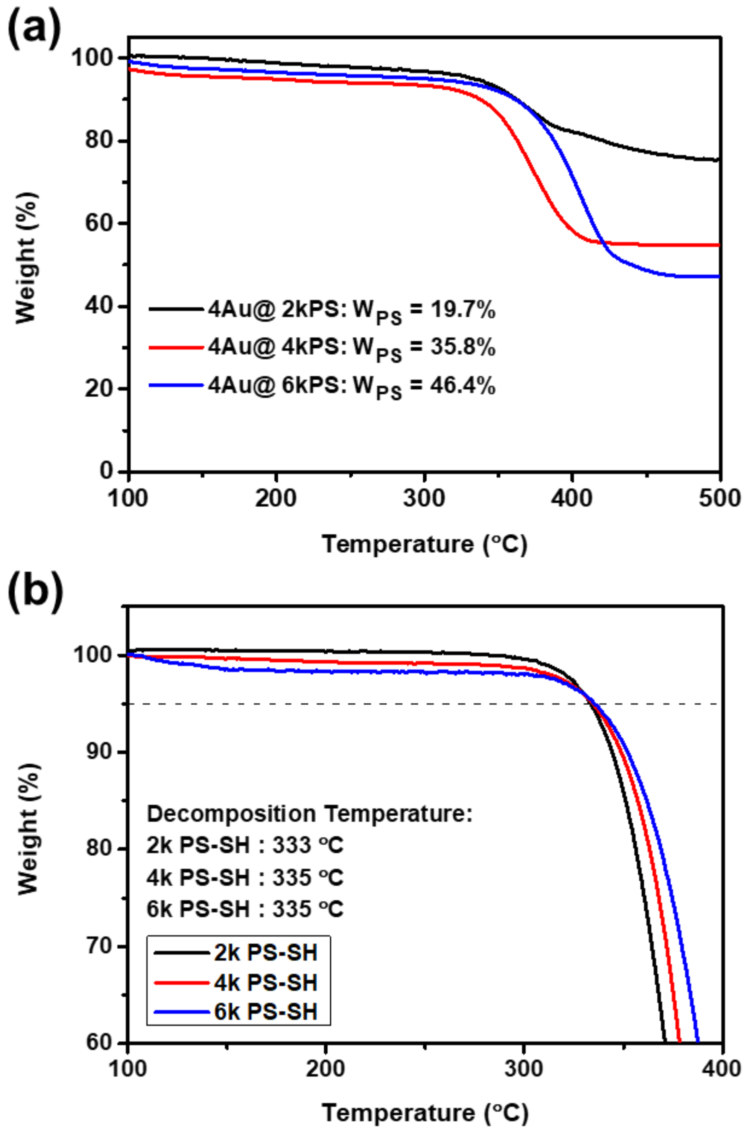


Figure S2. TGA analysis of (a) Au@PS and (b) only PS-SH ligands. The amount of PS-SH ligands in each sample was determined by calculating the weight loss from the thermal decomposition temperature of PS-SH (the temperature corresponding to 5 % weight loss in **Figure S2b**) to the temperature at which weight % reaches its minimum.

■ Calculation of Minimum Grafting Density Fully Covering the NP Surface.

The theoretical minimum value of grafting density for PS-SH ligands to effectively shield the gold surface from interacting with P4VP blocks can be calculated as[1]:

$$\Sigma_{\mathrm{min}} = \frac{1}{\pi}\left(\frac{R + R_{\mathrm{g}}}{R_{\mathrm{g}}R}\right)^2$$

where R is the radius of Au NP core, and the radius of gyration R_{g} = 1.15 nm for 2k PS-SH, R_{g} = 1.78 nm for 4k PS-SH, and R_{g} = 2.18 nm for 6k PS-SH.

Table S1. Detailed information of Au@PS used in this study.

PS-grafted Au NP	**Core Diameter (nm)**	**Ligand M_n (kg mol^{-1})**	**Overall Size d (nm)**	**d/L_{PS} (L_{PS}=10.2 ± 1.8 nm)**	**Grafting Density σ (chains nm^{-2})**
4Au@2kPS	4.3 ± 0.3	1.8	8.0 ± 0.5	0.78	1.14
4Au@4kPS	4.3 ± 0.3	4.3	11.4 ± 0.6	1.12	1.08
4Au@6kPS	4.3 ± 0.3	6.4	11.7 ± 0.8	1.15	1.13

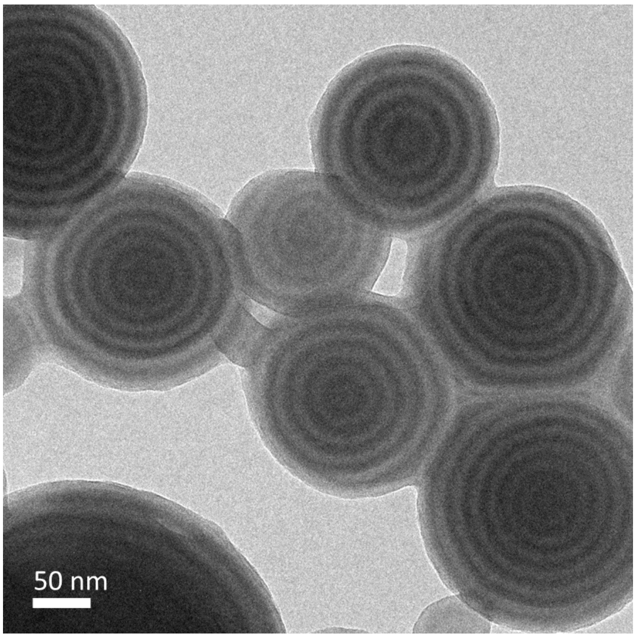


Figure S3. TEM image of pristine PS-*b*-P4VP particles.

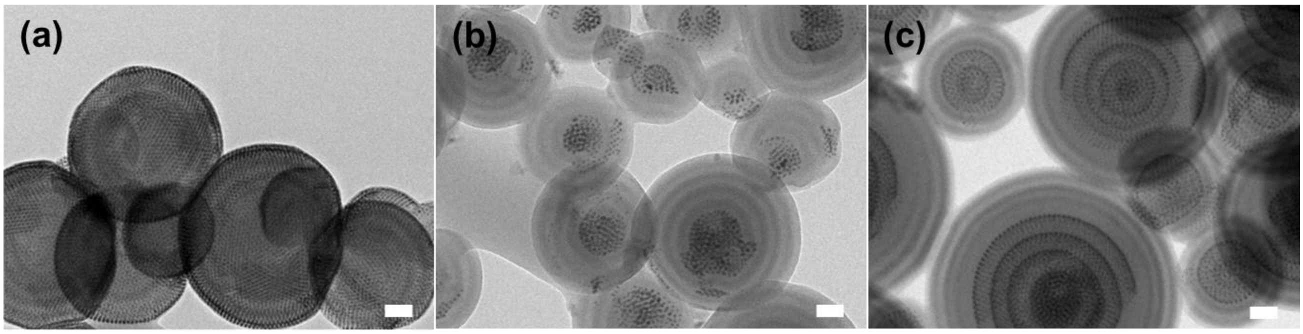


Figure S4. Low-magnification TEM images of PS-*b*-P4VP/Au@PS hybrid particles. TEM images of PS-*b*-P4VP particles containing (a) 4Au@2kPS, (b) 4Au@4kPS, and (c) 4Au@6kPS. Scale bars are 50 nm.

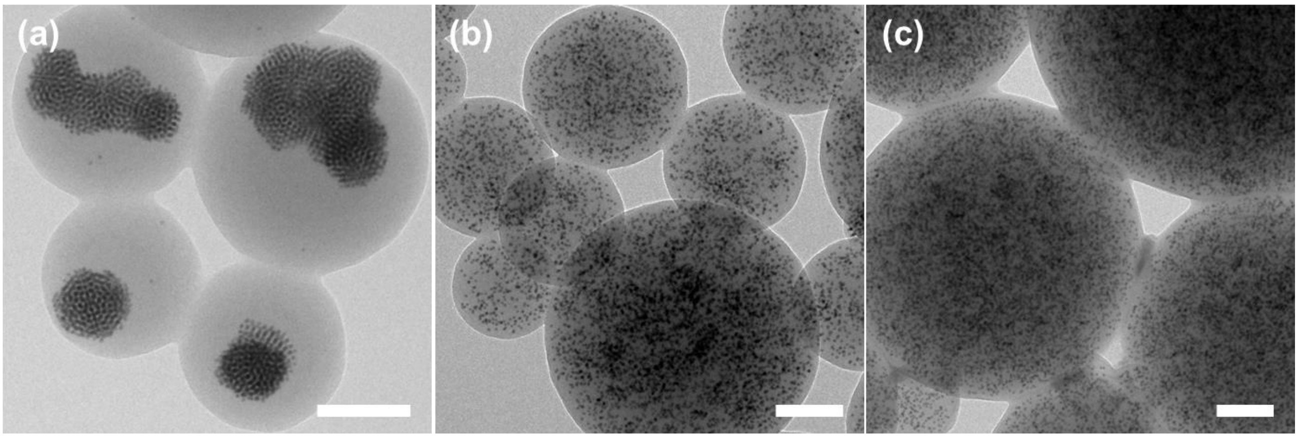


Figure S5. Characterization of Au@PS within a homopolymer PS (hPS) matrix. TEM images of (a) 9khPS/4Au@2kPS, (b) 9khPS/4Au@4kPS, and (c) 9khPS/4Au@6kPS hybrid particles. Scale bars are 100 nm.

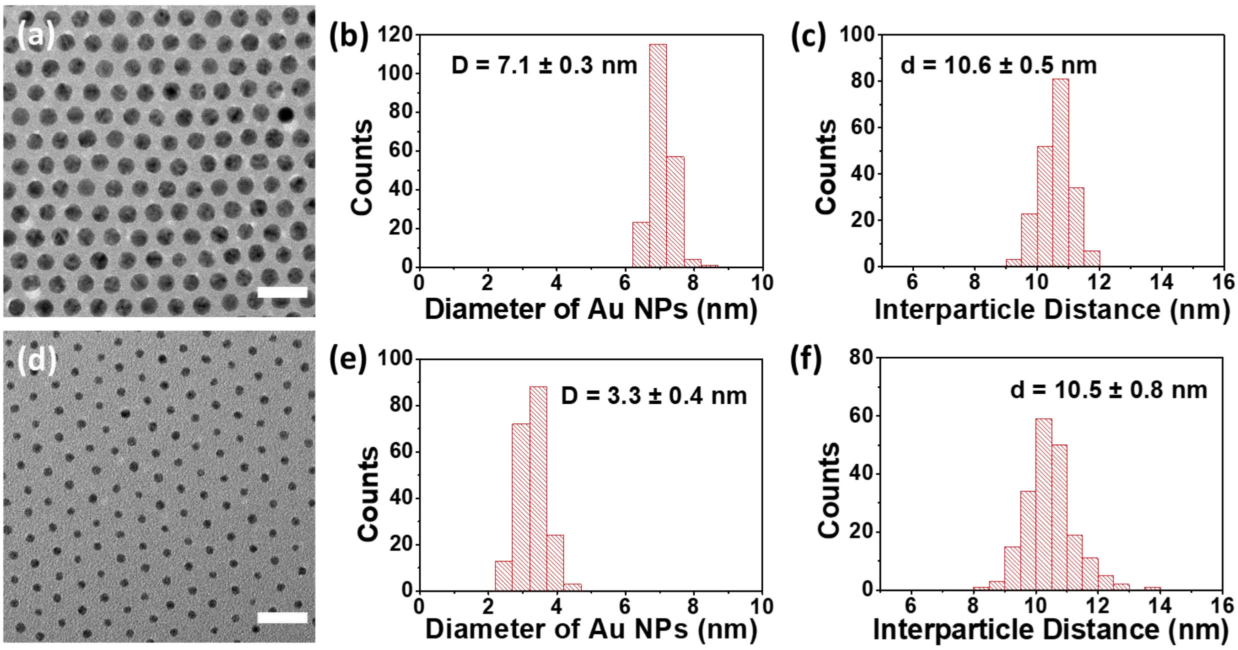


Figure S6. Characterization of Au@PS with different core sizes and M_n of ligands. TEM images and histograms of (a, b, and c) 7Au@2kPS, and (d, e, and f) 3Au@6kPS. Scale bars are 20 nm.

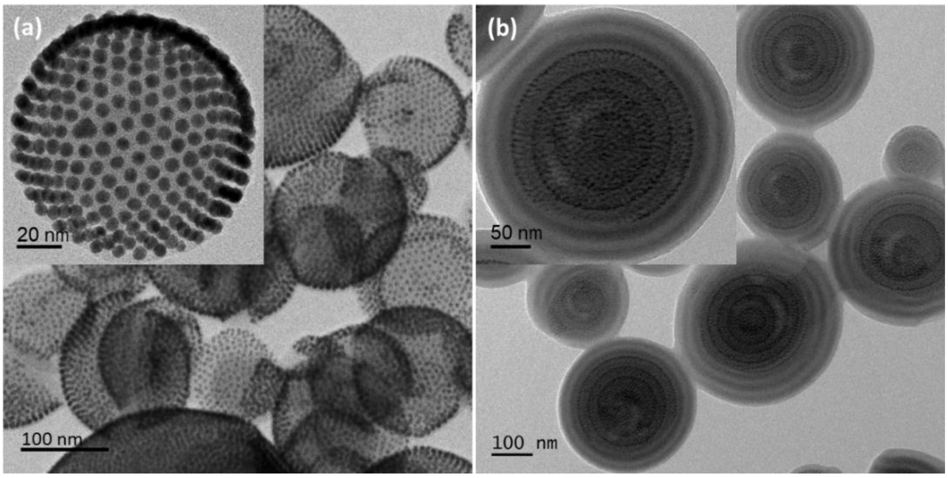
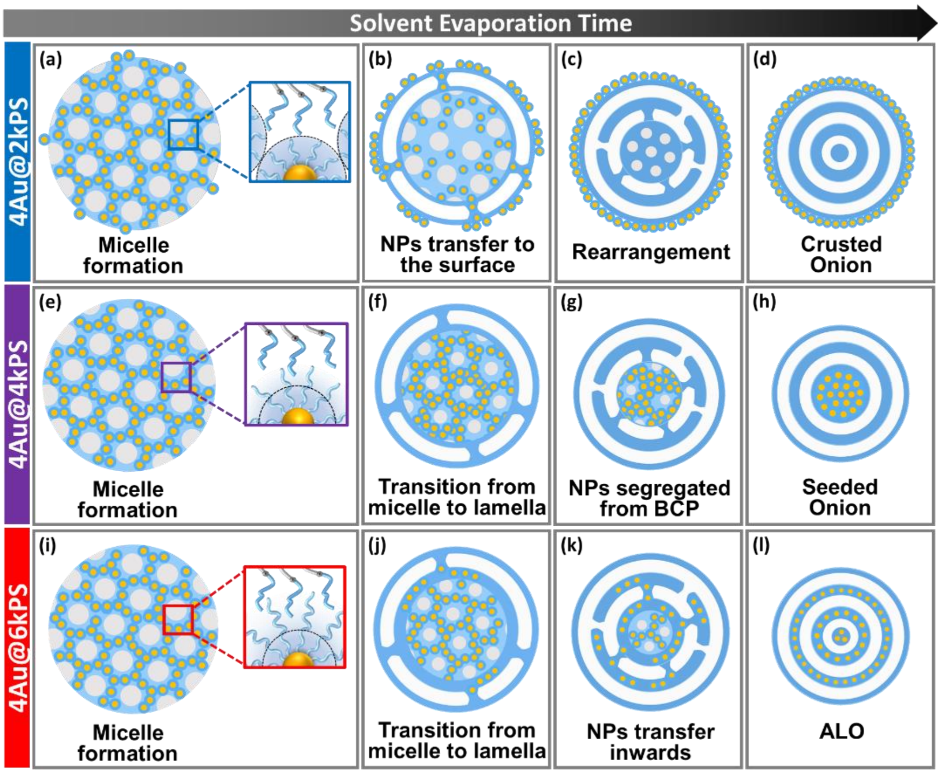


Figure S7. Effect of *P/N* values on Au@PS assembly within BCP particles. TEM images of PS-*b*-P4VP particles containing (a) 7Au@2kPS (P/N = 5.4, d/L_{PS} = 1.04) and (b) 3Au@6kPS (P/N = 1.5, d/L_{PS} = 1.03).



Scheme S1. Schematic illustration of (a-d) PS-*b*-P4VP/4Au@2kPS, (e-h) PS-*b*-P4VP/4Au@4kPS, and (i-l) PS-*b*-P4VP/4Au@6kPS particle formation process.

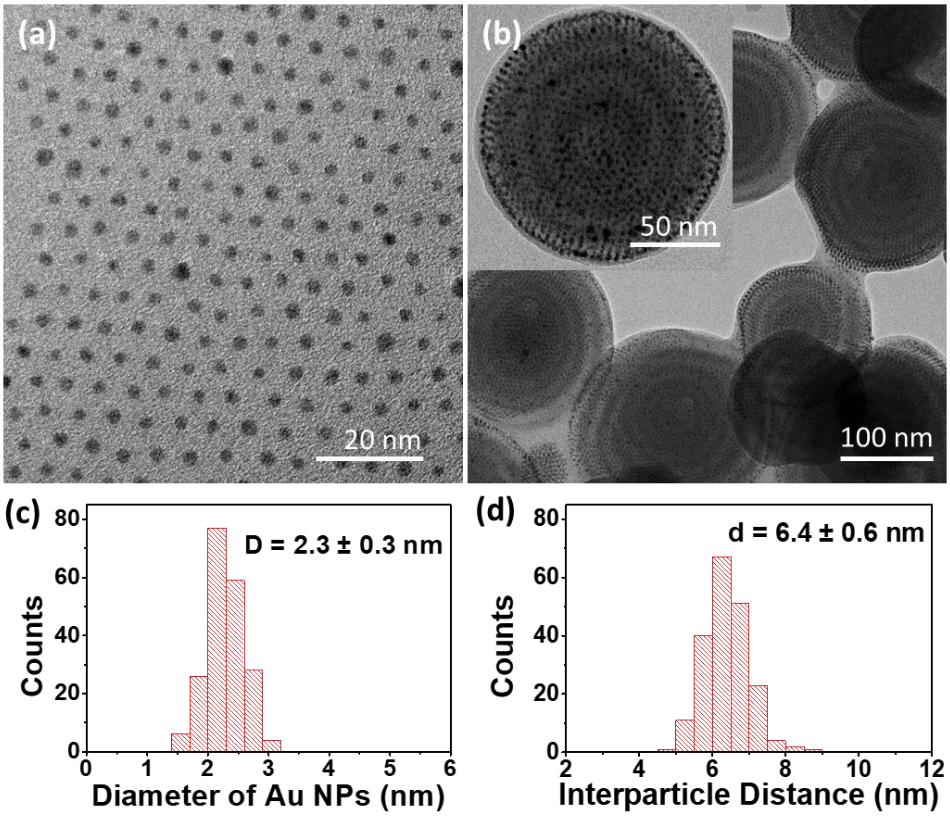


Figure S8. Characterization of 2Au@2kPS and the corresponding assembly structure within BCP particles. (a) TEM images and (c, d) histograms of 2Au@2kPS, and (b) TEM image of PS-*b*-P4VP particles containing 2Au@2kPS.

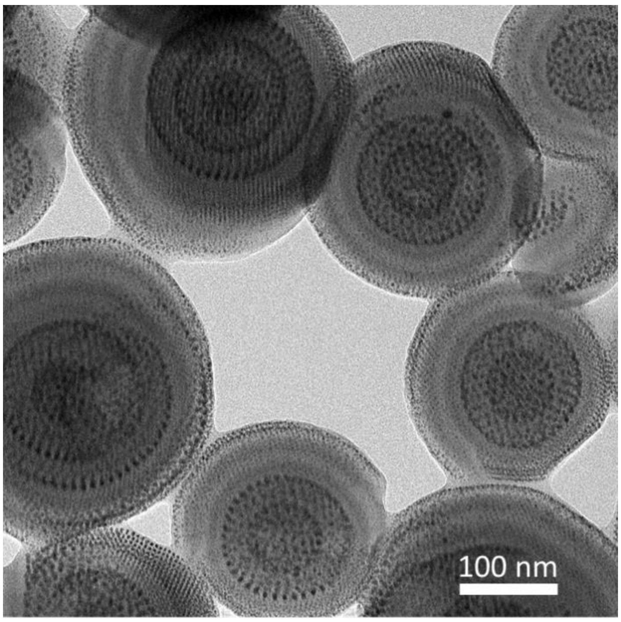


Figure S9. Low-magnification TEM image of PS-*b*-P4VP/Au@PS hybrid particles containing 2Au@2kPS and 4Au@6kPS.

References

(1) Yun, H.; Yu, J. W.; Lee, Y. J.; Kim, J.-S.; Park, C. H.; Nam, C.; Han, J.; Heo, T.-Y.; Choi, S.-H.; Lee, D. C.; Lee, W. B.; Stein, G. E.; Kim, B. J. Symmetry Transitions of Polymer-Grafted Nanoparticles: Grafting Density Effect. *Chem. Mater.* **2019**, *31*, 5264–5273.