

*Electronic supplementary information for:*

## Ultralong Gold Nanoparticles/Block Copolymers Hybrid Cylindrical Micelles: a Strategy Combining Surface Templated Self-Assembly and Rayleigh Instability

Jiangping Xu,<sup>ab</sup> Yutian Zhu,<sup>\*a</sup> Jintao Zhu,<sup>c</sup> Wei Jiang<sup>\*a</sup>

*<sup>a</sup>State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China. Email: ytzhu@ciac.jl.cn (Y. Z.); wjiang@ciac.jl.cn (W. J.); Fax: +86 431 85262126; Tel: +86 431 85262151*

*<sup>b</sup>University of Chinese Academy of Sciences, Beijing 100039, P. R. China*

*<sup>c</sup>Key Laboratory of Large-Format Battery Materials and System, Ministry of Education, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, P. R. China*

## Experimental Section

*Materials:* Hydrogen tetrachloroaurate trihydrate ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ , purity: 99.99%) was purchased from Alfa Aesar. Oleylamine (purity: 80-90%) and Triisopropylsilane (purity: 99%) were obtained from Aladdin. Amphiphilic diblock copolymer  $\text{PS}_{144}\text{-}b\text{-PAA}_{22}$  ( $M_n = 15000 \text{ g mol}^{-1}$  for PS block and  $M_n = 1600 \text{ g mol}^{-1}$  for PAA block,  $M_w/M_n = 1.10$ ) was purchased from Polymer Source. Other chemicals were supplied by Beijing Chemical Factory.

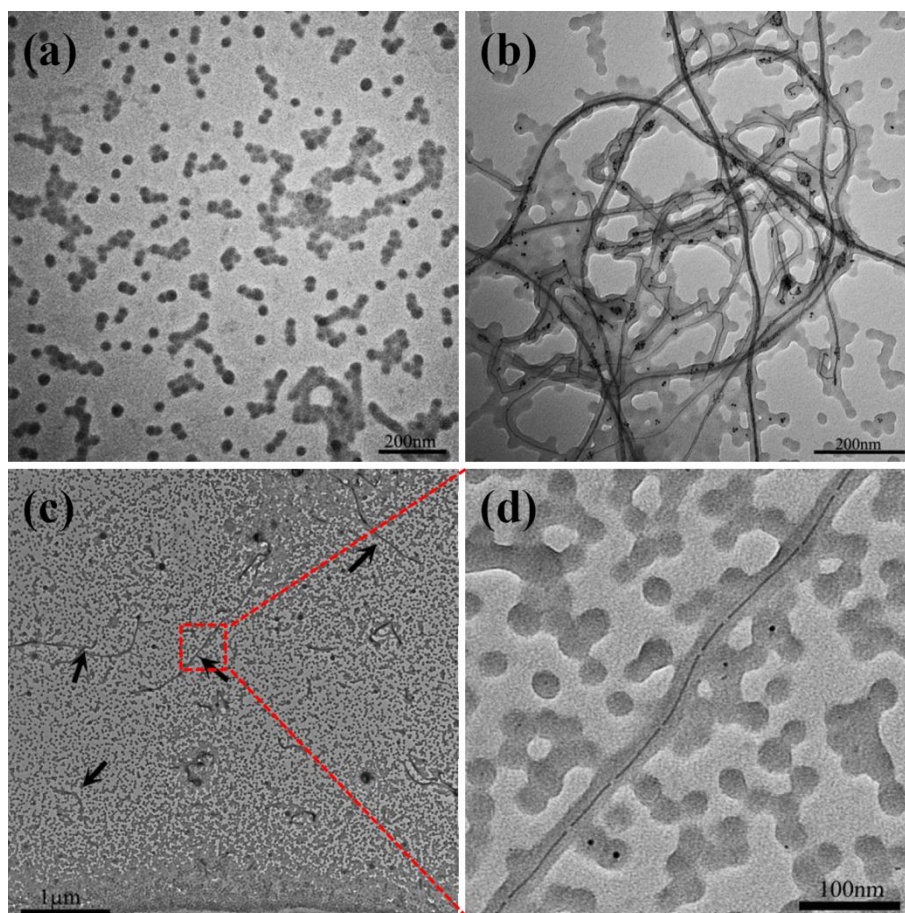
*Synthesis of ultrathin gold nanowires (AuNWs):* AuNWs were synthesized following a previously reported method.<sup>1</sup> The final ultrathin AuNWs with diameter of 1.8 nm were dispersed in THF.

*Preparation of hybrid cylindrical micelles:*  $\text{PS}_{144}\text{-}b\text{-PAA}_{22}$  (2 mg) was dissolved in DMF (500  $\mu\text{L}$ ). THF solution of as-synthesized AuNWs (100  $\mu\text{L}$ ) in different concentration was added to the polymer solution. Then water (80  $\mu\text{L}$ ) was dropwise added to the mixture. The mixture was stirred at 500 rpm for 7 days (or for varying times for the kinetic studies) at room temperature. After quenching in water, the hybrid micellar solution was repeatedly centrifuged for 3 times (10000 rpm, 10 min) to remove the empty micelles and the organic solvents. The micelles were redispersed in water. The AuNWs-loaded hybrid cylindrical micelles obtained after being stirred for 1 day were used for heating process. The micellar solution was put in a glass tube and then heated at 60 °C for 120 min (or for varying times for the kinetic studies).

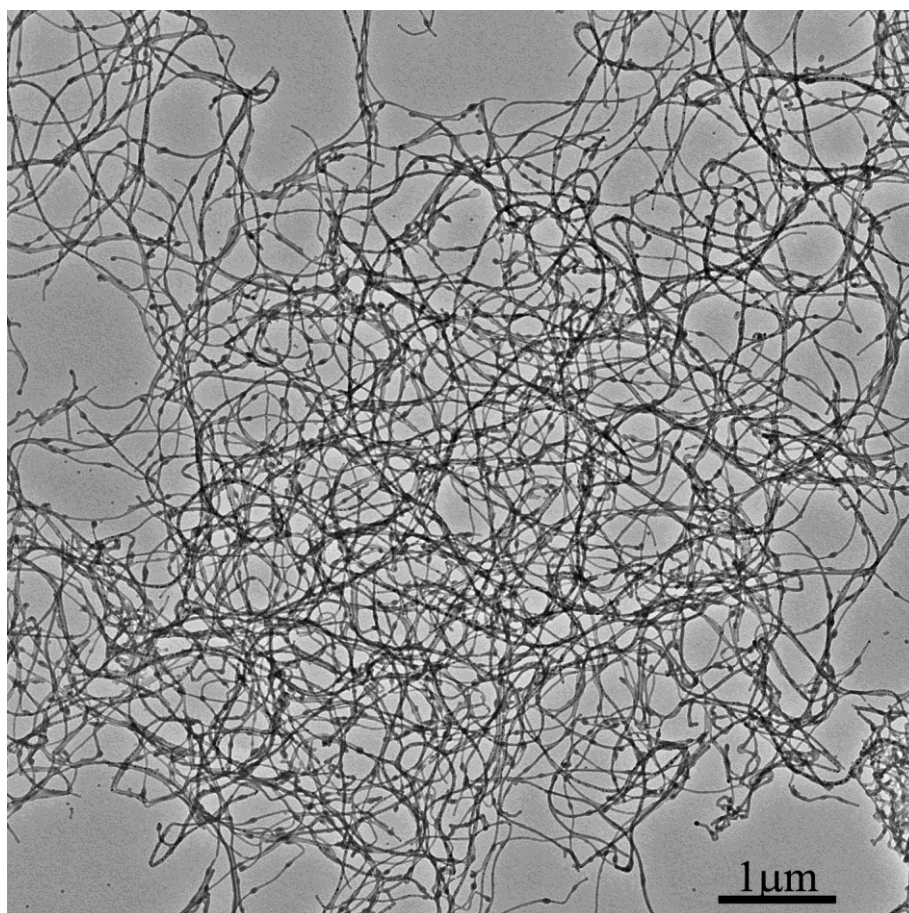
*Characterization:* The morphology of the micelles was examined by TEM (JEOL JEM-1011 and JEOL JEM-2100F) and SEM (FESEM, XL 30 ESEM FEG, FEI Company). UV-vis absorption spectra were recorded by using SP-756PC spectrophotometer (Shanghai Spectrum Instruments Co.,

Ltd). The structure parameters of the hybrid cylindrical micelles were obtained through measuring the TEM images by iTEM 5.1 (Build 1276), Olympus Soft Imaging Solutions GmbH.

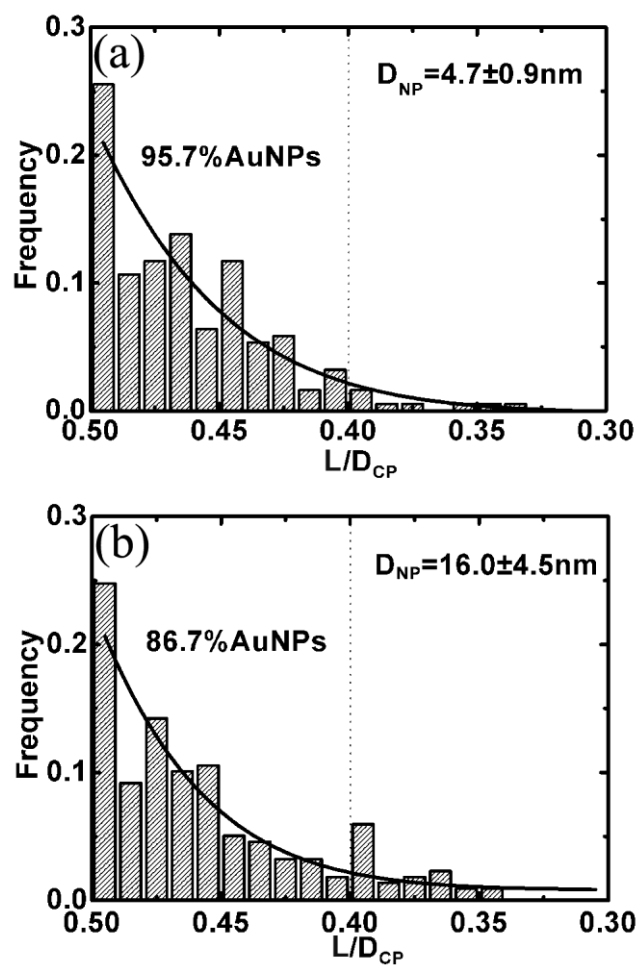
### Supporting Figures:



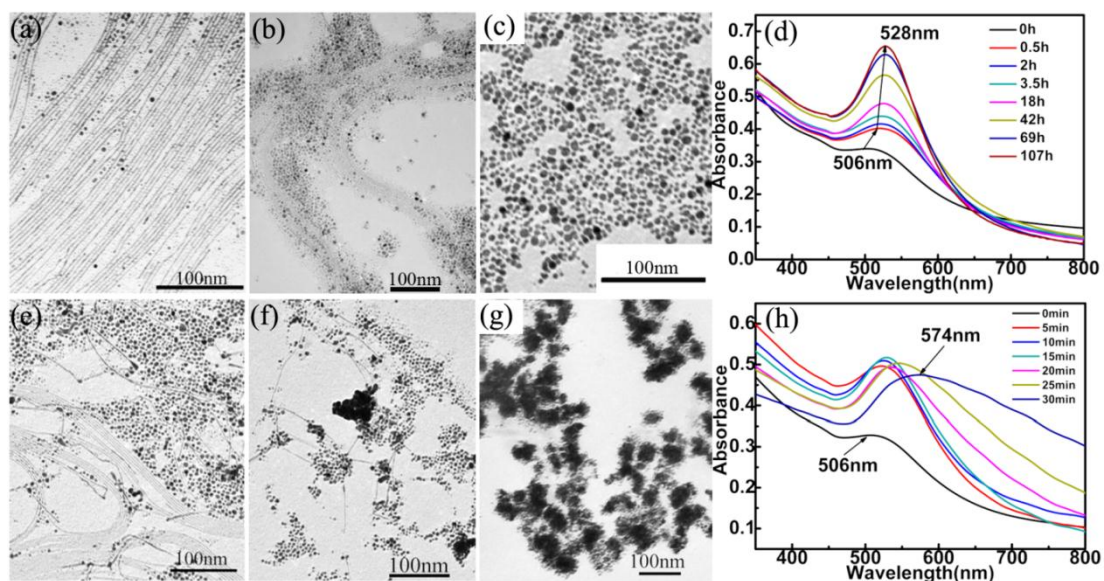
**Fig. S1** Bright field TEM images of (a) spherical micelles from self-assembly of neat  $\text{PS}_{144}\text{-}b\text{-PAA}_{22}$  in DMF/THF/ $\text{H}_2\text{O}$  (5:1:0.8, v/v/v) ternary mixed solvent. (b) Mixture hybrid cylindrical micelles with encapsulated AuNWs ( $0.28 \text{ mg mL}^{-1}$ ) and empty spherical micelles. The spherical micelles can be removed by repeated centrifugation. (c) A very low AuNWs concentration ( $0.08 \text{ mg mL}^{-1}$ ) leads to inefficient encapsulation. There are more empty spherical micelles and less hybrid cylinders (marked by black arrows) with less than 3 AuNWs in the core. The length of the hybrid cylinder is  $\sim 2 \mu\text{m}$ , which is similar to the length of AuNW. (d) Magnification of the area in red square of (c). A single AuNW is encapsulated in the cylinder core. Fragmentation of the AuNW can be clearly seen.



**Fig. S2** Low-magnification bright field TEM image of large area hybrid cylindrical micelles incorporated with AuNPs. The lengths are in the range of ~1-20 μm.



**Fig. S3** The radial distribution of AuNPs in the core of hybrid cylindrical micelles. The central localization extent of (a) smaller AuNPs ( $D_{NP} = 4.7 \pm 0.9 \text{ nm}$ ) is higher than that of (b) larger AuNPs ( $D_{NP} = 16.0 \pm 4.5 \text{ nm}$ ), i.e. 95.7% for the former and 86.7% for the later are localized in the central 4 vol % portion of the cylindrical micelles.



**Fig. S4** The instability of AuNWs in THF at room temperature (a-d) and 50 °C (e-h). At room temperature: (a) 0.5 h, short AuNWs and AuNPs; (b) 18 h, a large portion of AuNPs; (c) 107 h, AuNPs with diameters in the range of ~4-10 nm; (d) UV-vis spectra show the absorbance increases as the time extends, which means the concentration of AuNPs increases due to the fragmentation of AuNWs to AuNPs. A red shift from 506 nm to 528 nm indicates that the increase of the diameter of AuNPs. The transformation of AuNWs to AuNPs at room temperature is slow. At 50 °C: (e) 5 min, a large portion of AuNPs with diameters of ~5 nm; (f) 15 min, AuNPs and AuNP clusters; (g) 30 min, AuNP clusters and large AuNPs with diameters in the range of ~30-100 nm; (h) UV-vis spectra show a large red shift as the time extends, which indicates the apparent change of the diameter of the AuNPs. The morphological evolution at 50 °C is very rapid.

## References

1. H. J. Feng, Y. M. Yang, Y. M. You, G. P. Li, J. Guo, T. Yu, Z. X. Shen, T. Wu and B. G. Xing, *Chem. Commun.*, 2009, **15**, 1984-1986.