-Supporting Information-

One-step synthesis of composite vesicles: Direct polymerization and in situ over-oxidation of thiophene

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Experimental Section

Materials

Thiophene (99%, Alfa Aesar) was distilled before use and stored at 4 °C. Hydrogen tetrachloroaurate(III) (99.9%, Au 49% on metals basis, Alfa Aesar), sodium citrate tribasic dihydrate (99.0%, Sigma), SDS (99%, Alfa Aesar), ferric chloride (98%, Alfa Aesar) and aqueous H_2O_2 solution (35%, w/w, Alfa Aesar) were used as received. Copper specimen grids (200 mesh) with formvar/carbon support film (refjferred to as TEM grids in the text) were purchased from Beijing XXBR Technology Co. AuNPs (18 - 80 nm)[1] and gold nanorods (AuNRs)[2] were prepared following literature procedures. AgNPs (50 nm) were synthesized by using 3-4 nm Au seeds following literature procedures.[3] All solutions were prepared using ultrapure water (resistance > 18 MΩ cm^{-1}).

Fabrication of Au@Vesicle NPs

As synthesized citrate-stabilized AuNP solution (~40 nm, 0.75 mL) was concentrated to a total of 10 μL by centrifugation at 6000 rpm (2900 *g*) for 8 min. After removal of supernatant, the isolated AuNPs were added to a mixture of thiophene (0.075 mmol, 6.3 mg) and SDS (0 to 3.5 mM, 1.5 mL). Then the solution was vortexed for 10 s to make thiophene disperse in the aqueous solution as small droplets followed by addition of H_2O_2 (0.09 mmol, 35% aqueous solution, 8.75 mg) and $FeCl_3$ solution (1 mM, 13 μL). The final solution contained thiophene (50 mM), AuNPs (estimated 0.062 nM in number of particles),[4] SDS (0 to 3.5 mM, typically 2.5 mM), H_2O_2 (60 mM), $FeCl_3$ (9 μM), and H_2O (1.5 mL). After vortexing for 10 s, the reaction mixture was incubated at 70 ^{o}C for 12 h to ensure complete reaction. To isolate Au@vesicle NPs, the reaction mixture was centrifuged at 6000 rpm for 8 min, the supernatant was removed and the concentrated NP solution was collected at the bottom of the Eppendorf tubes.

Au@vesicle NPs with thinner walls of about 10 nm were prepared by use of low concentration of thiophene (15 mM) and the corresponding decreased concentration of H_2O_2 (18 mM) and $FeCl_3$ (2.7 μM) under otherwise identical conditions.

Further growth cycles were carried out using the isolated Au@vesicle NPs instead of citrate-stabilized AuNPs, following the mixing sequence above, the final solution contained thiophene (50 mM), Au@vesicle NPs, SDS (2.5 mM), H_2O_2 (60 mM), $FeCl_3$ (9 μM), and H_2O (1.5 mL).

Citrate-stabilized AuNPs of 18 nm and 80 nm were also applied to fabricate polythiophene-based composite vesicles using the above method.

As-synthesized AuNRs (0.75 mL) were purified by first centrifuging at 6000 rpm for 10 min and then dispersing the concentrated AuNRs in water. This purification was repeated once more to further remove the excess CTAB. After these purification steps, the AuNRs were used to fabricate polythiophene-based composite vesicles using the above method. AgNPs were also incorporated in the polymer vesicles using this method.

Fabrication of Au@PTh Core-Shell NPs

Au@PTh core-shell NPs were obtained at high concentration of SDS solution (5 to 7.5 mM) under otherwise identical conditions with the above fabrication of Au@vesicle NPs. The final reaction mixture contained thiophene (50 mM), AuNPs (estimated 0.062 nM), SDS (5 to 7.5 mM, typically 5 mM), H_2O_2 (60 mM), $FeCl_3$ (9 μM), and H_2O (1.5 mL).

Control Experiments Investigating the Liquid in Vesicle Cavities

The as-prepared Au@vesicle NPs were isolated, and incubated in THF for 12 h to dissolve the hypothesized thiophene monomer or oligomers in the vesicle cavities. The Au@vesicle NPs were then isolated and redispersed in aqueous SDS solution. Further polymer growth cycles were carried out using the isolated Au@vesicle NPs instead of citrate-stabilized AuNPs, following the mixing sequence above. The final reaction mixture contained thiophene (50 mM), the isolated Au@vesicle NPs, SDS (2.5 mM), H_2O_2 (60 mM), $FeCl_3$ (9 μM), and H_2O (1.5 mL).

Over-Oxidation of Au@Vesicle NPs by H_2O_2

The as-prepared Au@vesicle NPs were isolated, and then incubated in aqueous H_2O_2 solution (1%, large excess) at 70 ^{o}C for the over-oxidation. Control experiments showed that the presence/absence of catalytic amount of $FeCl_3$ in this step did not make a difference. After 3 h, the color of the solution changed from dark brown to light red. One half of the solution was extracted, and the over-oxidized Au@vesicle NPs were isolated and used for an additional growth cycle. Further polymer growth cycle was carried out using the isolated Au@vesicle NPs instead of citrate-stabilized AuNPs, following the mixing sequence above. The final reaction mixture contained thiophene (50 mM), the isolated Au@vesicle NPs, SDS (2.5 mM), H_2O_2 (60 mM), $FeCl_3$ (9 μM), and H_2O (1.5 mL). After reaction, the color of the solution changed from light red to dark brown, indicating the formation of new polythiophene. The other half of the over-oxidized Au@vesicle NPs was incubated at 70 ^oC for further over-oxidation. After 12 h, the solution became colorless, suggesting the complete loss of conjugated polymer by over-oxidation and the aggregation of AuNPs.

Characterization

Transmission electron microscopy (TEM) images were collected on a JEM-1400 (JEOL) operated at 100–120 kV. Ultraviolet-visible (UV-vis) spectra were collected on a Cary 100 spectrophotometer. Fourier transform infrared (FT-IR) spectra were collected on a FT-IR spectrometer (Perkin-Elmer System 2000) using KBr pellets (32 scans), and the spectra were recorded with a resolution of 4 cm^{-1}. Atomic force microscopy (AFM) images were collected on a commercial instrument (Digital Instrument, Nanoscope III, and Dimension 3000TM) in tapping mode at room temperature in air. X-ray photoemission spectroscopy (XPS) analysis was performed using a Kratos-Axis spectrometer with monochromatic Al Kα (1486.71 eV) X-ray radiation (15 kV and 10 mA) and hemispherical electron energy analyzer.

Preparation of TEM Samples

$(NH_4)_6Mo_7O_{24}$ was used as the negative stain in all TEM images reported in this paper, so that empty polymer nanoparticles and polymer shells appear white against the stained background. TEM grids were treated with oxygen plasma in a Harrick plasma cleaner/sterilizer for 45 s to improve the surface hydrophilicity. A sample solution was carefully mixed with stain solution on the surface of a plastic Petri dish ([$(NH_4)_6Mo_7O_{24}$] = 4 mM); the hydrophilic face of the TEM grid was then placed in contact with the sample solution. A filter paper was used to wick off the excess solution on the TEM grid, which was then dried in air for 5 min.

References:

(1) G. Frens, *Nat. Phys. Sci.* 1973, **241**, 20.

(2) B. Nikoobakht and M. A. El-Sayed, *Chem. Mater.* 2003, **15**, 1957.

(3) a) G. Chen, Y. Wang, M. X. Yang, J. Xu, S. J. Goh, M. Pan and H. Y. Chen, *J. Am. Chem. Soc.* 2010, **132**, 3644; b) N. R. Jana, L. Gearheart and C. J. Murphy, *Langmuir* 2001, **17**, 6782; c) J. Zhang, Y. Fu, M. H. Chowdhury and J. R. Lakowicz, *J. Phys. Chem. C* 2008, **112**, 18.

(4) H. Wang, J. Xu, J. Wang, T. Chen, Y. Wang, Y. W. Tan, H. Su, K. L. Chan and H. Cheng, *Angew. Chem., Int. Ed.* 2010, **49**, 8426.

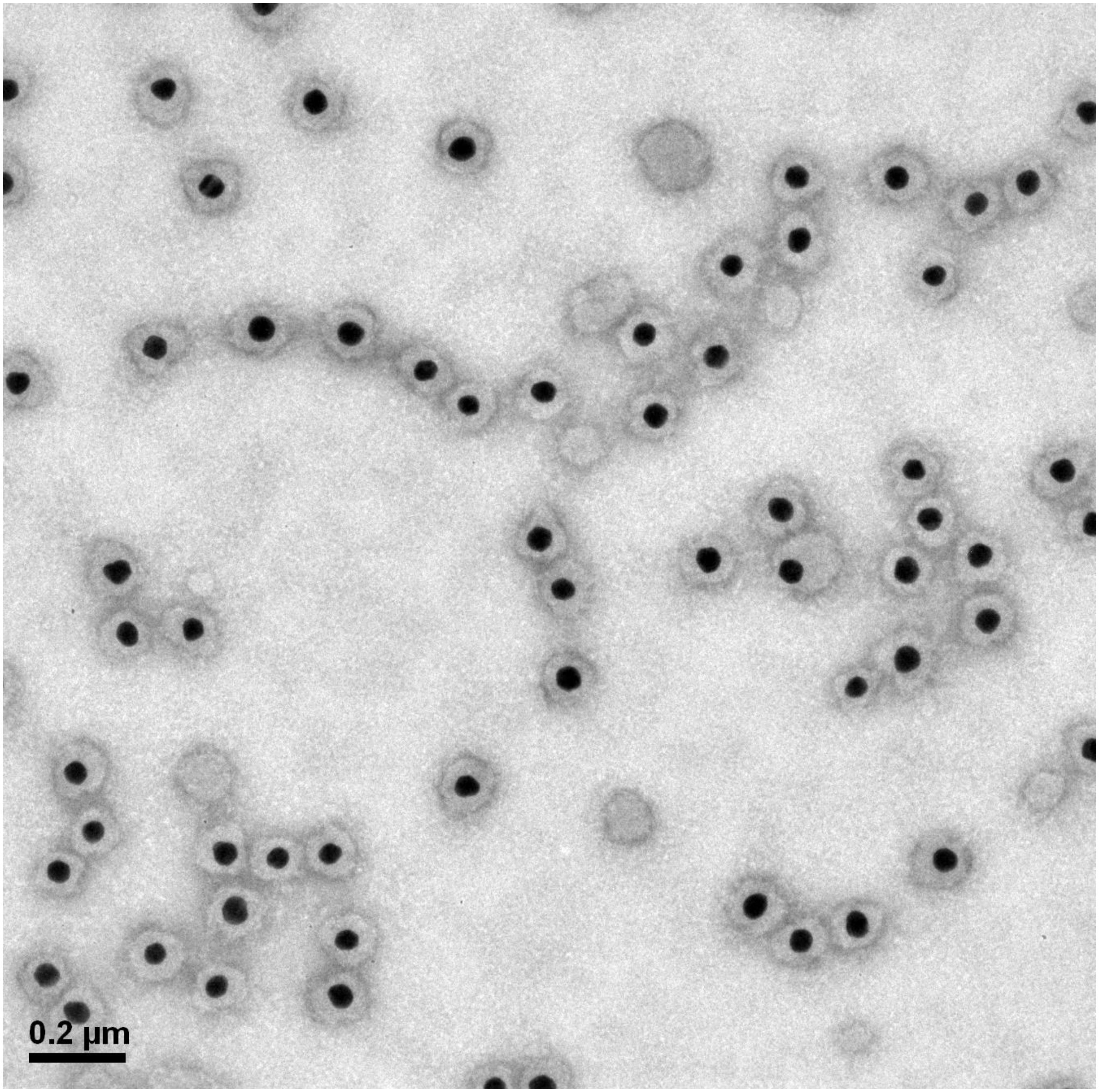

Figure S1. TEM image of the Au@PTh core-shell NPs, d_{Au} = 40 nm, [SDS] = 5 mM, t = 12 h (large-area view of Figure 1b).

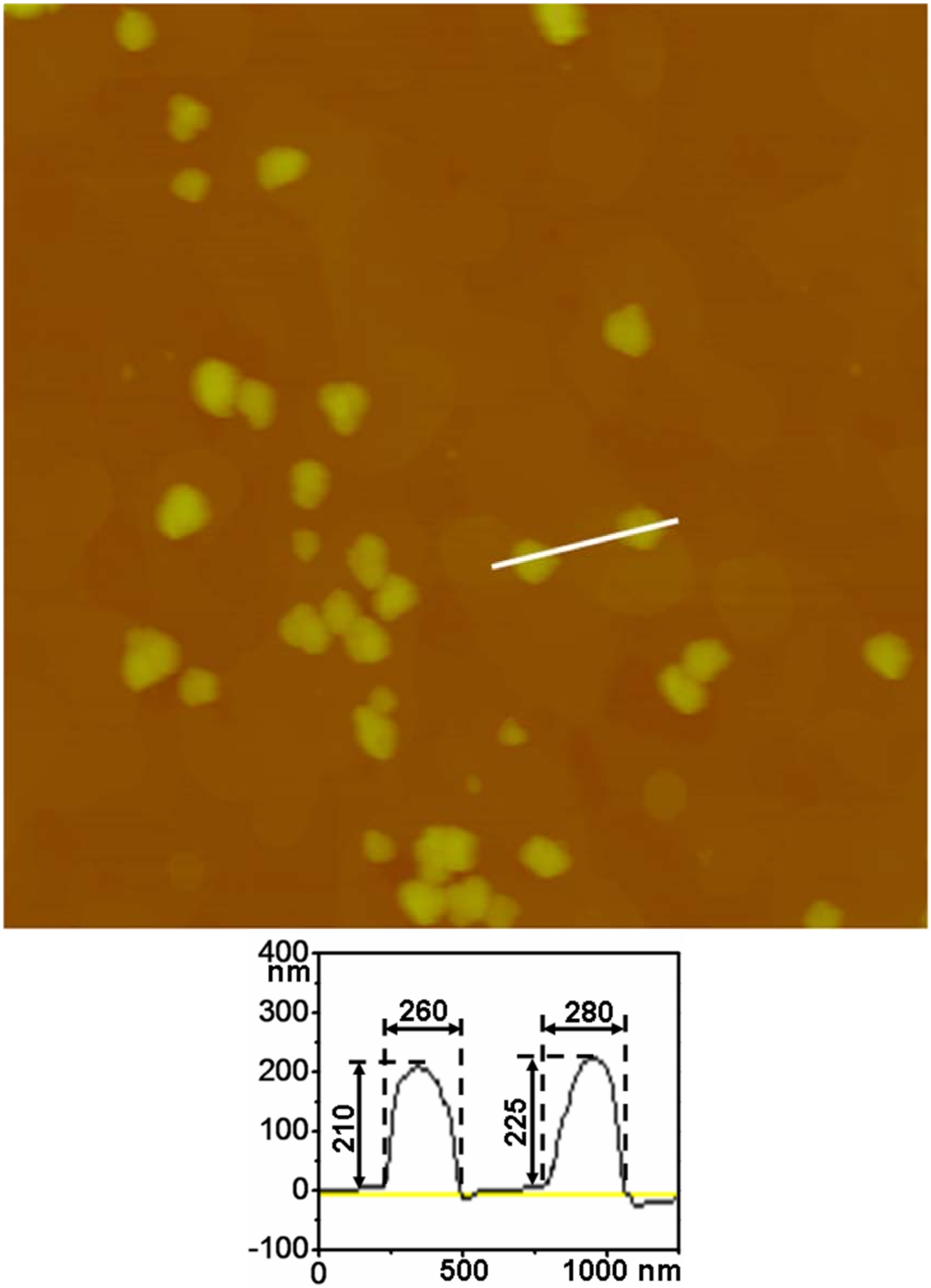

Figure S2. AFM image of Au@vesicle NPs, d_{Au} = 40 nm, [SDS] = 2.5 mM, t = 12 h, and the cross-sectional height profile along the white line is shown at the bottom.

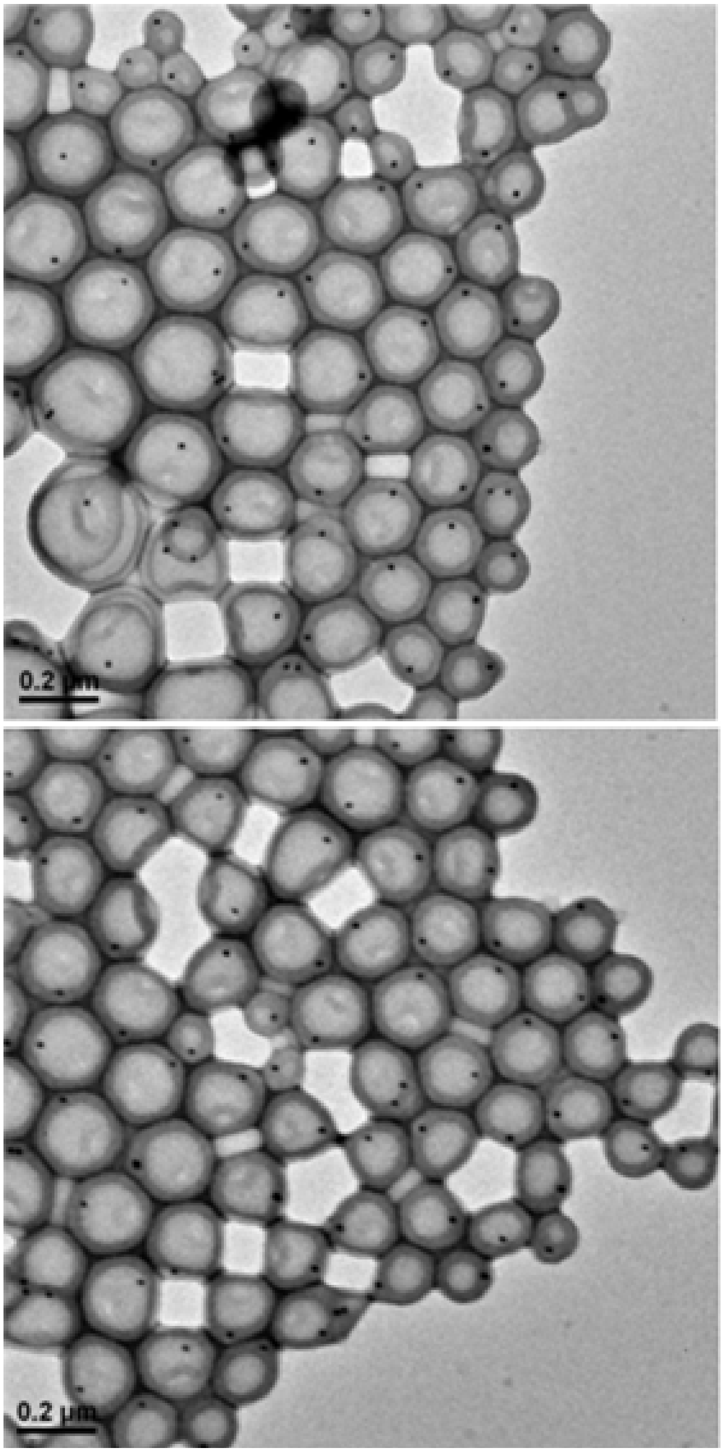

Figure S3. TEM images of the Au@vesicle NPs, d_{Au} = 18 nm, [SDS] = 1 mM, (large-area view of Figure 3a). Most (98% out of 132 nanocomposites) of the vesicles have only one cavity, though some of the AuNPs were aggregated.

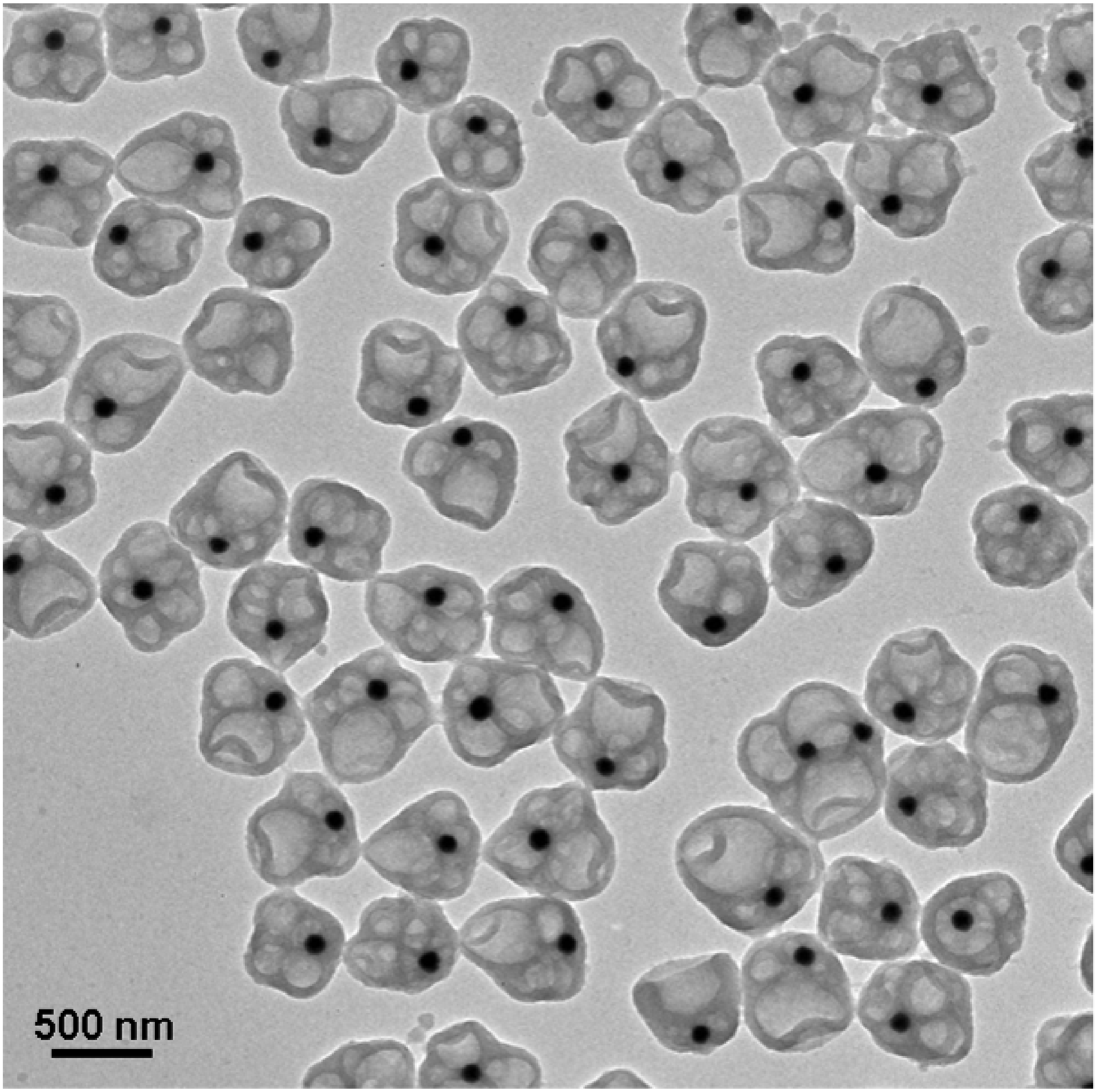

Figure S4. TEM image of the Au@vesicle NPs, $d_{\mathrm{Au}} = 80$ nm, [SDS] = 2.5 mM, (large-area view of Figure 3b).

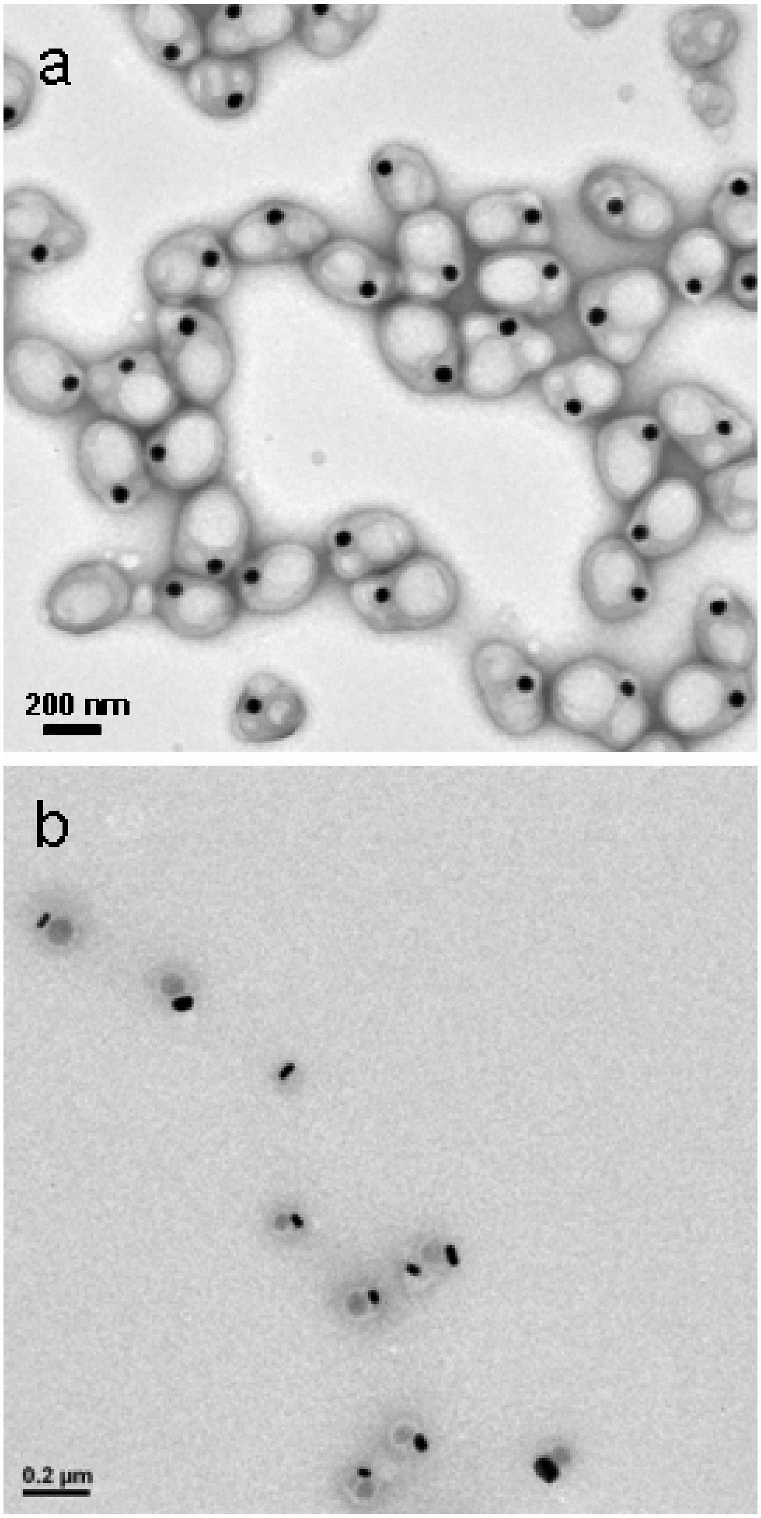

Figure S5. TEM images of (a) Ag@vesicle NPs, d_{Ag} = 50 nm, [SDS] = 2.5 mM, t = 12 h, and (b) AuNR@vesicle NPs, d_{AuNR} = 62 nm, l_{AuNR} = 30 nm, [SDS] = 2.5 mM, t = 12 h.

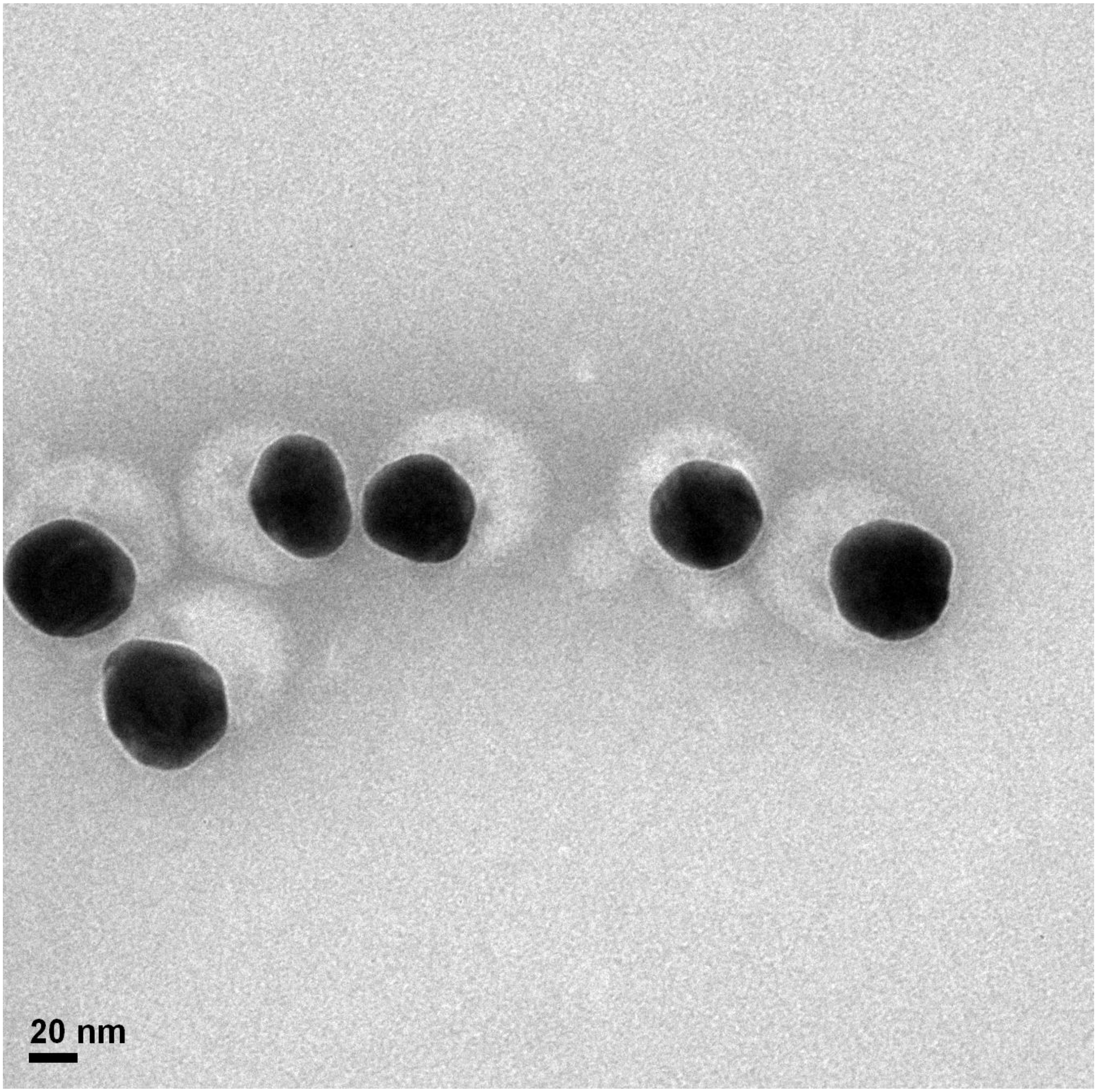

Figure S6. TEM image of the Au@vesicle NPs, d_{Au} = 40 nm, [SDS] = 2.5 mM, t = 1.5 h (large-area view of Figure 3c).

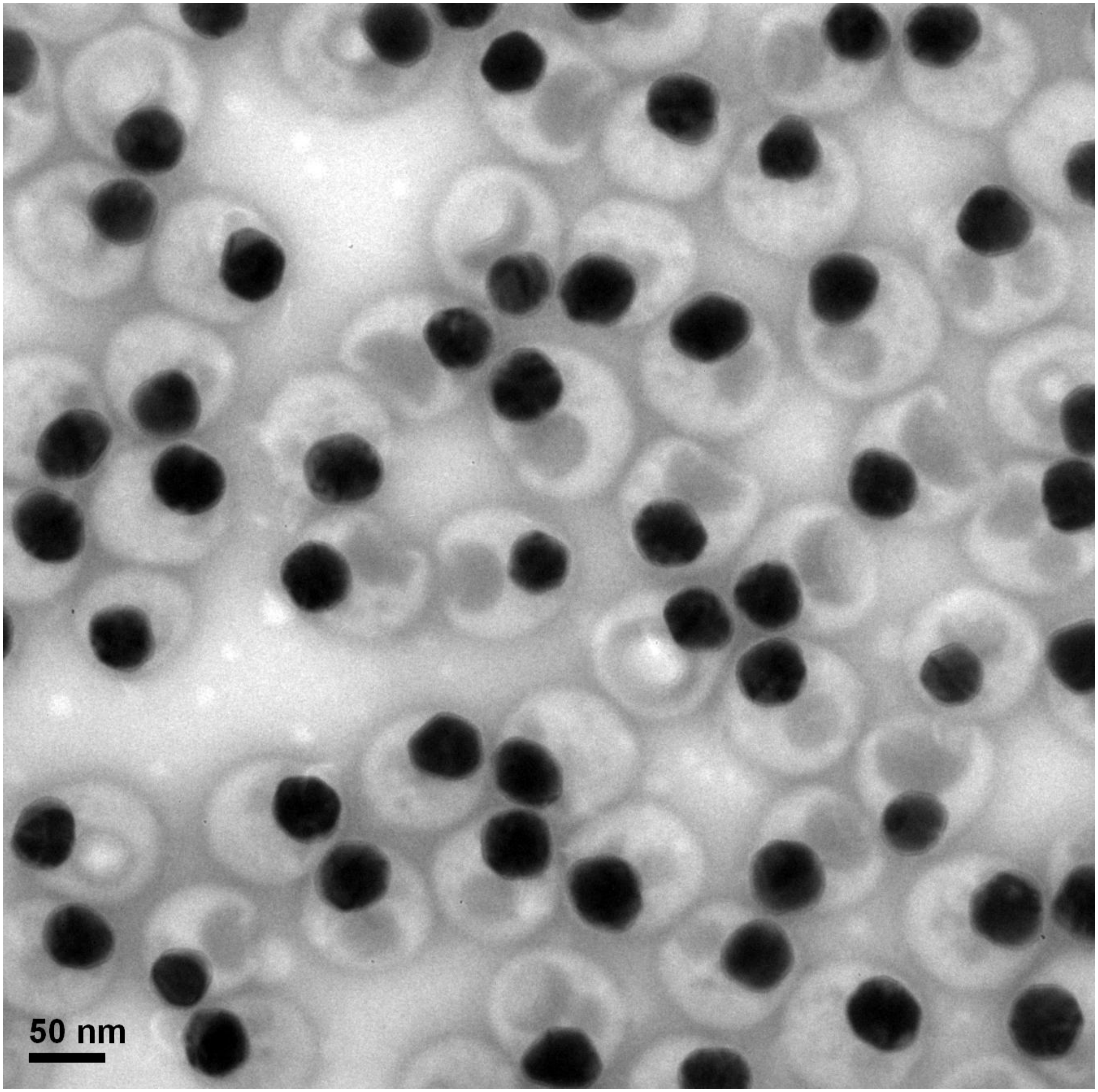

Figure S7. TEM image of the Au@vesicle NPs, d_{Au} = 40 nm, [SDS] = 2.5 mM, t = 2.5 h (large-area view of Figure 3d).

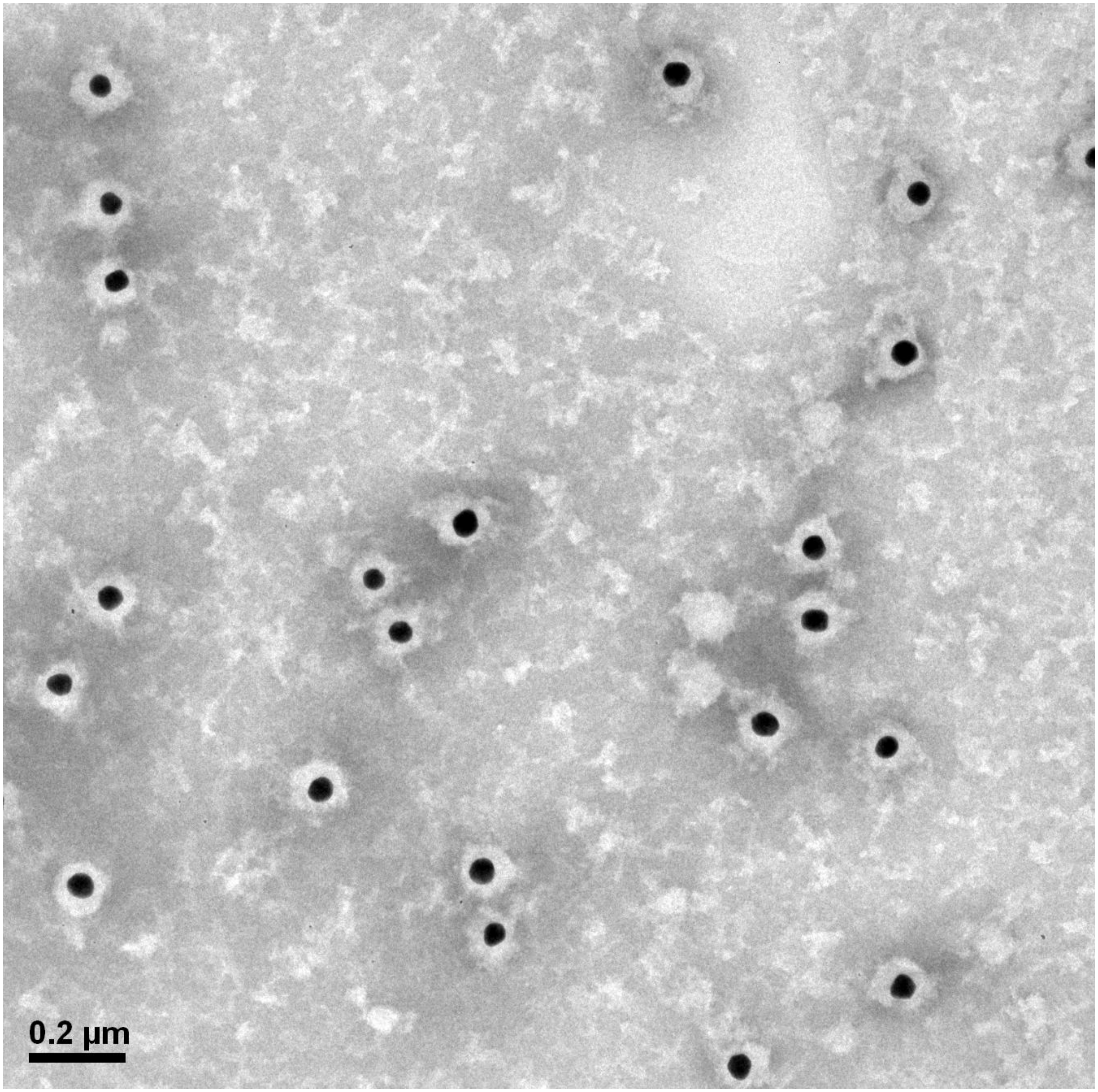

Figure S8. TEM image of the Au@PTh core-shell NPs, d_{Au} = 40 nm, [SDS] = 5 mM, t = 12 h, before purification. The polymer NPs in the dark brown supernatant can identified as the white particles.

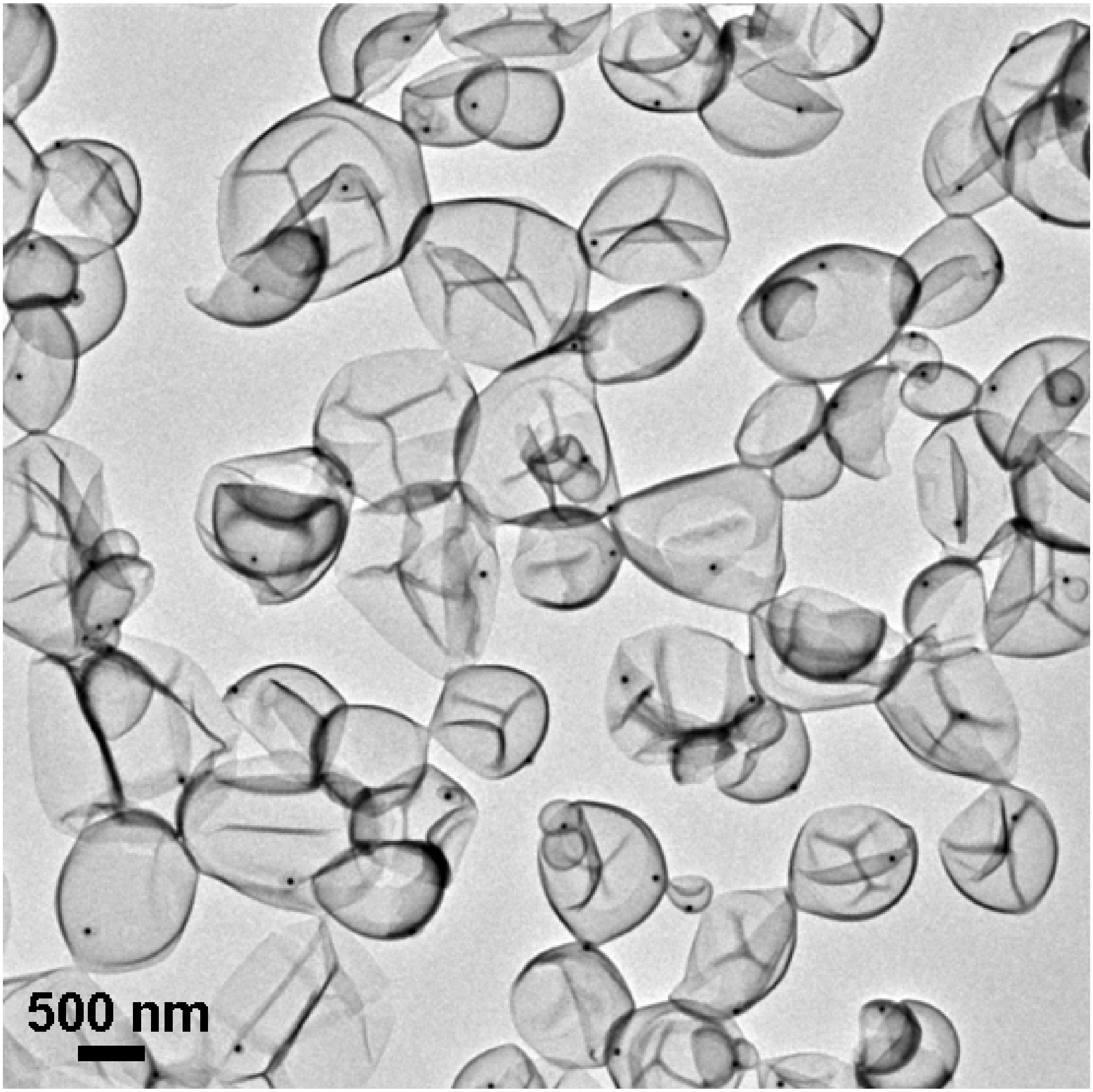

Figure S9. TEM image of the Au@vesicle NPs, d_{Au} = 40 nm, [SDS] = 0.8 mM, t = 12 h (large-area view of Figure 3f).

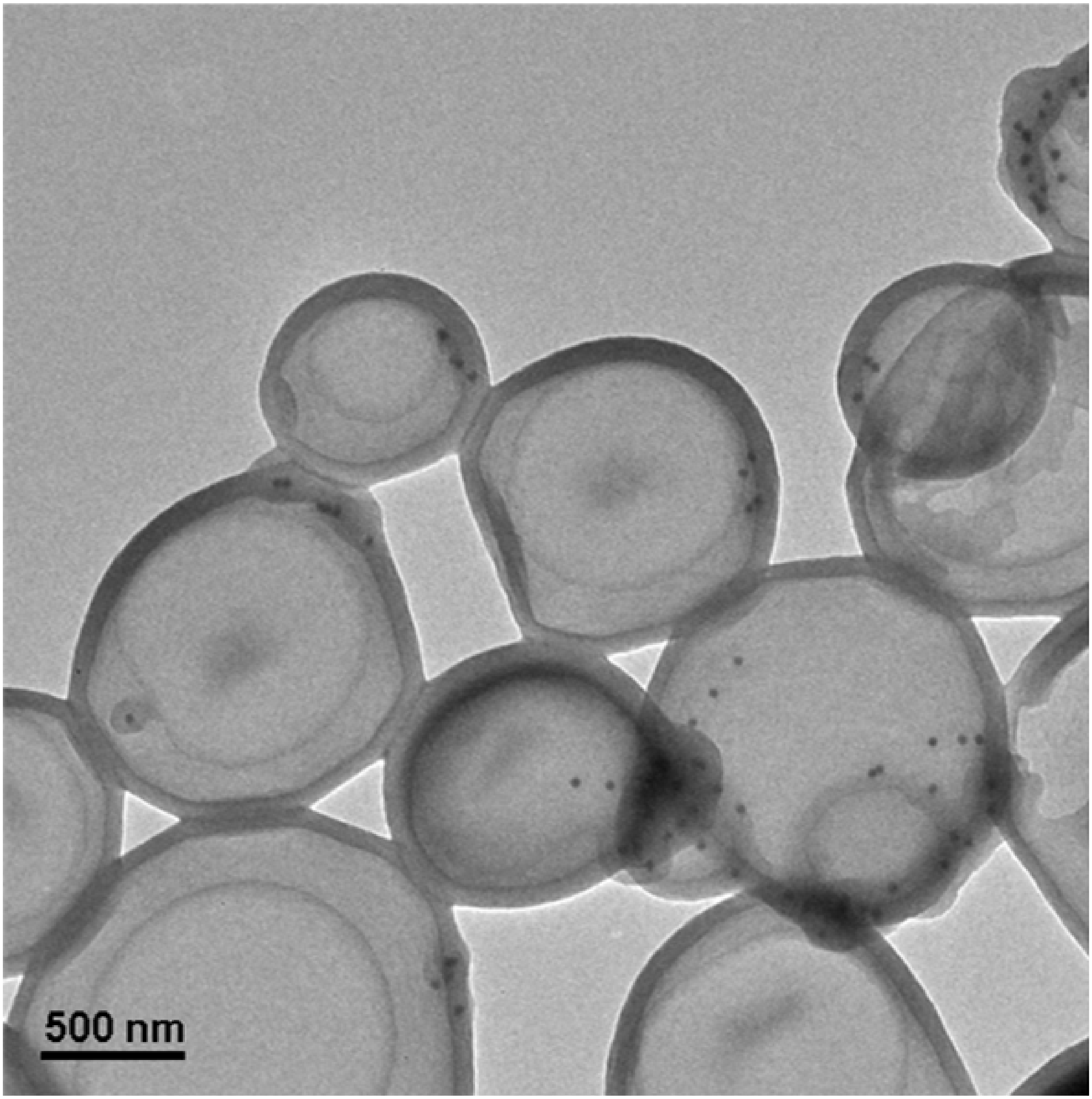

Figure S10. TEM image of the Au@vesicle NPs formed in the absence of SDS, d_{Au} = 40 nm, t = 12 h (large-area view of Figure 3g).

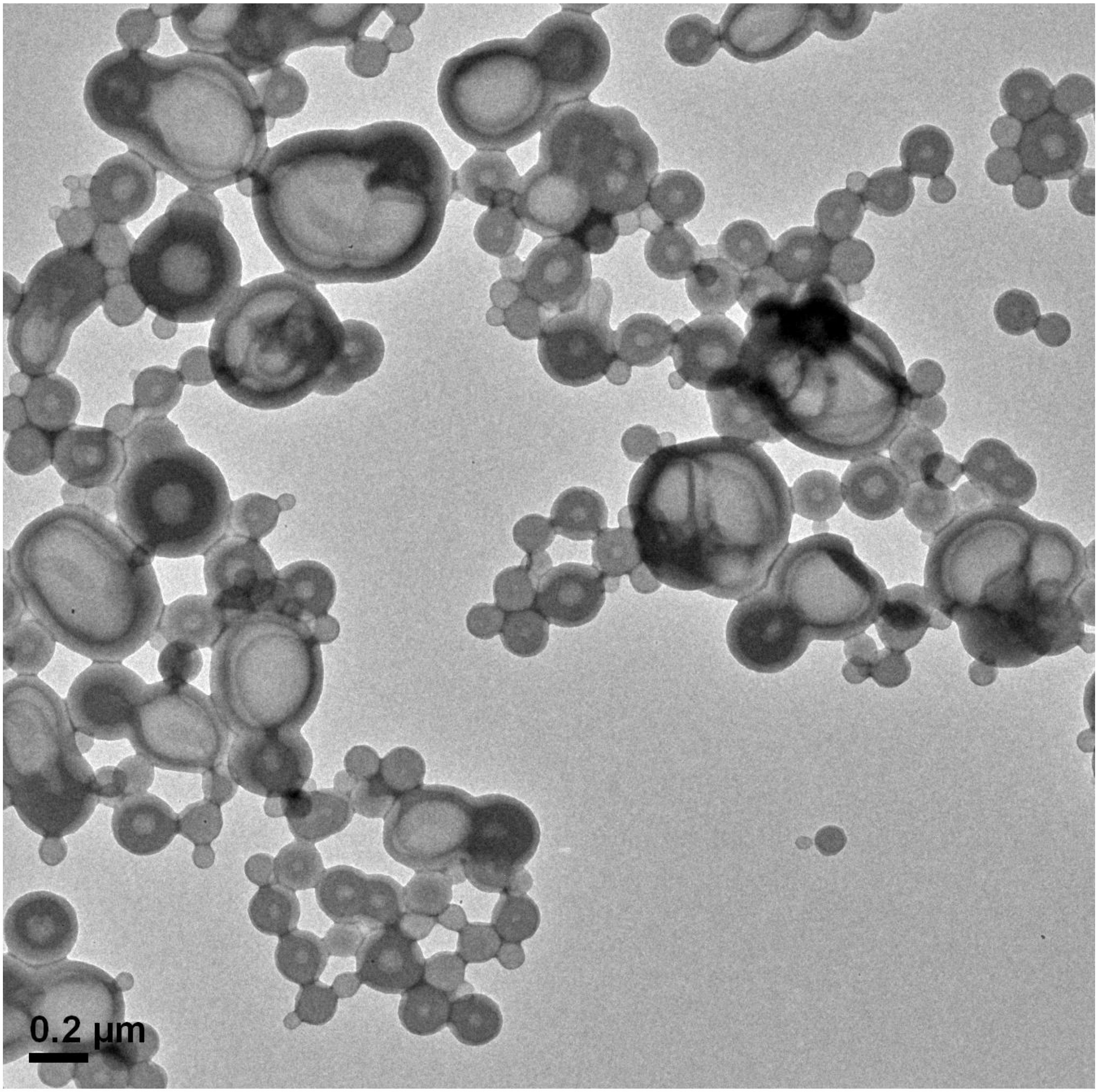

Figure S11. TEM image of the polymer vesicles formed in the absence of SDS and Au NPs (large-area view of Figure 3h).

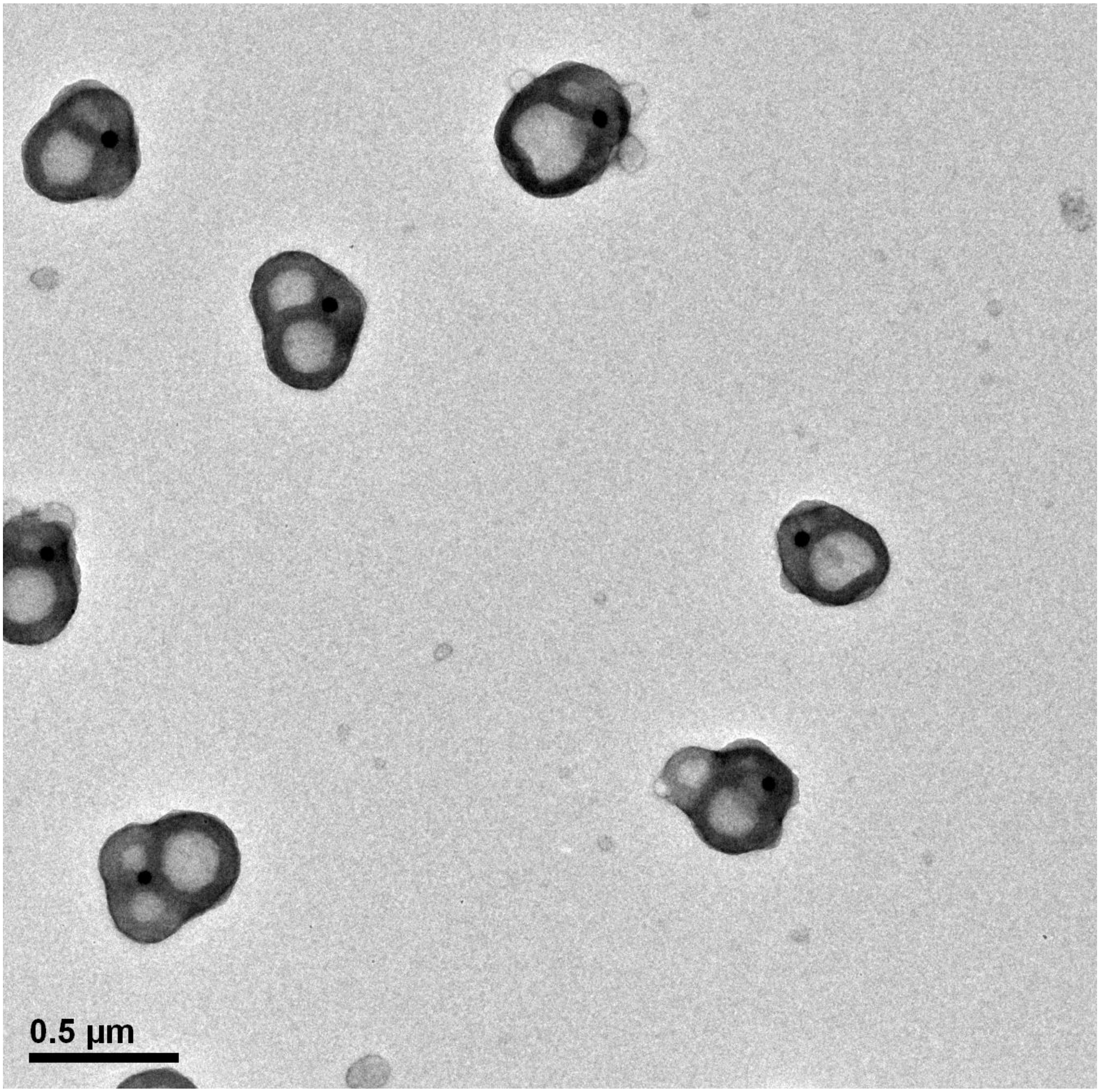

Figure S12. TEM image of Au@vesicle NPs after 2 growth cycles, [SDS] = 2.5 mM (before the formation of the vesicles in Figure 4a).

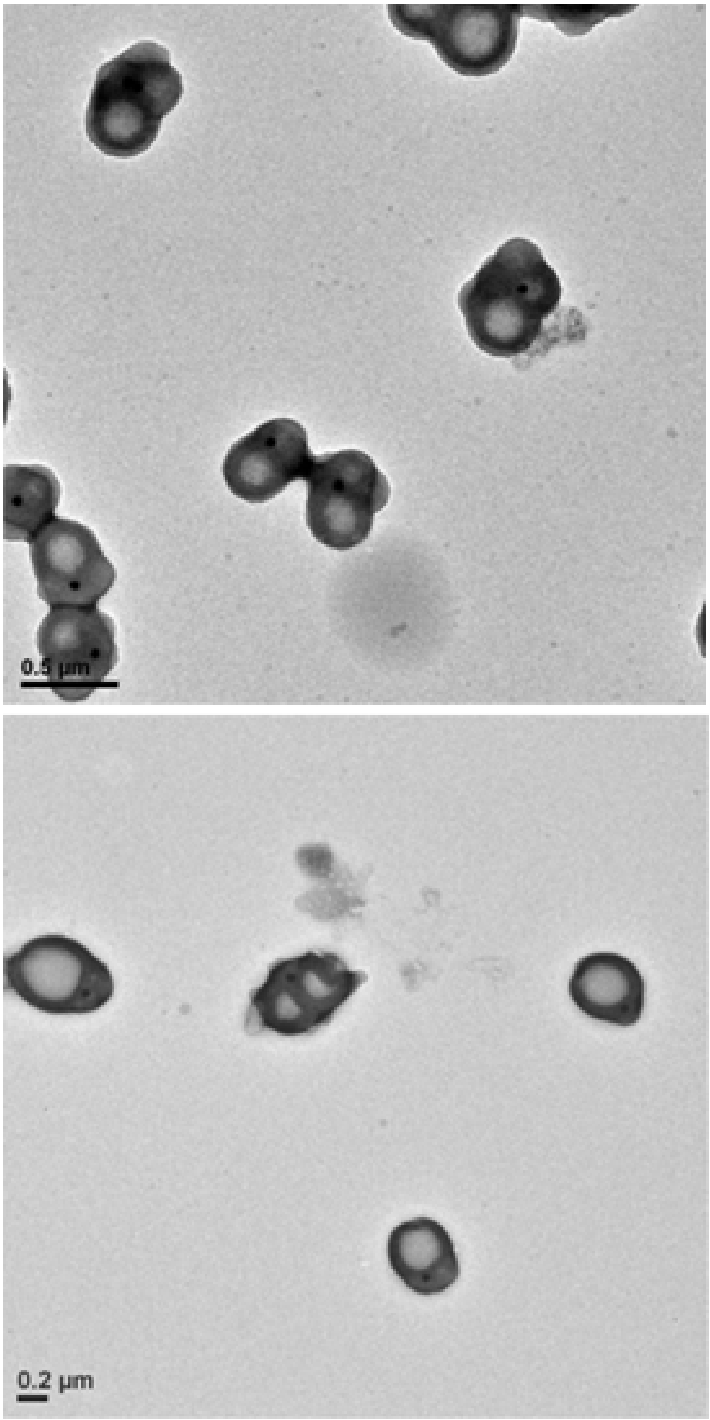

Figure S13. TEM images of Au@vesicle NPs after 3 growth cycles, [SDS] = 2.5 mM. The average diameter of the cavity is 210 nm and the average thickness of the cavity wall is 65 nm calculated from 11 vesicles.

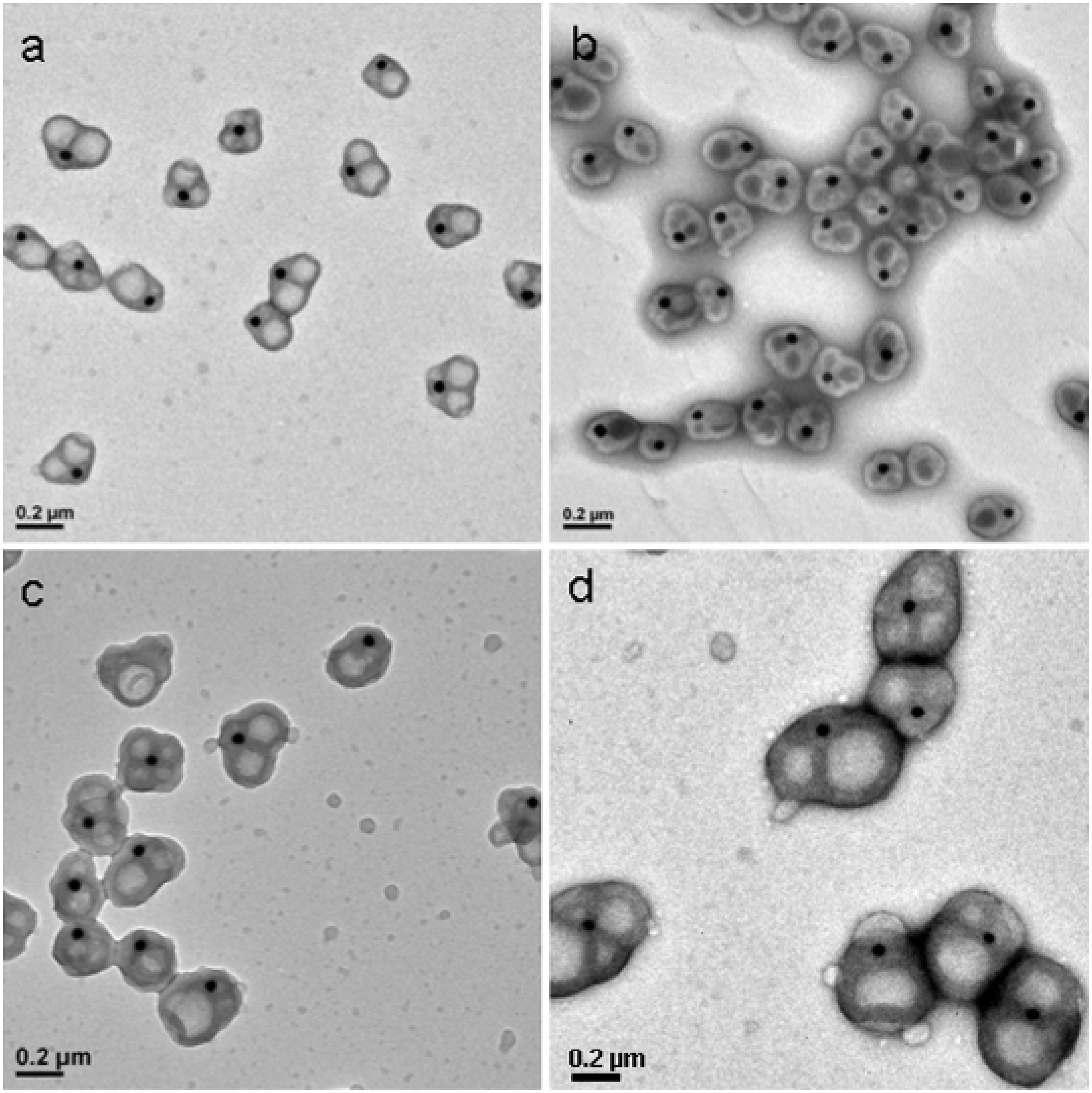

Figure S14. TEM images of (a) Au@vesicle NPs, (b) sample a after incubating in THF, (c) sample b after the 2nd growth cycle, and (d) after the 3nd growth cycle, respectively, d_{Au} = 40 nm, [SDS] = 2.5 mM.

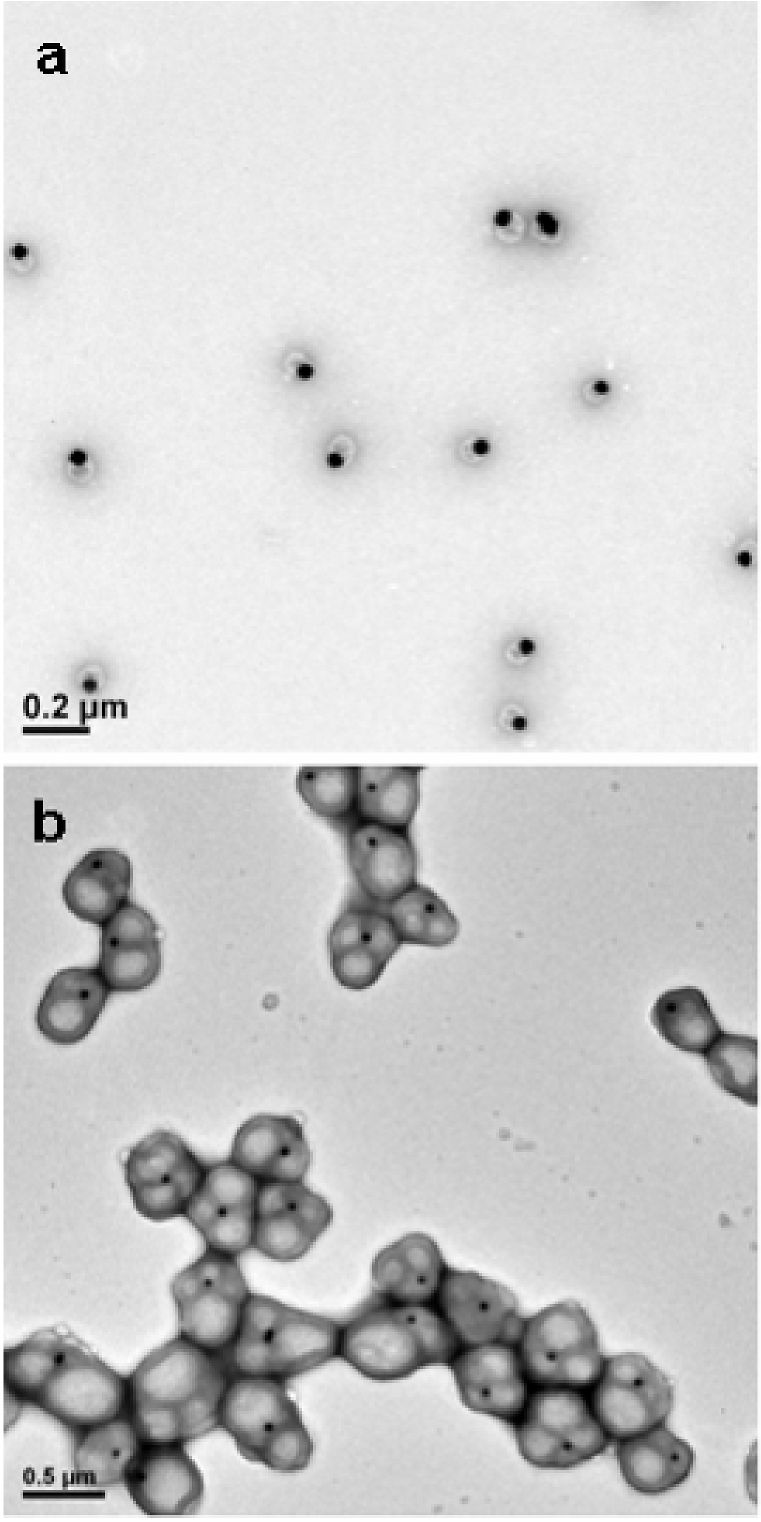

Figure S15. TEM images of (a) Au@vesicle NPs after oxidation by H_2O_2, t = 2 h; (b) sample a after purification and an additional growth cycle (large-area view of Figure 4b and 4c, respectively).

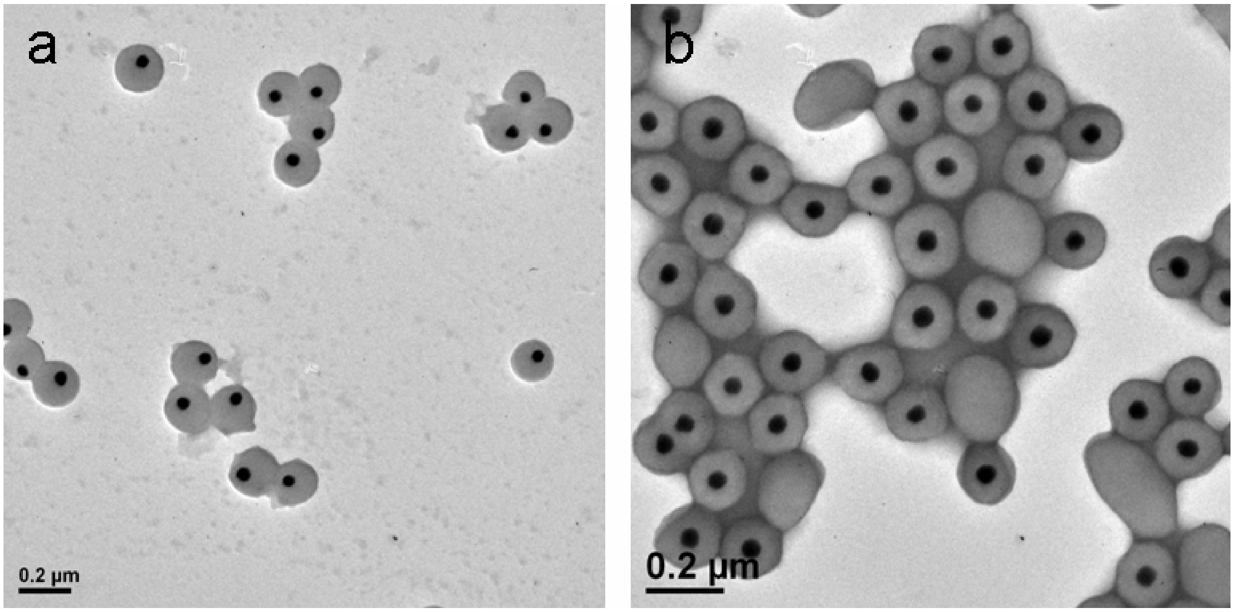

Figure S16. TEM images of (a) Au@polyaniline and (b) Au@polypyrrole core-shell NPs. The nanocomposites were prepared following the same method for the preparation of thiophene-based Au@vesicle NPs, but aniline or pyrrole was used instead of thiophene. The final reaction mixture contained aniline or pyrrole (50 mM), AuNPs (estimated 0.062 nM), SDS (2.5 mM), H_2O_2 (60 mM), $FeCl_3$ (9 µM), and H_2O (1.5 mL).