-Supporting Information-

Facile fabrication of triple-layer (Au@Ag)@Polypyrrole core-shell and (Au@H₂O)@Polypyrrole yolk-shell nanostructures

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Experiment section

All solutions were prepared using ultrapure water (resistivity > 18 M $\Omega \cdot \text{cm}^{-1}$). Pyrrole (98%, Alfa Aesar) were 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) and AgNO₃ (99%, Sigma) were used as received. Copper specimen grids (200 mesh) with formvar/carbon support film (referred to as TEM grids in the text) were purchased from Electron Microscopy Sciences. Transmission electron microscopy (TEM) images were collected on a JEM-1400 (JEOL) operated at 100 ~ 120 kV. Raman spectra were collected from sample solutions in a cuvette (pathlength = 1.00 cm) on an R-3000HR spectrometer (Raman Systems Inc.) using red LED laser (λ = 785 nm). Ultraviolet-visible (UV-vis) spectra were collected on a Cary 100 spectrophotometer.

Preparation of TEM Samples. $(NH_4)_6Mo_7O_{24}$ was used as the negative stain in all TEM images reported in this paper unless specifically mentioned, so that 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 ([$(NH_4)_6Mo_7O_{24}$] = 6.8 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.

Synthesis of triple-layer (Au@Ag)@PPy with $d_{Au}=17$ nm. The gold seeds were prepared by the citrate-reduction method.¹ The citrate-stabilized AuNP solution (3 × 1.5 mL) were concentrated to a total of 10 µL by centrifugation at 14000 rpm (16000 g) for 15 min. After removal of the supernatant, the isolated NPs were added to a solution containing pyrrole (1.5 mL, 5 mM) and SDS (0.2 mL, 40 mM). Then the solution was vortexed for 5 s followed by addition of AgNO₃ solution (1.5 mL, 5 mM). The total volume of the final mixture was 3.2 mL, where [pyrrole] = 2.3 mM, [SDS] = 2.5 mM, [AgNO₃] = 2.3 mM. After vortexing for 10 s, the reaction mixture was incubated at room temperature for 12 h to ensure complete reduction of AgNO₃. To isolate (Au@Ag)@PPy, reaction mixture was centrifuged at 12000 rpm (12000 g) for 12 min, the isolated NPs were dispersed in SDS solution (3.6 mM) to prevent further aggregation of the NPs in water.

Synthesis of triple-layer (Au@Ag)@PPy with $d_{Au}=60$ nm. The process is similar to that of the above, except the concentrations used: [pyrrole] = 0.8 mM, [AgNO₃] = 2 mM and [SDS] = 8 mM.

Etching of triple-layer (Au@Ag)@PPy. 0.5 mL of the as-synthesized reaction mixture (d_{Au} =17 nm) was centrifuged and the isolated NPs were added into 1 mL solution containing NH₃·H₂O (7.5 M) and SDS (1.8 mM). The mixture was incubated for 12 h on a shaker. After that, the solution was centrifuged at 12000 rpm (12000 g) for 12 min and the isolated (Au@H₂O)@PPy NPs were redispersed in SDS solution (3.6 mM) for further characterization. As for the NPs with d_{Au} =60 nm, the centrifugation was conducted at 6000 rpm (3000 g) for 6 min with otherwise similar experiment conditions.

References

1. G. Frens, Nat. Phys. Sci., 1973, 241, 20.



Figure S1. TEM images of $(Au@Ag)@PPy (d_{AuNP} = 17 \text{ nm})$ at low and high magnification.



Figure S2. TEM image of Ag@PPy prepared in absence of AuNP seeds.



Figure S3. UV-Vis spectra of synthetic mixture with (lower panel, (Au@Ag)@PPy NPs) and without (upper panel, Ag@PPy) AuNP seeds. Spectra were taken at 0, 1 h, 2 h, 4 h and 12 h after addition of AgNO₃. The latter spectra were collected after the solution was diluted 10 times.



Figure S4. TEM image of $(Au@Ag)@PPy (d_{AuNP} = 17 \text{ nm})$ before purification.



Figure S5. TEM image of the resulting product from a control experiment without SDS.



Figure S6. TEM images of isolated (Au@Ag)@PPy redispersed in either water (a, c, e, g) or SDS solution (3.6 mM, b, d, f, h), after the 1st, 2nd, 3rd and 4th centrifugation-resuspension cycle, respectively. Sample c, e and g have to be sonicated before TEM sample preparation. Scale bars: 200 nm.



Figure S7. Etched (Au@H₂O)@PPy (after purification, $d_{AuNP} = 17$ nm) at low and high magnification.



Figure S8. TEM images of (Au@Ag)@PPy (after purification, $d_{AuNP} = 60$ nm) at low and high magnification. The embedded AuNP seeds cannot be easily discerned owing to the thick Ag layer.



Figure S9. Etched (Au@H₂O)@PPy (after purification, $d_{AuNP} = 60$ nm).