

Supporting Information

Universal chitosan-assisted synthesis of Ag-included heterostructured nanocrystals for label-free *in situ* SERS monitoring

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EXPERIMENTAL SECTION

Reagents and materials. Tellurium dioxide powder (TeO_2 , 99.99%) and p-NTP were purchased from Aladdin Chemistry Co., Ltd. Hexadecyltrimethylammonium bromide (CTAB, 99%) and sodium dodecyl sulfate (SDS, 99%) were purchased from Sigma-Aldrich. Hydrazine monohydrate (85%, AR), potassium tetrachloroplatinate (II) (K_2PtCl_4 , AR), tetrachloroauric (III) acid hydrate ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$, AR), palladium (II) Chloride (PdCl_2 , AR), Chitosan, acrylic acid polymers (PAA, AR), ascorbic acid (AA, AR), silver nitrate (AgNO_3), polyvinyl pyrrolidone (PVP), sodium borohydride (NaBH_4) and sodium hydrate (NaOH, AR) were supplied by Sinopharm Chemical Reagent Co., Ltd. Ultrapure water with a conductivity of $18.25\text{ M}\Omega\text{ cm}$ was used throughout the experiments, and all chemicals were used without further purification.

Synthesis of Te nanowires. Te NWs were prepared according to the method reported by Chang et al.¹ Typically, hydrazine monohydrate (10 mL) was added to a beaker containing tellurium dioxide (0.032 g) at room temperature under constant magnetic stirring. The solution changed color from colorless to blue after 50 min, indicating the formation of Te NWs. To terminate the reaction and stabilize the Te NWs, the mixture was diluted 10-fold with SDS (10 mM), which was then subjected to a centrifugation/wash cycle to remove most of the matrices, including SDS and hydrazine.

Synthesis of Pd (or PdPt) nanotubes and Ag/Pd (or Ag/PdPt) heterostructured nanotubes. In a typical synthesis, Te NWs ($\sim 0.04\text{ mmol}$) from the previous experiment were dispersed in 10 mL of chitosan solution (0.5 mg mL^{-1}) under

constant magnetic stirring at 25 °C. After 15 min, PdCl₂ (5 µmol) was added to the solvent containing TeNWs. The solution changed color from blue to grey-black after 10 min. The mixture was subjected to a centrifugation/wash cycle to remove most of the matrices. When PdCl₂ (3 µmol) and K₂PtCl₄ (2 µmol) mixture solution were used instead of PdCl₂ precursor under the same conditions, PdPt alloy nanotubes were obtained.

In the preparation of Ag/Pd (or PdPt) heterostructured nanotubes, Pd (or PdPt) nanotubes were dispersed in the chitosan (0.01 mg mL⁻¹) and PVP (10 mM) solution. After 15 min, AgNO₃ solution (10 mM) was added to the solvent containing Pd (or PdPt) nanotubes. After another 15 min, 80 uL AA solution (0.1 M) was added to the solvent, which was subjected to a centrifugation/wash cycle after 10 min.

Synthesis of porous PdPt bimetallic nanotubes and Ag/PdPt heterostructured nanotubes. The synthesis of porous PdPt nanotubes was carried out according to our previously reported method with minor modifications.² Briefly, Te NWs (~ 0.05 mmol) were dispersed in 100 mL of CTAB solution (5 mM) under constant magnetic stirring. After 30 min, the mixture, which included PdCl₂ (5 µmol), K₂PtCl₄ (0.01 mmol) and 0.4 mL NaOH (0.1 M), was added to the solvent containing Te NWs. After 30 min, the mixture was subjected to a centrifugation/wash cycle.

Then, the product was dispersed in the chitosan solution (0.5 mg mL⁻¹). After 15 min, AgNO₃ solution (10 mM) was added to the solvent. After another 15 min, 80 uL AA solution (0.1 M) was added to the solvent, which were subjected to a centrifugation/wash cycle after 10 min.

In contrast, chitosan solution was changed to PVP solution (10 mM), CTAB solution (10 mM), SDS solution (10 mM), or PAA solution (10 mM) under the same conditions.

Synthesis of porous Au/PtAu nanotubes and Ag/Au/PtAu heterostructured nanotubes. The synthesis of porous Au/PtAu nanotubes was carried out according to our previously reported method.³ In a typical synthesis, TeNWs (~ 0.05 mmol) from the previous experiment were dispersed in 100 mL CTAB solution (5 mM) under constant magnetic stirring at 30 °C. After 30 min, the mixture including 0.4 ml NaOH (0.1 M) and K₂PtCl₄ (0.01 mmol) was added to the solvent containing Te NWs. The solution changed color from blue to grey-black after 30 min, indicating the formation of Te/Pt core-shell nanostructures. Then HAuCl₄ (2.0 µmol) was added to the solvent. The color of the solution was gray-black after 25 min, indicating the formation of porous Au/PtAu nanotubes. The mixture was subjected to a centrifugation/wash cycle to remove most of the matrices.

Then, the product was dispersed in the chitosan solution (0.5 mg mL⁻¹) according to the above method. In contrast, chitosan solution was changed to PVP solution (10 mM).

In situ monitoring of the catalytic reaction with SERS. The catalytic reaction monitored by SERS were collected out by the following approach. First, 10 uL p-NTP ethanol solution (1.0 mM) was added to 0.1 mL of colloidal suspension of Ag/Pd heterostructured nanotubes. Then 10 uL freshly prepared aqueous solution of NaBH₄ (0.5 M) solution was added to the above mixture to start the catalytic reaction. SERS

spectra were collected directly from the colloidal suspension at different reaction times. During the process of collecting SERS spectrum, a short working distance 5x objective was used and the date acquisition time was approximately 10 s. The whole SERS measurement was taken at room temperature.

Characterization. Transmission electron microscopy (TEM) measurements were performed on a JEM-2100F high-resolution transmission electron microscopy at an accelerating voltage of 200 kV. Scanning transmission electron microscopy (STEM), elemental maps and cross-sectional line profiles were carried out under the high-angle annular dark field (HAADF) mode on a FEI TECNAIF-30 microscope operated at 300 kV. Samples for TEM analysis were prepared by depositing a single drop of diluted nanostructures dispersion in water on copper grids. The composition was determined by inductively coupled plasma atomic emission spectrometer (ICP-AES, IRIS Intrepid II XSP, Thermo Fisher Scientific, USA). The X-ray diffraction (XRD) analysis was carried out on a Bruker D8 Advance X-ray diffractometer with Cu K α radiation. Ultraviolet-Visible (UV-vis) absorption spectra were recorded on Nicolet Evolution 300 Ultraviolet-Visible spectrometer.

All Raman spectra were recorded at room temperature using an inVia Raman spectrometer (Renishaw, UK) equipped with a confocal microscope (Leica, German). The samples were excited with a He-Ne laser (633 nm) for corresponding characterization with an output power of 20.0 mW.

References

1. Z.-H. Lin, Z. Yang and H.-T. Chang, Cryst. Growth & Des., 2007, 8, 351.
2. K. Cai, Z. Zhi, K. Chen, L. Huang, J. Wang, F. Shao, Y. Wang and H. Han, Chem. Commun., 2013, 49, 6024.
3. K. Cai, J. Liu, H. Zhang, Z. Huang, Z. Lu, M. F. Foda, T. Li and H. Han, Chem. Eur. J., 2015, 21, 7556.

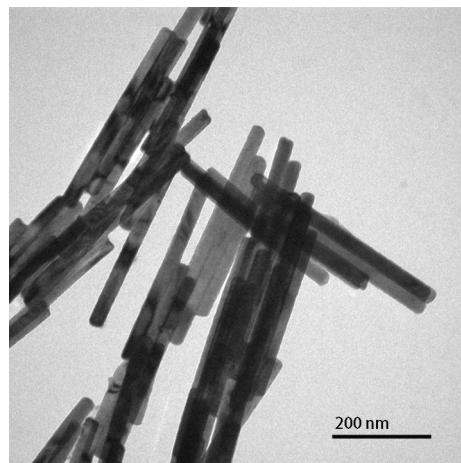


Figure S1. TEM image of Te nanowires.

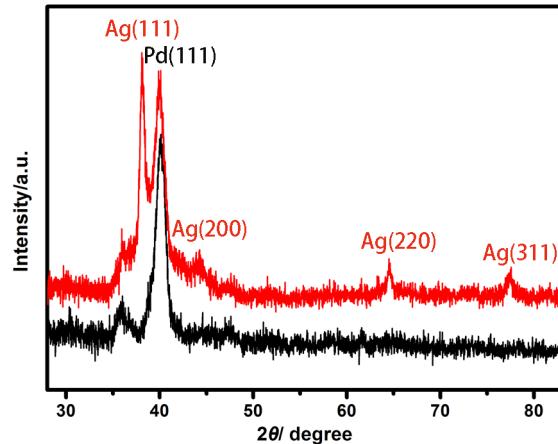


Figure S2. XRD of Pd NTs (black line) and Ag/Pd OHNTs (red line).

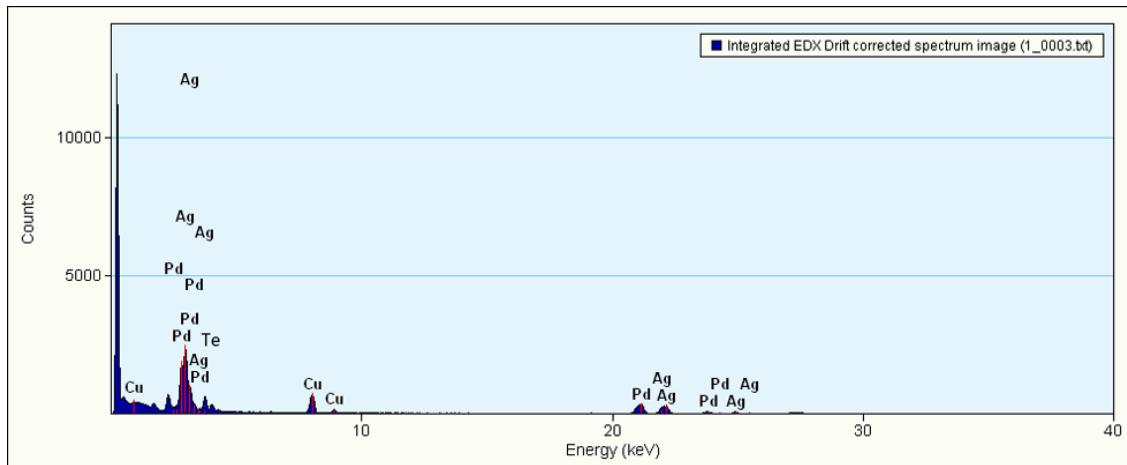


Figure S3. EDS spectrum of Ag/Pd OHNTs.

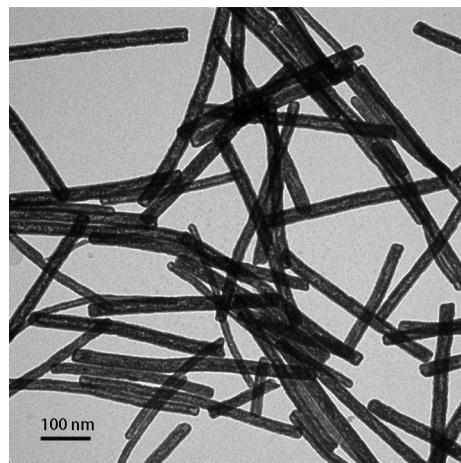


Figure S4. TEM image of PdPt NTs.

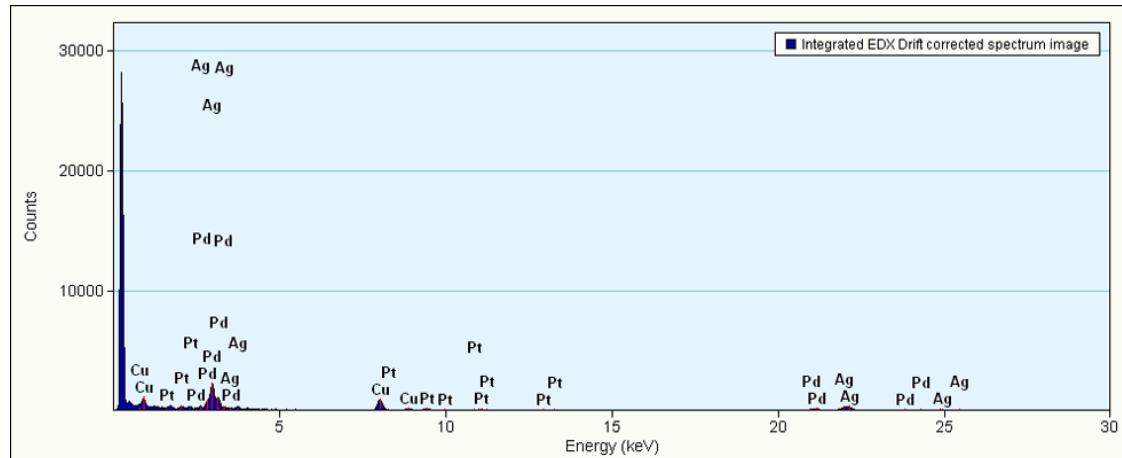


Figure S5. EDS spectrum of Ag/PdPt OHNTs.

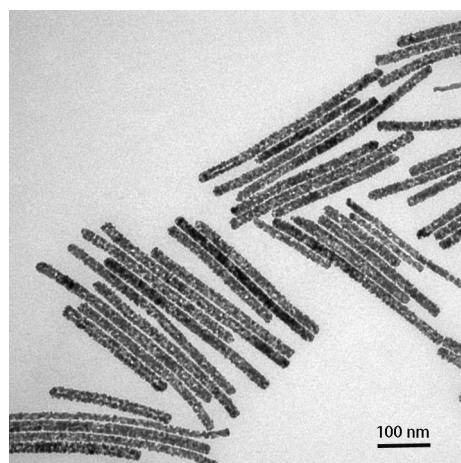


Figure S6. TEM image of porous PdPt NTs.

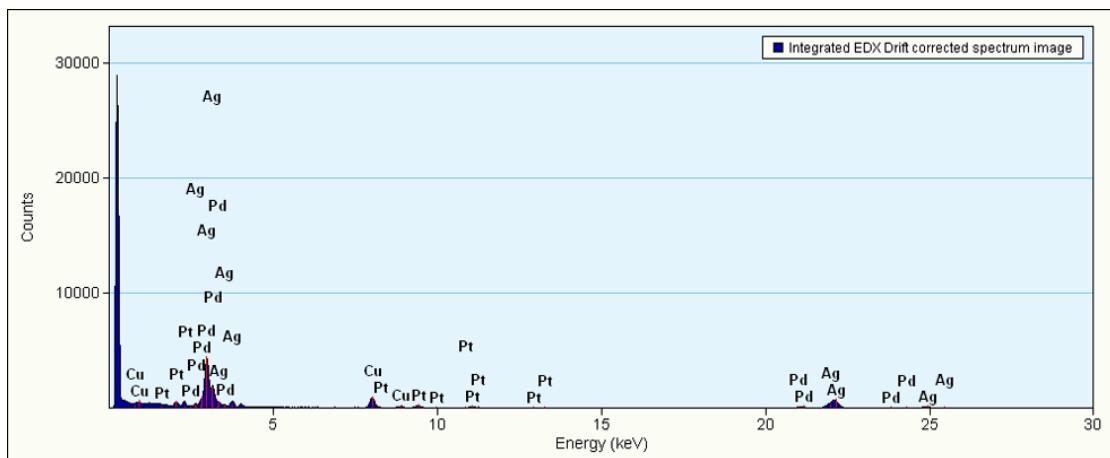


Figure S7. EDS spectrum of porous Ag/PdPt OHNTs.

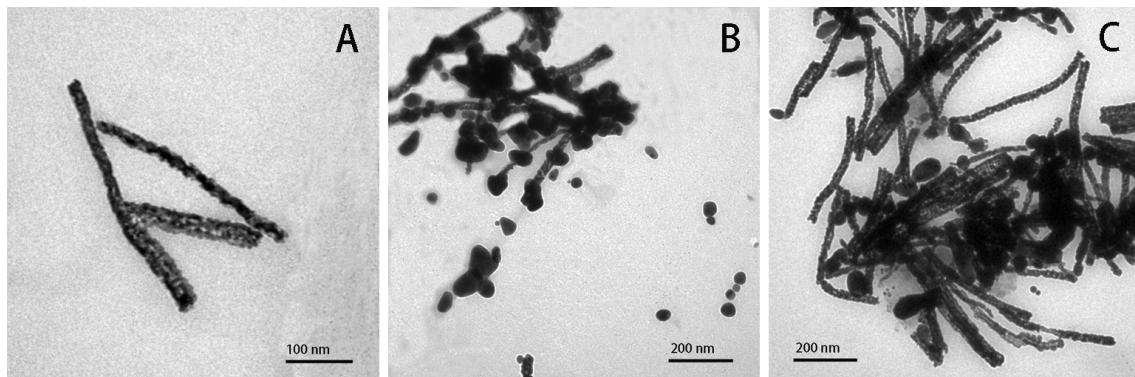


Figure S8. TEM images of products using CTAB (A), SDS (B) and PAA (C) instead of chitosan in the synthesis of porous Ag/PdPt OHNTs.

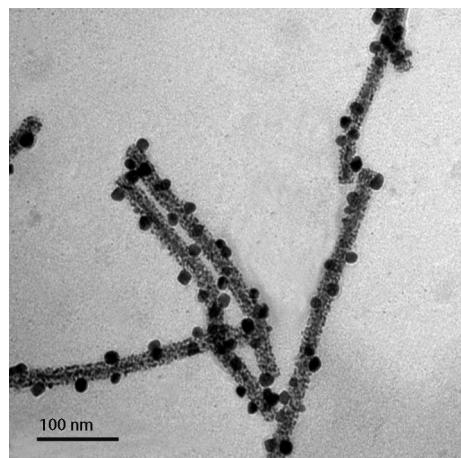


Figure S9. TEM images of Au/PtAu heterostructured nanotubes.

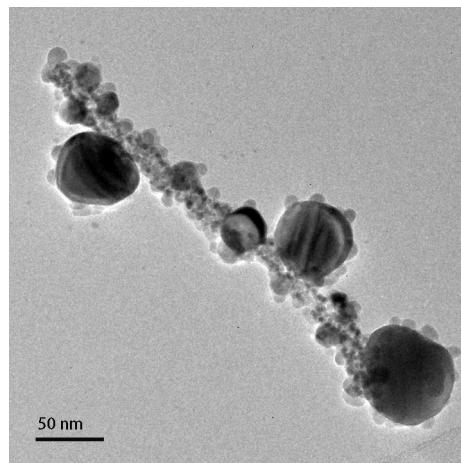


Figure S10. TEM images of Ag/Au/PtAu heterostructured nanotubes.

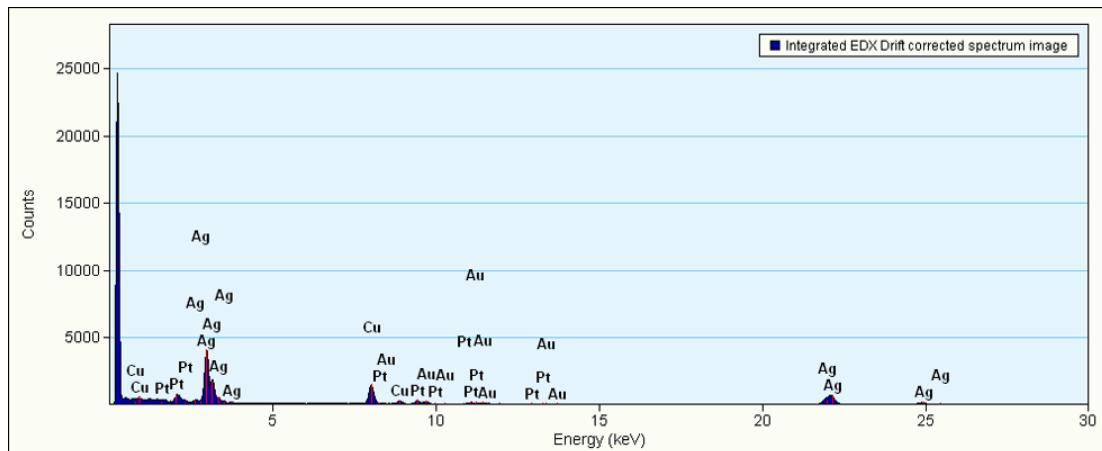


Figure S11. EDS spectrum of Ag/Au/PtAu heterostructured nanotubes.

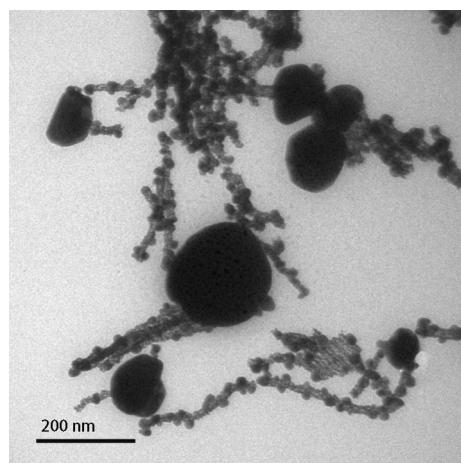


Figure S12. TEM images of the products by using PVP instead of chitosan in the synthesis of Ag/Au/PtAu heterostructured nanotubes.

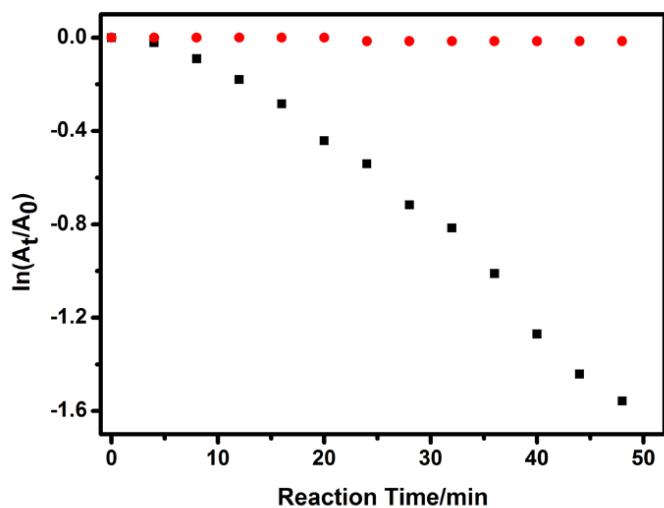


Figure S13. Plot of $\ln(A_t/A_0)$ of p-NTP as a function of time for the reaction catalyzed by Ag/Pd OHNTs.

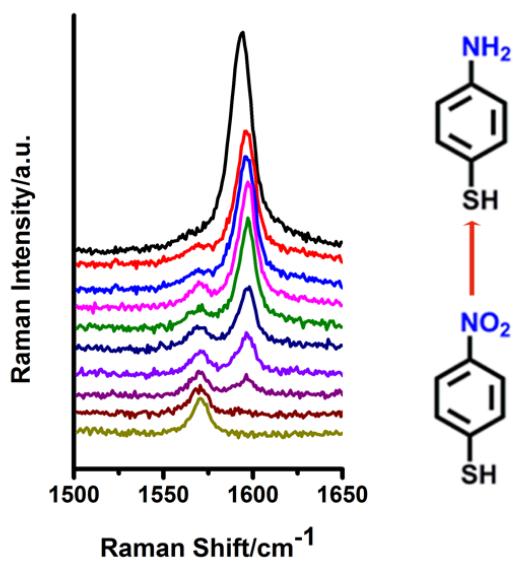


Figure S14. SERS spectra recorded from the reaction suspension collected at different reaction times. From bottom to top: SERS spectra recorded at 0, 1, 2, 3, 4, 5, 6, 7, 8 and 12 min after addition of NaBH_4 solution.