

Supplementary Information

to

Rapid Synthesis of Hybrids and Hollow PdO Nanstructures by Controlled In-situ Dissolution of a ZnO Nanorod Template: Insights into the Formation Mechanism and Thermal Stability

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I. ZnO nanorods :

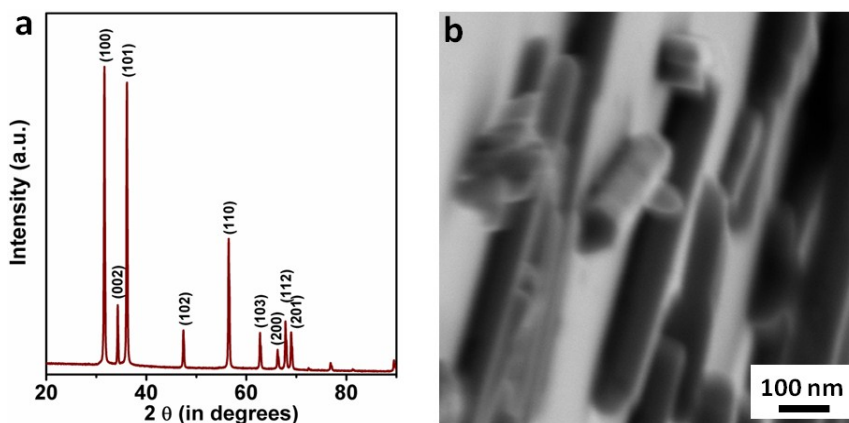


Figure S1: (a) XRD data of as-synthesized ZnO nanorods. (b) Cross-sectional SEM image of ZnO nanorods.

II. ZnO-PdO nanorods :

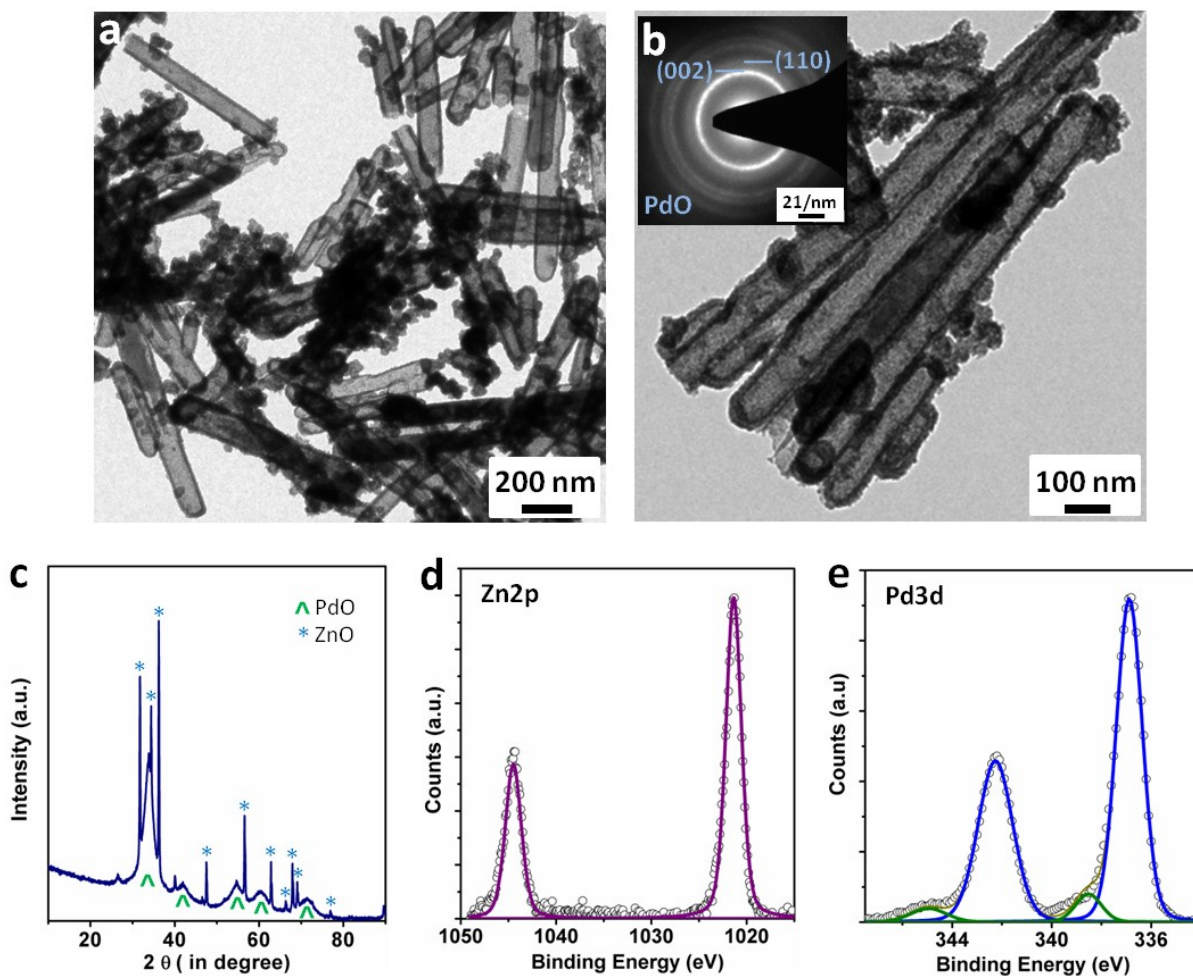


Figure S2: (a) Low magnification TEM image showing PdO nanotubes (ZP-1). (b) High magnification TEM image of PdO nanotubes. Inset shows the diffraction pattern from the same set of nanotubes. (c) XRD data of the synthesized PdO nanotubes. (d) Core level XPS spectra of Zn2p obtained from the PdO nanotube sample showing +2 oxidation state of Zn. (e) Pd3d XPS spectra of the same sample shows that Pd is in +2 oxidation state predominantly with trace amounts of Pd in higher oxidation state.

III. Control experiment without ZnO :

In the control experiments the same procedure was repeated without addition of ZnO. In a typical experiment, 'x' mg of PdCl₂ dissolved/dispersed in 'v' ml of water was subjected to microwave irradiation under closed vessel condition for 't' minutes at 'T' degree Celsius. (refer table 1 in main paper for 'x', 'v', 't', 'T')

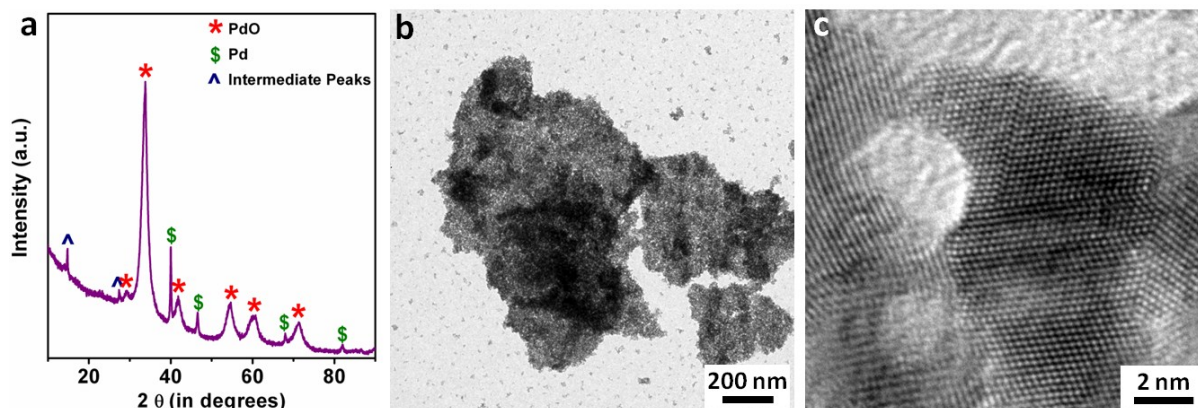


Figure S3: (a) XRD data of the product formed as a result of the reaction without ZnO (ZP 1-control). (b), (c) BF & HR TEM images showing formation of randomly shaped PdO crystal aggregates without ZnO.

IV. Effect of loading :

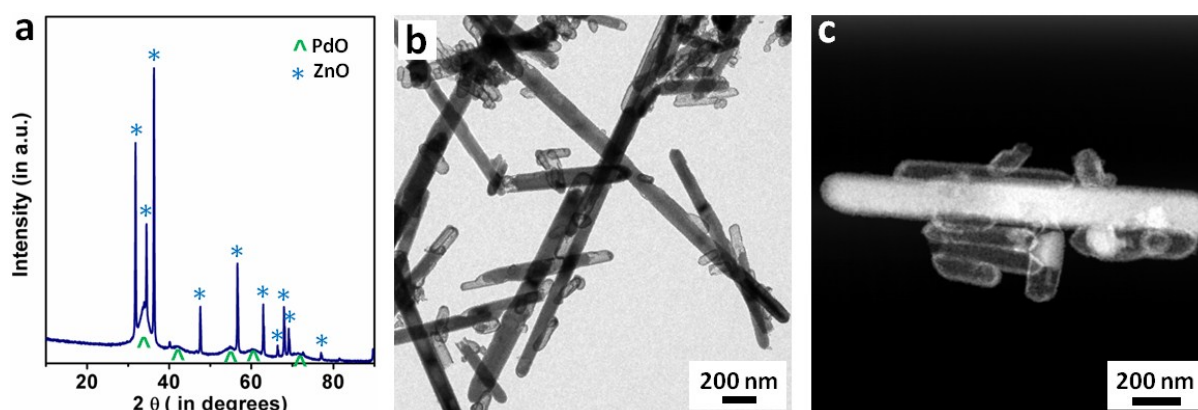


Figure S4: (a) XRD data of the hollow + hybrid sample (ZP-2). (b), (c) Low magnification BFTEM and HAADF STEM image showing that the dissolution of ZnO is suppressed at lower PdCl₂:ZnO ratio.

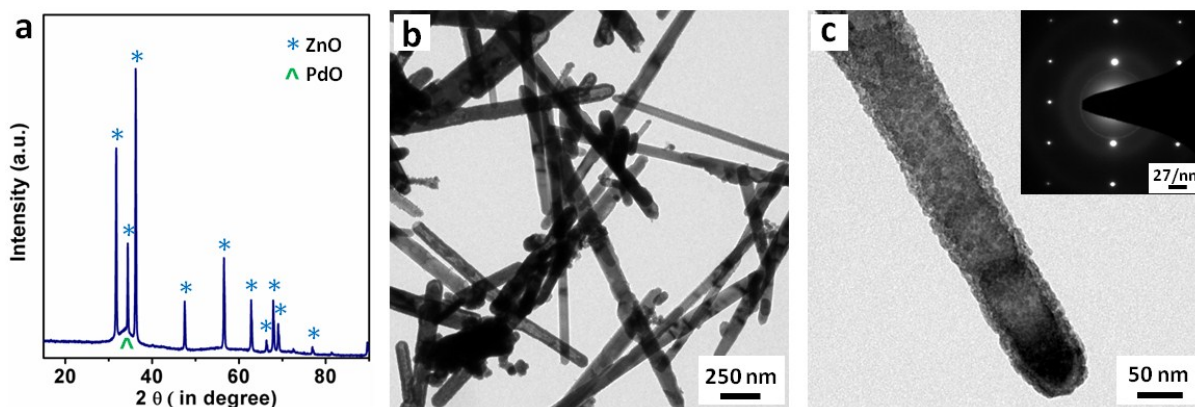


Figure S5: (a) XRD and (b), (c) BF TEM images of ZnO-PdO hybrid nanorods obtained at low starting ratio of PdCl₂:ZnO (ZP-3).

Increasing loading – hybrid to hollow

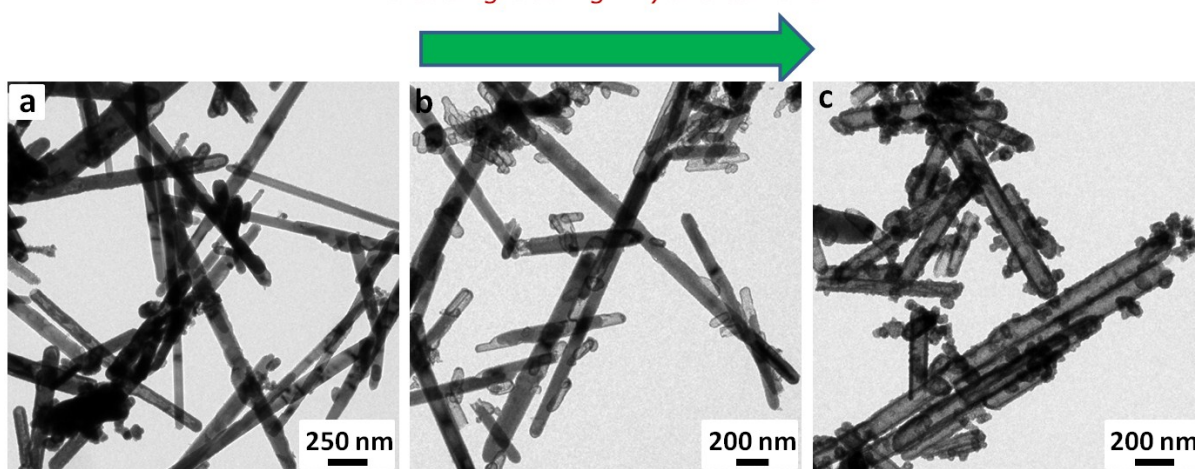


Figure S6: Low magnification TEM images of samples at different loading. (a) At low loading primarily PdO attached ZnO nanorods are formed. PdO preferentially attaches to ZnO nanorods with smaller diameter. Trace amounts of PdO nanotubes with smaller inner diameter is also present. (b) As loading is increased, more of PdO nanotubes are formed. Etching of ZnO is incomplete in nanorods with bigger diameter. (c) Further increasing the loading leads to predominant formation of PdO nanotubes.

Table ST 1 : H⁺ ion concentration for different loading.

Sample name	Amount of PdCl ₂ and water used	Calculation of [H ⁺] from amount of PdCl ₂ and water used	Calculation of [H ⁺] from the final pH in the corresponding control experiment without ZnO
ZP-1	20 mg in 6 ml	3.76 X 10 ⁻² M	4.00 X 10 ⁻² M
ZP-2	10 mg in 6 ml	1.88 X 10 ⁻² M	3.25 X 10 ⁻² M
ZP-3	2.5 mg in 18 ml	1.57 X 10 ⁻³ M	1.64 X 10 ⁻³ M

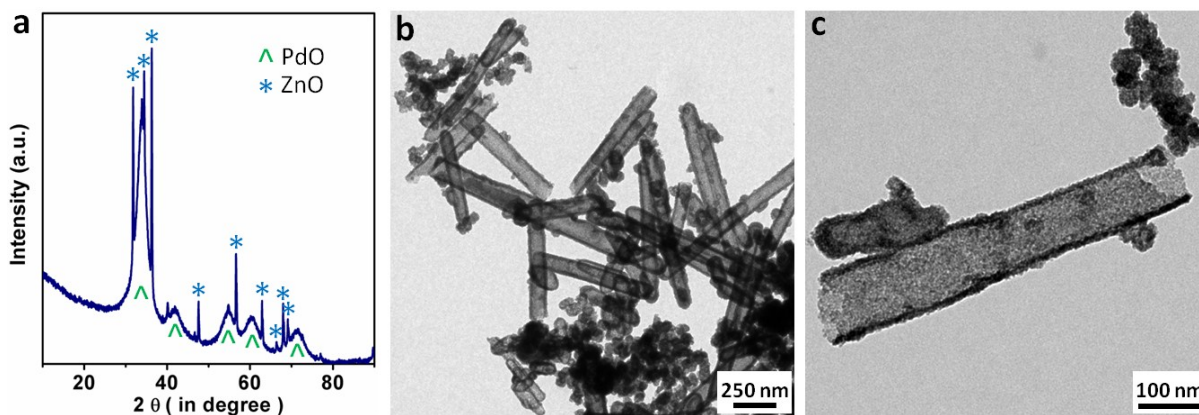


Figure S7: (a), (b), (c) XRD data and TEM images of the PdO nanotube sample prepared with higher starting ratio of $\text{PdCl}_2:\text{ZnO}$ (ZP-4).

V. Effect of temperature :

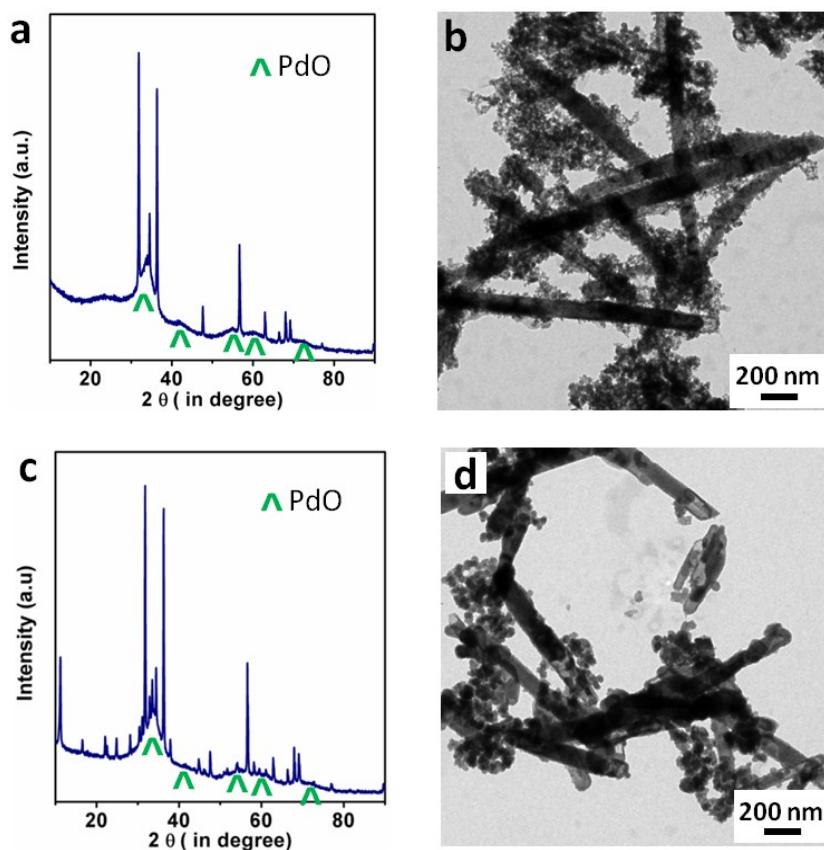


Figure S8: XRD data and BFTEM images of PdO nanotube sample prepared at (a), (b) 100°C, (c), (d) room temperature (ZP-6, 7).

VI. Ex-situ dissolution :

1 mg of PdO nanotube sample (ZP-5) was added to HCl/H₂O solution set to a pH of 4/3/2. It was stirred for an hour. The product was washed with water several times till the pH of the supernatant reaches ~7. Finally it was washed with acetone and left over night for drying.

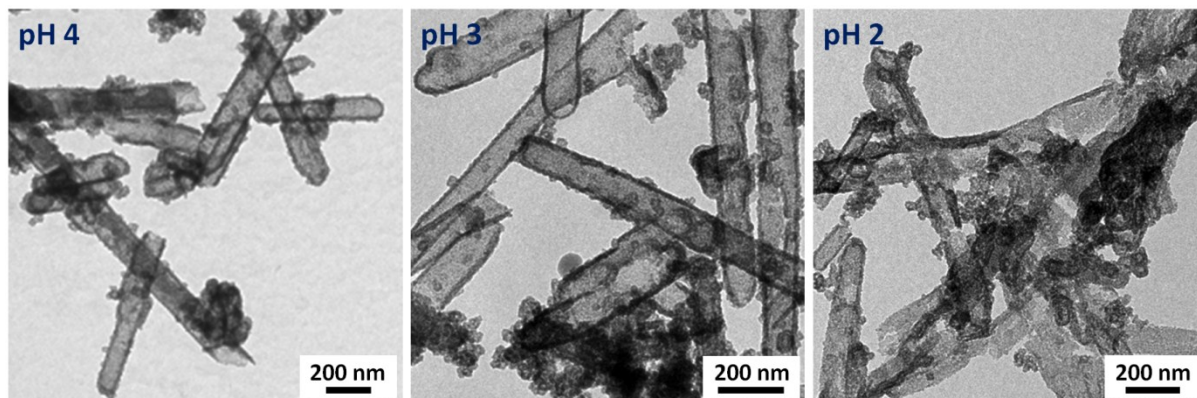


Figure S9: Low magnification TEM images of HCl/H₂O treated (different pH) PdO nanotubes.

VII. Synthesis of Pd attached ZnO :

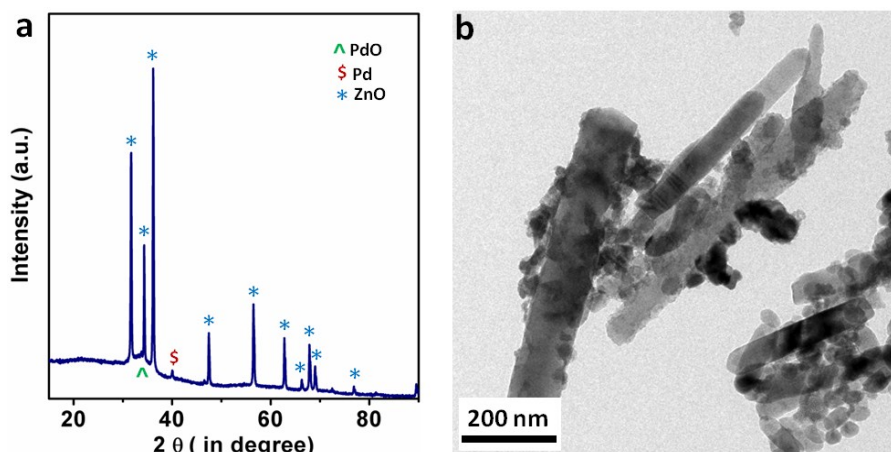


Figure S10: (a) PdO nanotube synthesis reaction done at low loading with additional presence of Na₃Ct to form Pd attached ZnO nanorods. A sharp peak corresponding to (111) plane of Pd is observed indicating sintering of Pd particles. (b) TEM image of the same, showing formation of large aggregates of Pd.

VIII. Conversion of PdO to Pd nanotubes :

On TEM support membrane: An extremely dilute suspension of PdO nanotubes (ZP-1) was prepared by dispersion of the nanotubes in acetone. Few microlitres were drop-casted and dried on a TEM support membrane. It was dipped in freshly prepared NaBH_4 (10 mg in 1 ml) solution for ~ 20 s and washed with water.

In solution: 4 mg of PdO nanotube sample (ZP-1) was suspended in 2 ml of water by vigorous stirring. To the stirring solution, freshly prepared NaBH_4 solution (10 mg in 1 ml) was added. The color of the PdO solution changes from brown to black, instantly. It was kept stirring for ~ 5 minutes, after which the product was washed several times with water and finally with acetone.

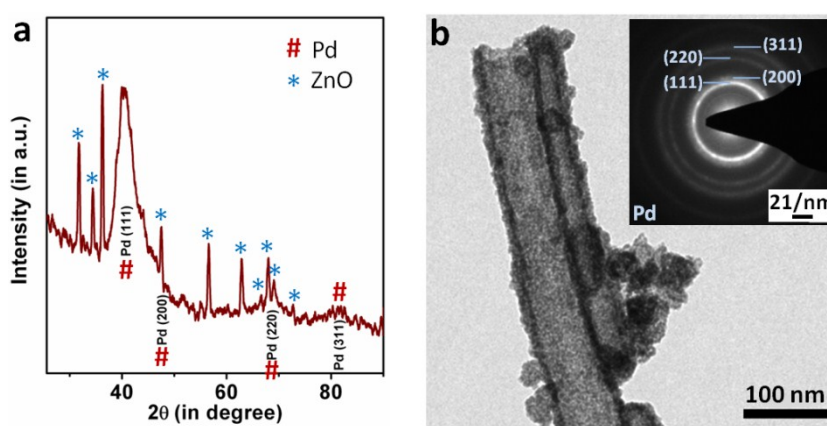


Figure S11: (a) XRD data of Pd nanotubes obtained by reduction of PdO nanotubes with NaBH_4 solution. (b) TEM image showing the obtained Pd nanotubes. Inset shows diffraction pattern from the same region.

IX. Thermal stability :

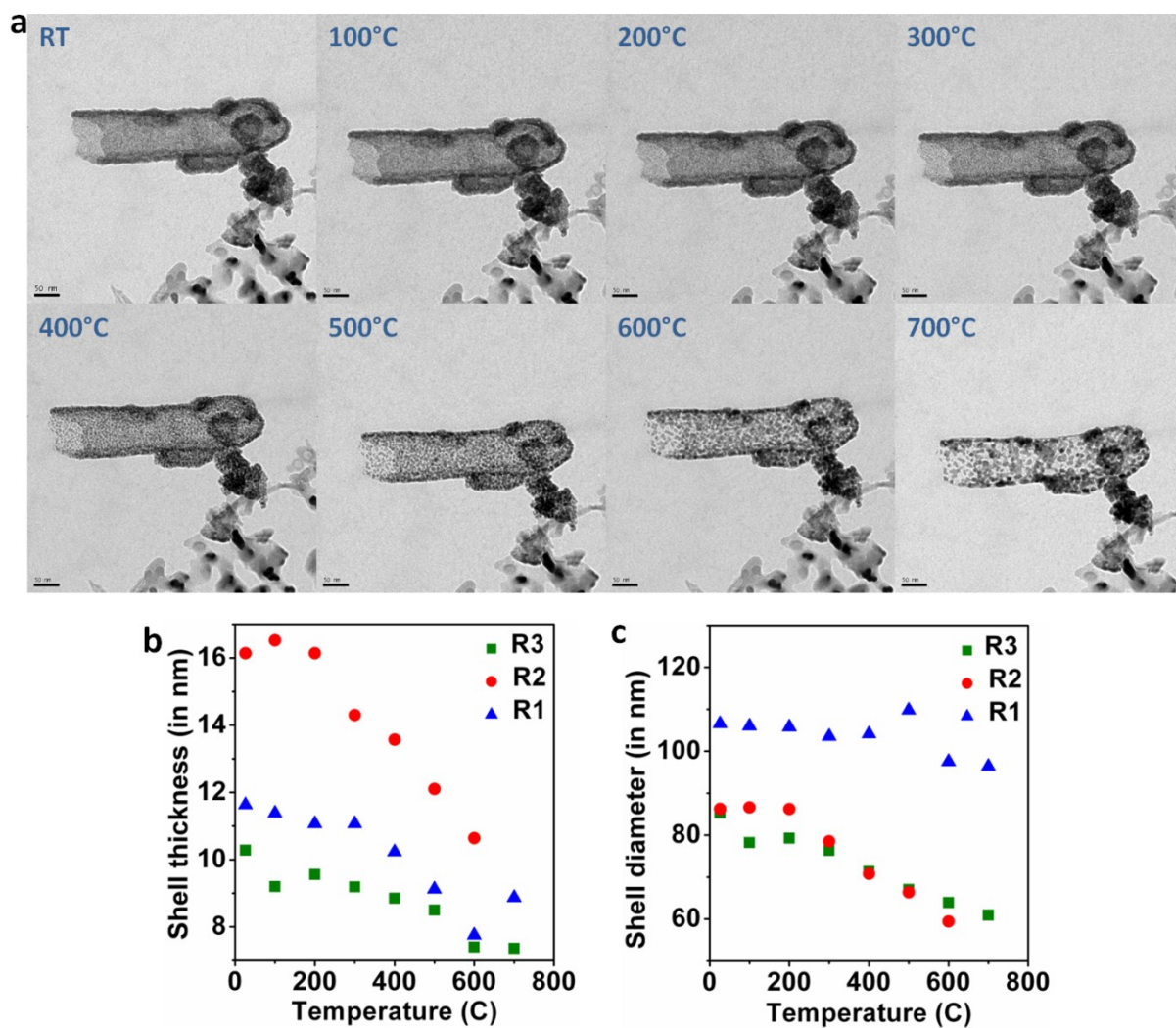


Figure S12: (a) TEM images (Scale marker- 50 nm) of the same PdO nanotube at different temperature. (b), (c) Shell thickness and diameter of 3 different nanotubes (marked as R1, R2 & R3) at different temperature.