Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Template-Free, Hollow and Porous Platinum Nanotube Derived from Tobamovirus and its Three-Dimensional Structure at the Nanoscale.

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Supporting Figure Legends

Figure S1. SEM images of (A) ToMV-Pt at concentration 0.05 mg/mL. (B) 10 µL purified ToMV-Pt was diluted 300 times with Milli-Q water, vortexed for 2 min and sonicated for 2 s. 5 µL of the resulting suspension was imaged and shows that well-dispersed ToMV-Pt rods with various length from nano to micron size visible, with the longer lengths due to end-to-end interactions.

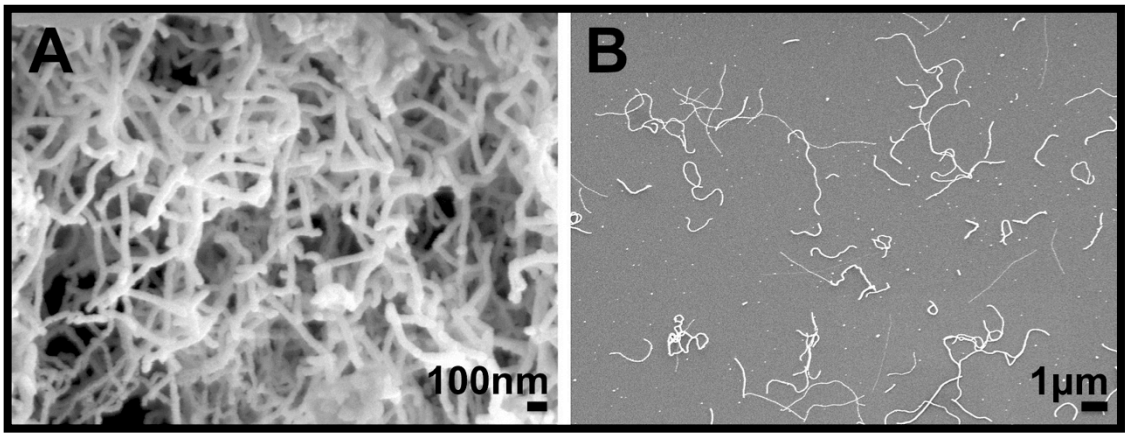


Figure S2. TEM image of ToMV stained with 3 % PTA on a SiN before (A) and after (B) heating at 250 °C in air for 30 mins. Arrows show a "shadow" left behind after decomposition of the ToMV.

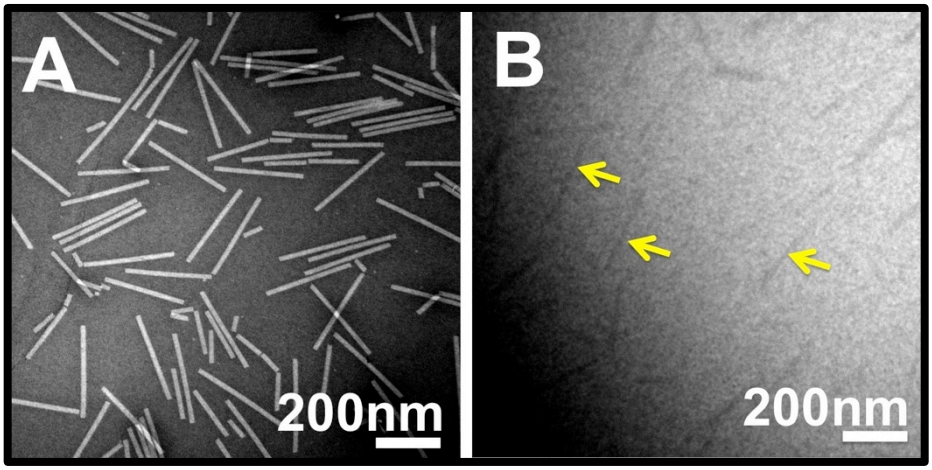


Figure S3. Comparison of Pt NTs before and after heating. TEM images were acquired from identical areas of the SiN membrane before and after annealing of ToMV-Pt at 400 °C in air for 4 h. Images A, B and C are before heating, showing outer diameter of 50(±5) nm. A', B', and C' show the same areas after heating.

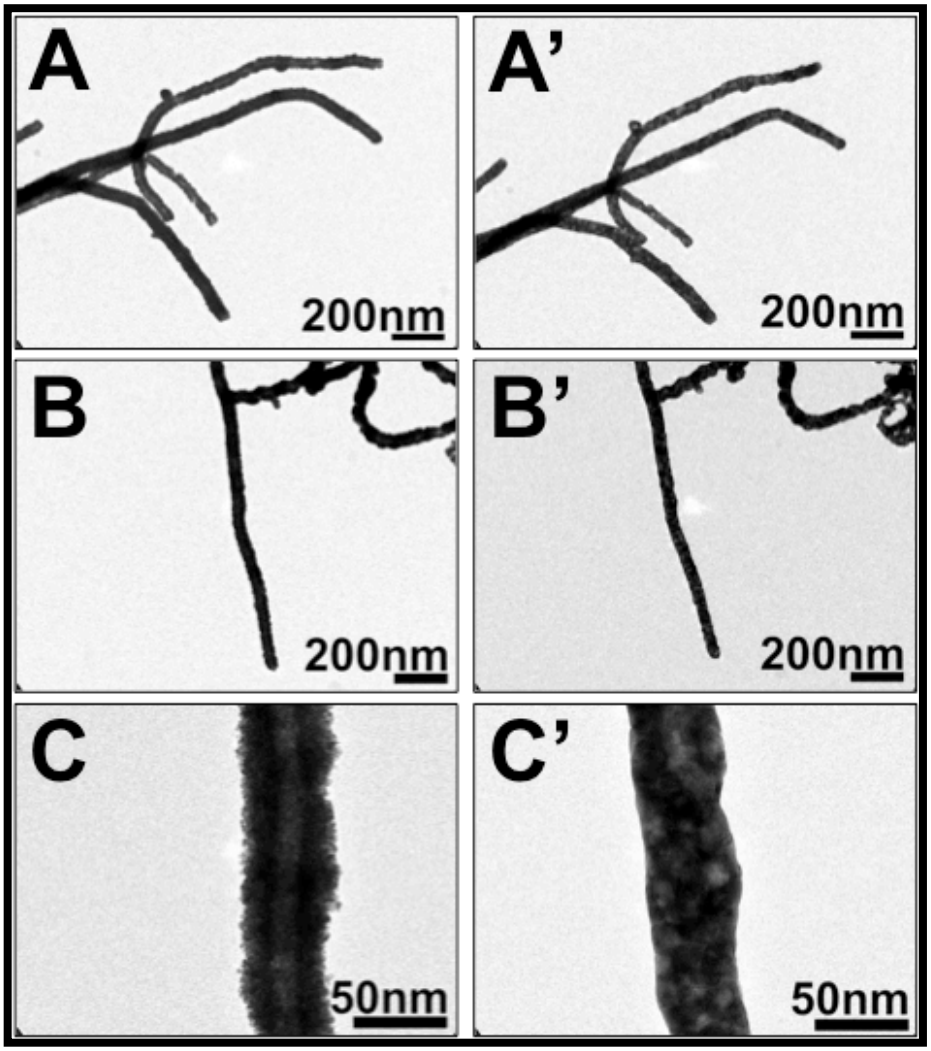


Figure S4. FE-SEM image shows that Pt-NTs have retained their morphology even after sudden cooling. Freshly prepared purified ToMV-Pt was loaded onto a silicon oxide wafer and annealed at 300 °C in air for 4 h, and cooled in atmospheric air to 25 °C over ~5 min. No visible damage is observed .

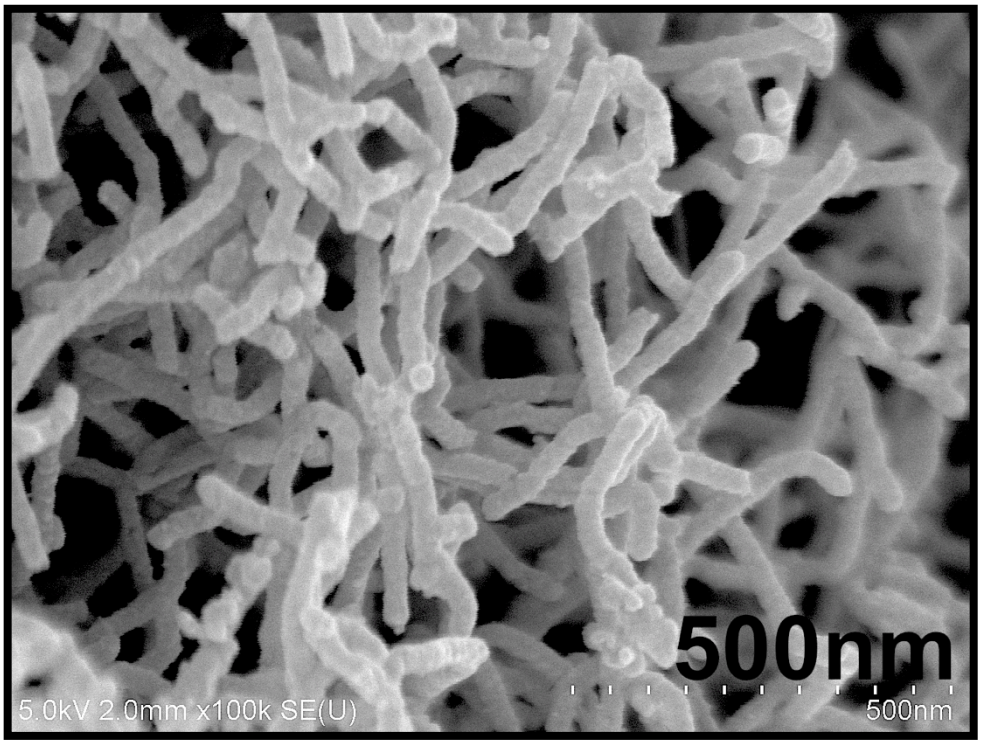


Figure S5. FE-SEM image shows Pt-NT synthesis at 400 °C in air overnight; no visible damage was observed.

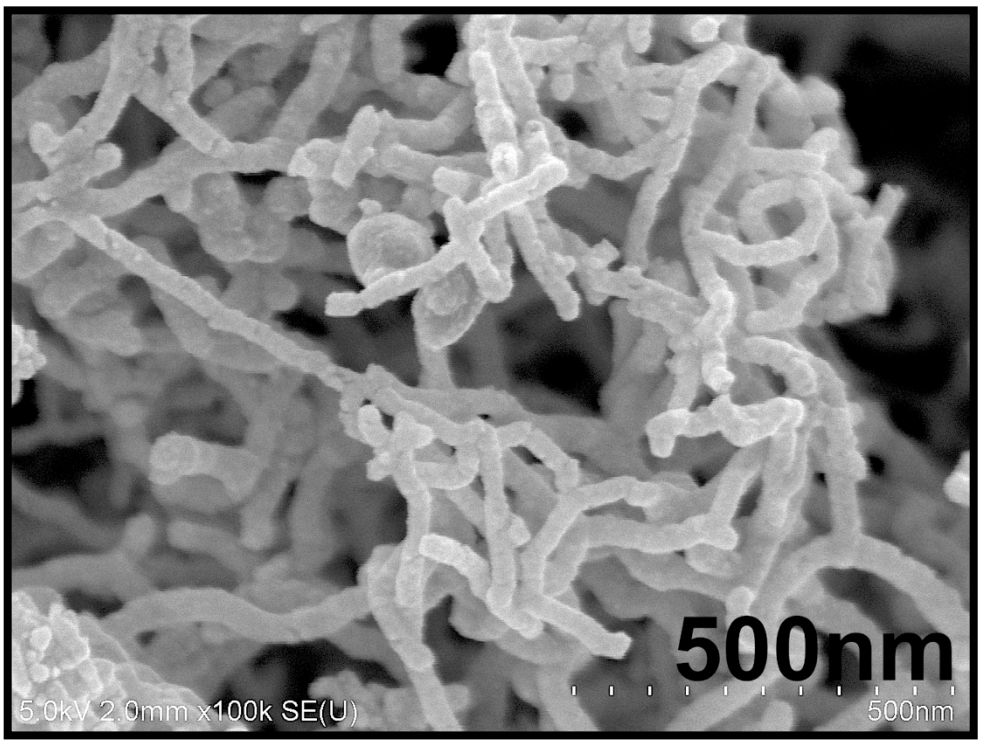


Figure S6. TEM images show the structure of the Pt-NT is preserved even after heating at 600 °C for 4 h in air. (A) A long end-to-end Pt-NT tube imaged using a 200 kV TEM. (B) The outer surfaces of the Pt-NT were smoother and Pt particles fused to form larger particles. White arrow shows presence of the inner hollow channel. (C) High resolution TEM images shows inter-fringe distances of 0.23 nm, equivalent to the Pt (111) plane of *fcc* platinum, similar to that found for ToMV-Pt and 400 °C annealed Pt-NT. (D) High-angle annular dark field scanning transmission electron microscopy (HAADF –STEM) of Pt-NT showing a tube of approximately 50 nm outer diameter with central hollow channel of approximately 12 nm (black arrow) and variously sized of voids.

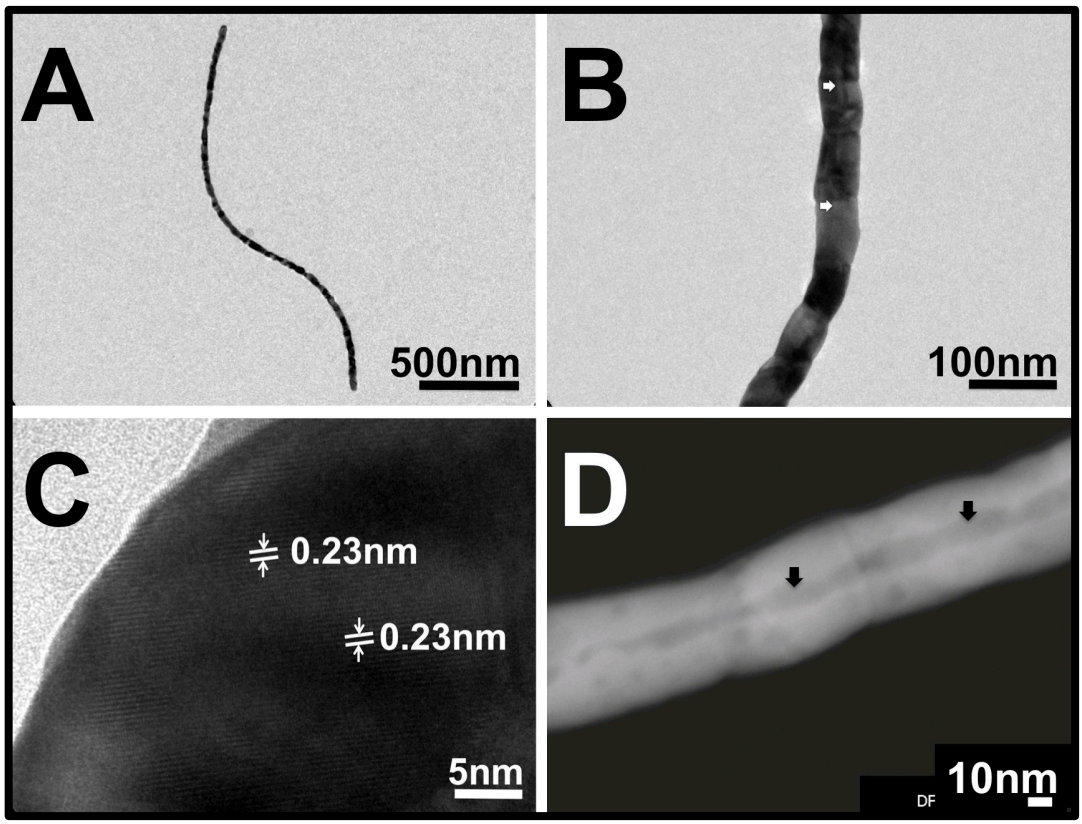


Figure S7. 2D-STEM dark field image showing Pt-NTs produced after annealing of ToMV-Pt. The hollow central channel (black line) and cavities throughout (black patches) are visible.

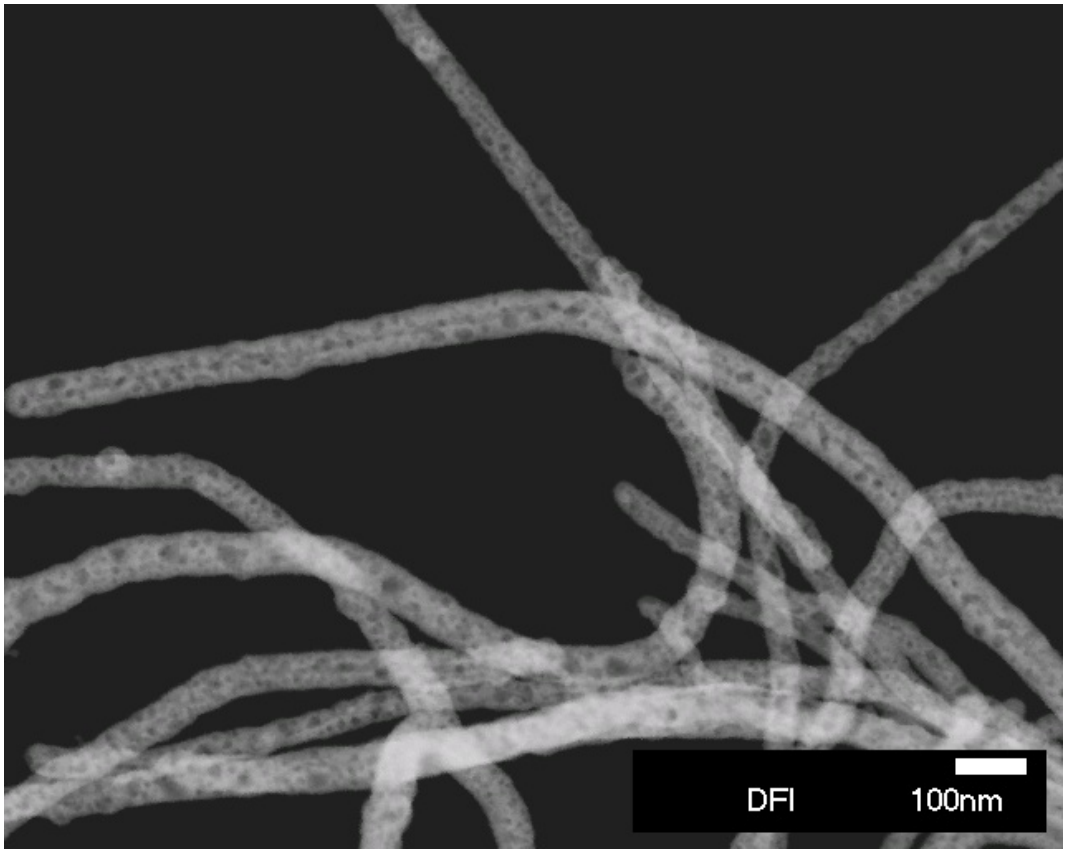


Figure S8. EDS line scanning in STEM dark field mode of ToMV-Pt. (A) Profiles were taken along the cyan colored line with five spots chosen for analysis. (B) The profile line (pink) for the middle three spots showed high platinum intensities. Silicon (Si) and nitrogen (N) signals arise from SiN membrane and copper TEM holder respectively.

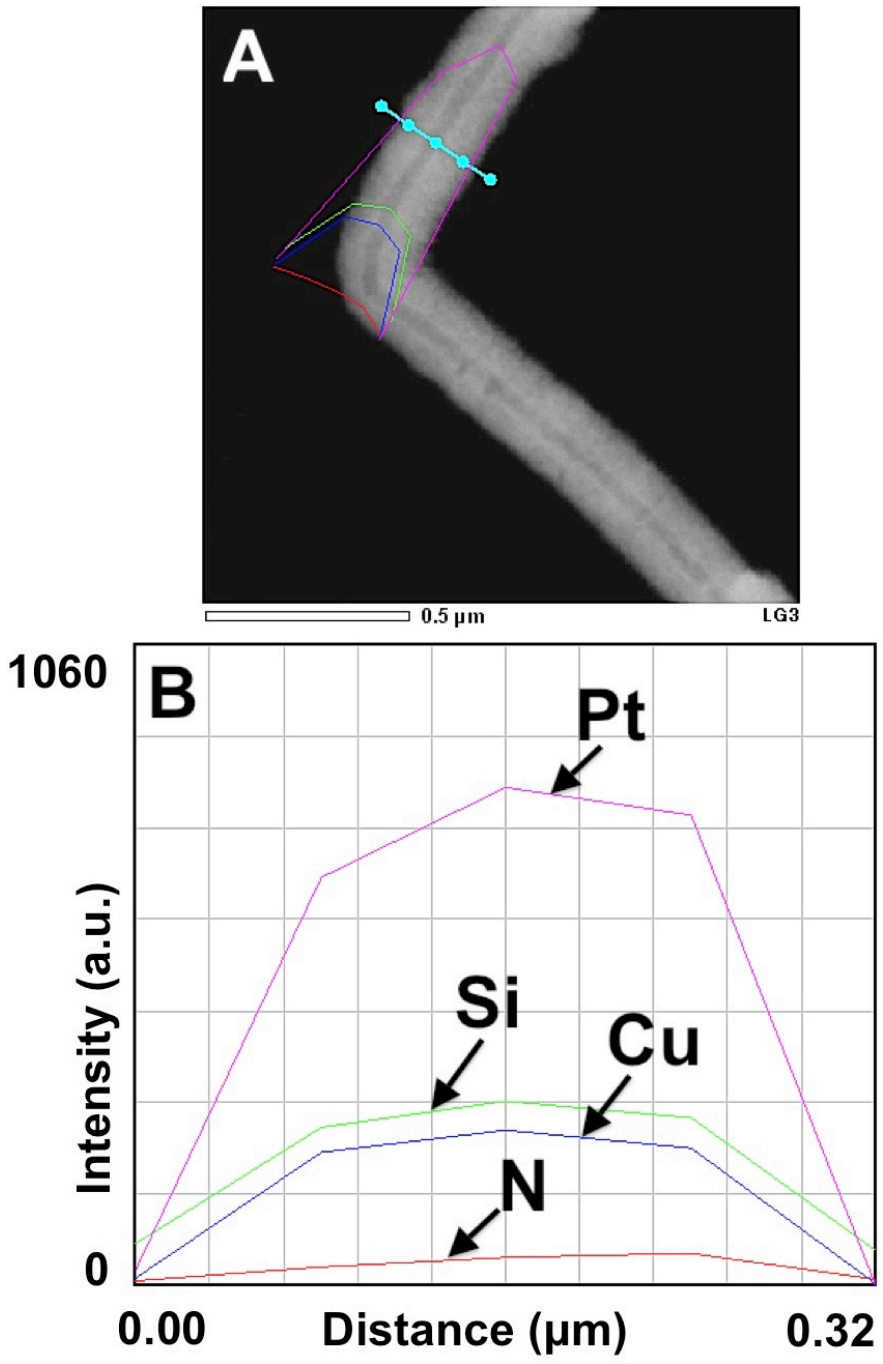


Figure S9. EDS line scanning of Pt-NT in STEM dark field mode; (A) Profiles were taken along the cyan colored line with five spots chosen for analysis. (B) The profile line (pink) for the middle three spots showed high platinum intensities. Silicon (Si) and nitrogen (N) signal arises from SiN membrane and carbon (C) and oxygen (O) signals mainly from TEM chamber respectively. A barium TEM holder is used to minimize the copper noise.

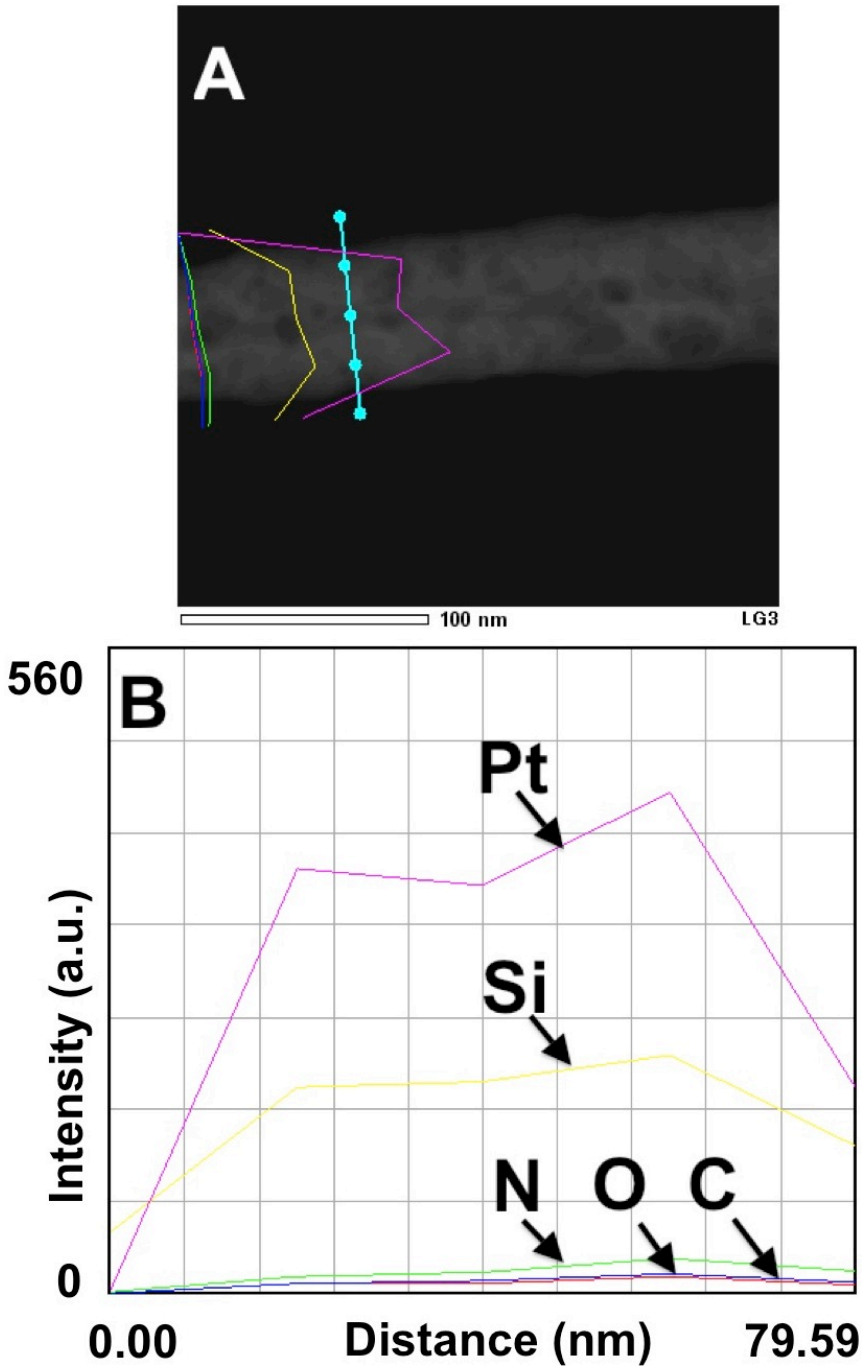


Figure S10. SEM images showing (A) ToMV-Pt and (B) Pt-NT; after argon (Ar^+) sputtering for 40 s.

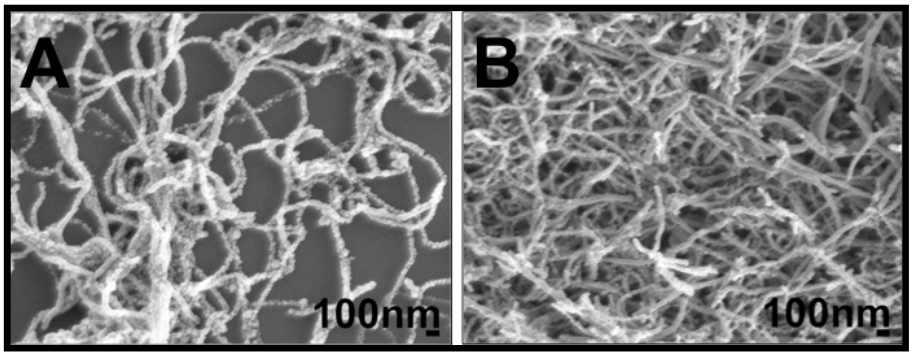


Figure S11 N 1s (~401 eV), C 1s (~285 eV) and O 1s (~532 eV) XPS spectra of ToMV-Pt. There are notable high intensity features at the high binding energy side. These are likely due to heavy charging effects due to presence of adsorbed protein, which is absent after annealing (see Figure S12).

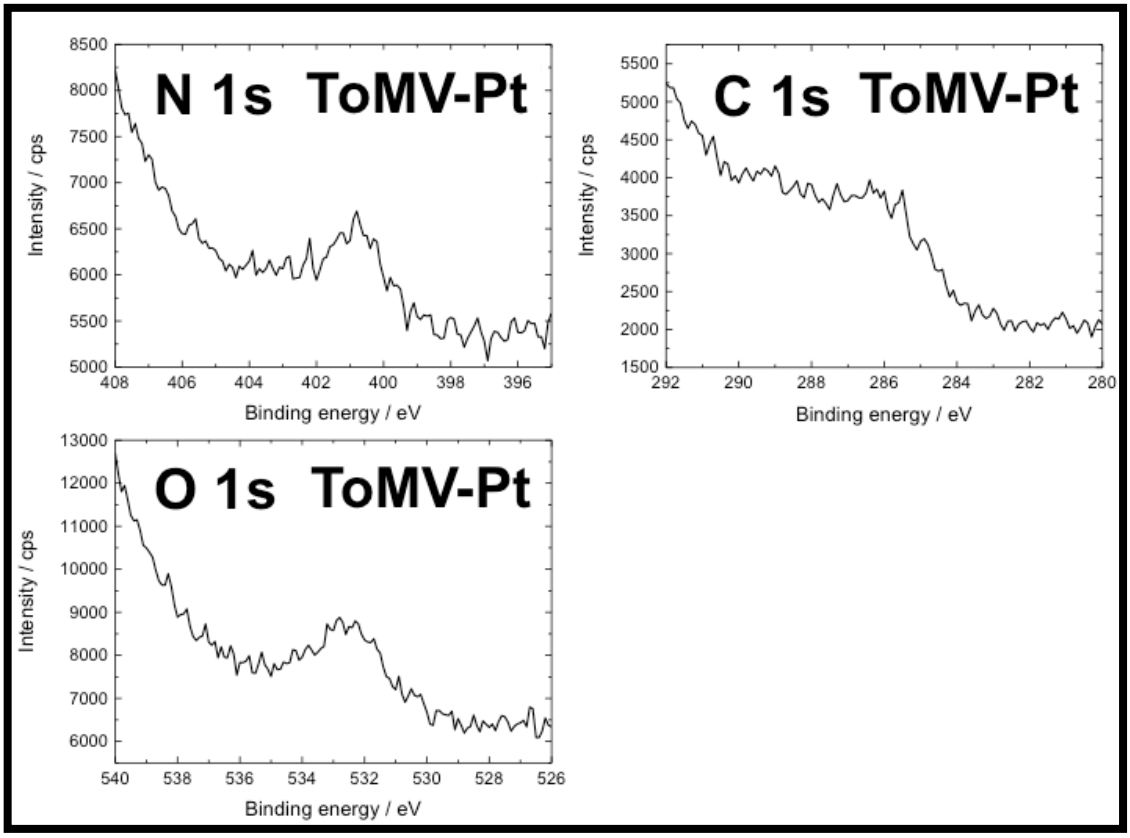


Figure S12 : N 1s (~401 eV), C 1s (~285 eV) and O 1s (~532 eV) XPS spectra of Pt-NT.

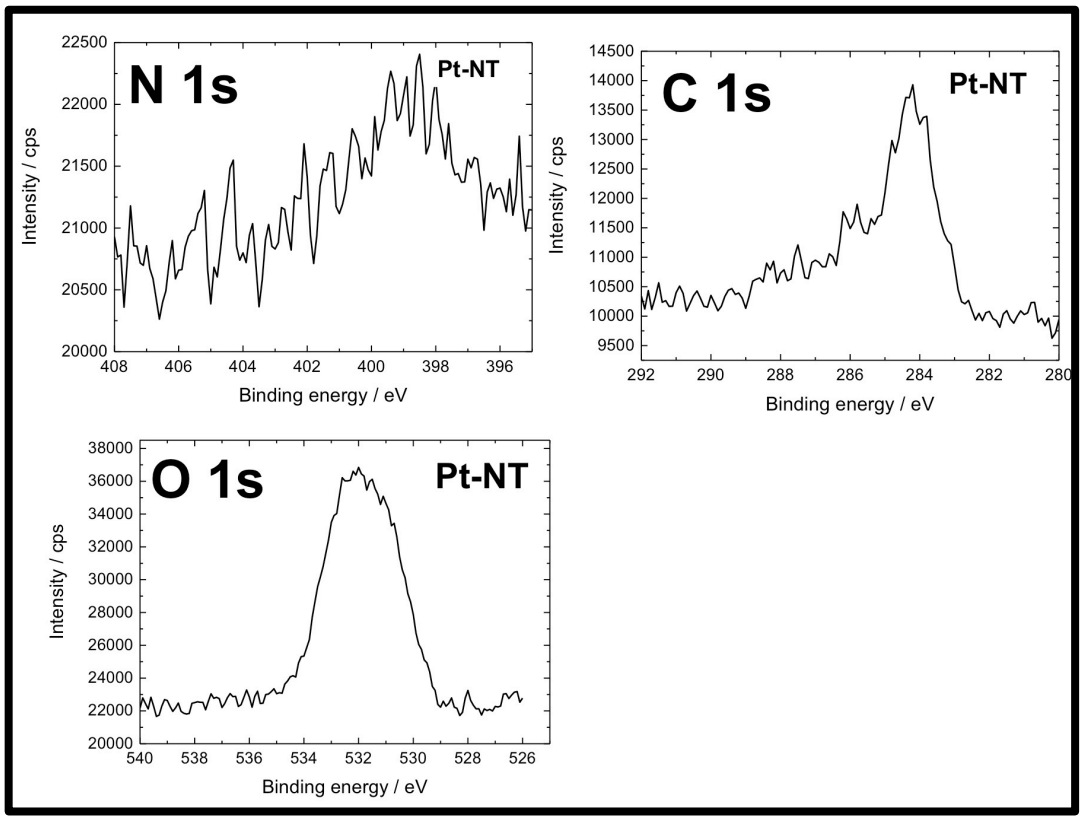


Figure S13 N1s XPS spectra of ToMV-Pt over 40 s of sputtering with readings taken at 5 s intervals. Increases in the peak area and intensity at ~401 eV were observed over time. The high intensity observed at the high binding energy side is due to the charging effect of protein as described earlier and is absent from the 5 s sputtering time point onwards.

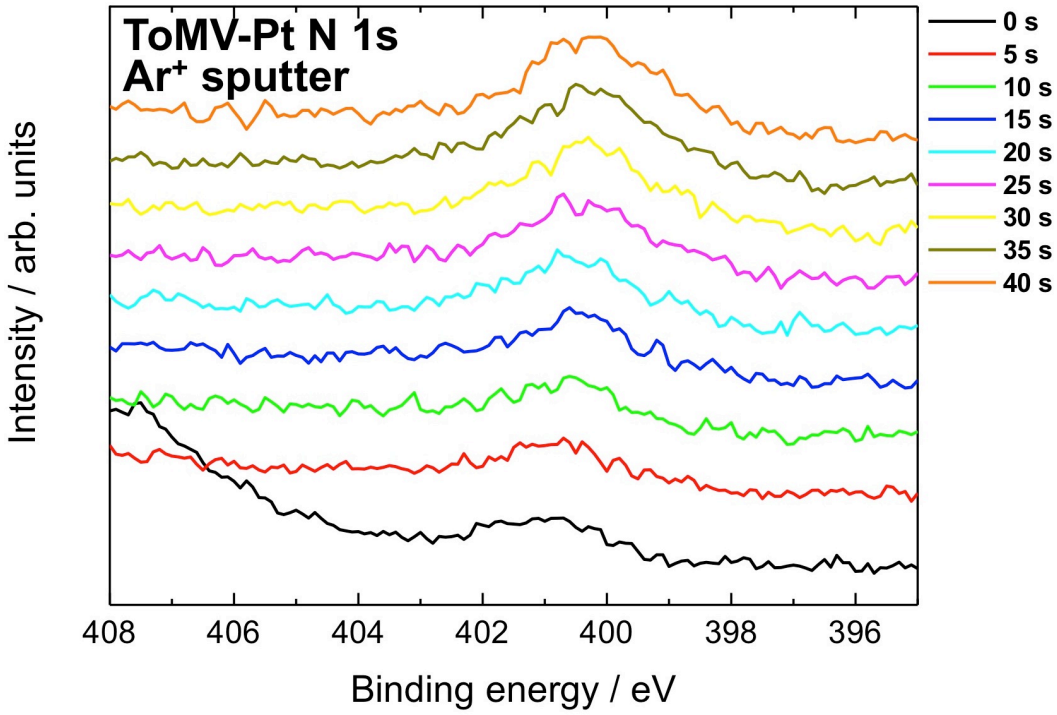


Figure S14: N1s XPS spectra of Pt-NT over 40 s of sputtering with readings taken at 5 s intervals. Increases in the peak area and intensity at ~401 eV were observed over time, indicating that nitrogenous impurities can be removed by Ar^+ sputtering treatment.

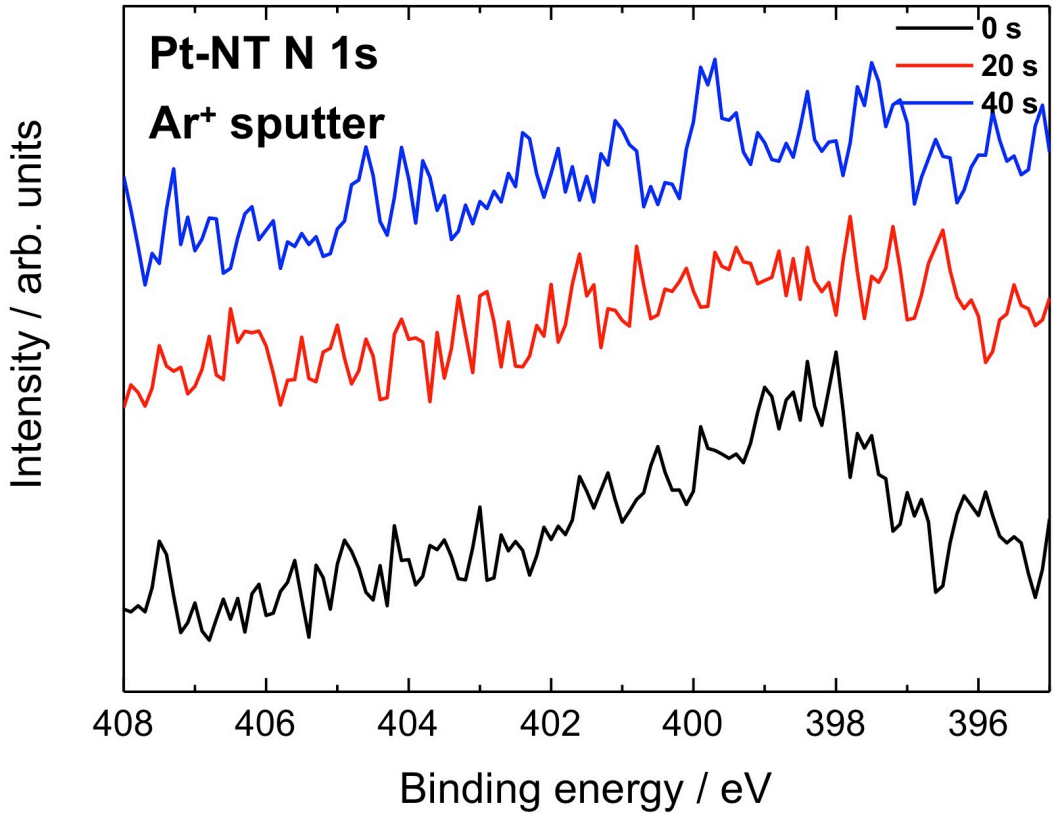


Figure S15: Comparison of the effect of sputtering time for ToMV-Pt and Pt-NT. The graphs shows peak area vs sputtering times (0 s, 20 s and 40 s). (A) shows the increasing peak area of the Pt $4f_{7/2}$ for samples ToMV-Pt (black line) and Pt-NT (red line), respectively. Results indicate an argon ion sputtering cleaning effect on the platinum surfaces and reduction of platinum complex impurity (PtO_2) leaving behind metallic Pt^0. (B) The graph of the nitrogen (N 1s) peak area vs sputtering time (s), the distance to the template ToMV is decreased due to sputtering, resulting in an increasing nitrogen signal in the case of ToMV-Pt (black); but in the case of Pt-NT (red), annealing at 400 °C likely results in removal of the nitrogenous core but leads to deposition of nitrates on the external surface which is visible at the 0 s time point but is quickly removed by sputtering.

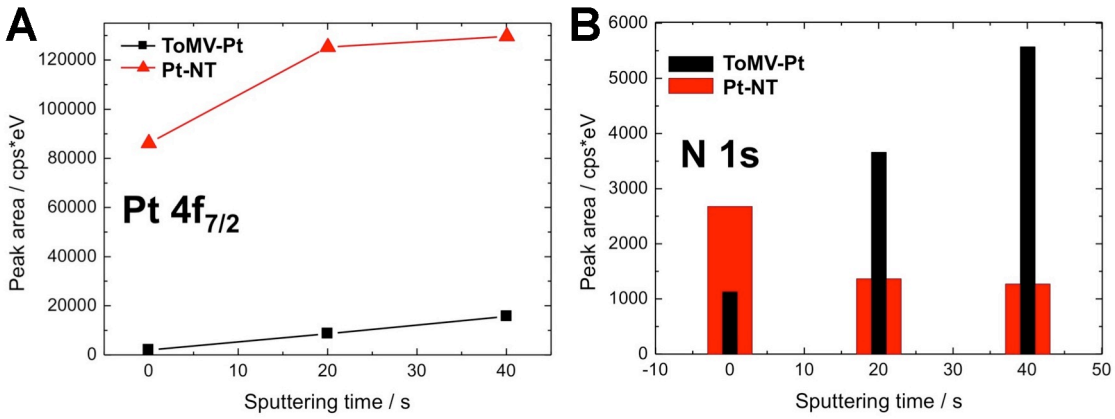


Figure S16: 3D-TEM tomographical volume reconstruction of Pt-NT with Pt shown in yellow at X-axis slice. White arrow show the central hollow channel and green arrows point to cavities reaching almost to the outside of the thick walled tube.

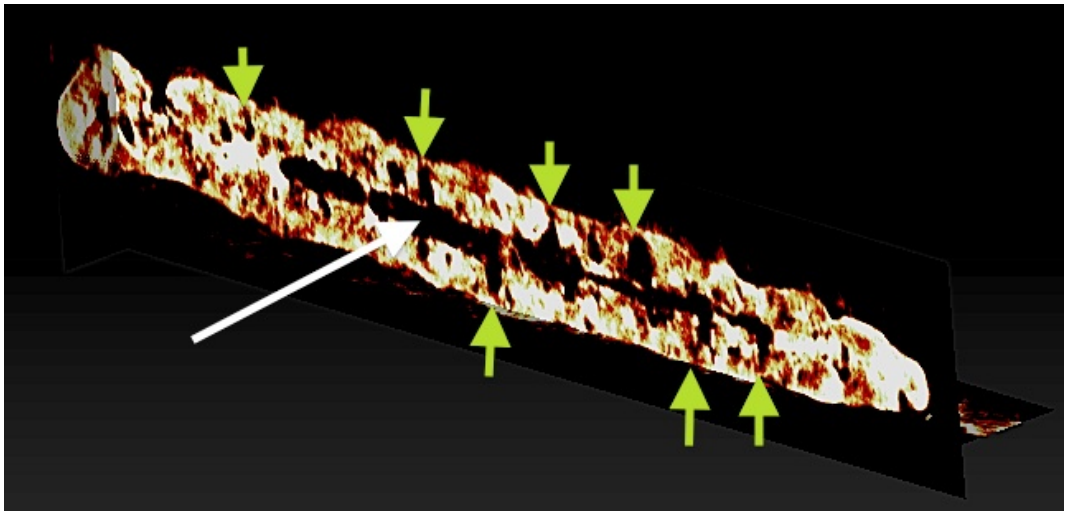
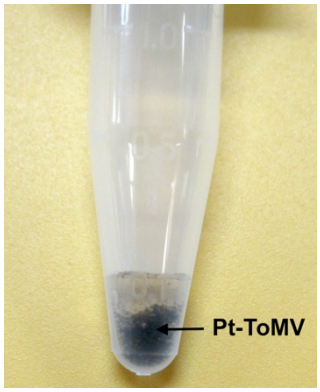


Figure S17: Completed mineralization reaction showing a black precipitate Pt-ToMV settled at the bottom of the tube.



Supplementary Movie File M1: 3D TEM of a single Pt-NT. Platinum is shown in red while cavities are shown in black. The central channel initially occupied by the virus is clearly visible.

Supplementary Movie File M2: 3D TEM data showing "slicing" of a single Pt-NT orthogonal to the longitudinal axis. Pt is shown in white with cavities shown in red.

Supplementary Movie File M3: 3D TEM data showing "slicing" of a single Pt-NT along the longitudinal axis. Pt is shown in white with cavities shown in red.