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

Journal:	*RSC Advances*
Manuscript ID:	RA-ART-05-2014-004681.R1
Article Type:	Paper
Date Submitted by the Author:	08-Aug-2014
Complete List of Authors:	Shah, Sachin; RIKEN, Heddle Initiative Research Unit Shah, Shama; RIKEN, Heddle Initiative Research Unit Ito, Eisuke; Advanced Industrial Science and Technology (AIST), Functional Thin Films Team, Research Center for Photovoltaic Technologies Heddle, Jonathan; RIKEN, Heddle Initiative Research Unit

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

Sachin N. Shah [a#*], *Shama S. Shah* [a#b], *Eisuke Ito* [c] , *Jonathan G. Heddle* [a*]

Keywords: Platinum, metallic nanotube, ToMV, mineralization, 3D-TEM, nanosensors.

Abstract

We describe a simple method for production of hollow, porous and template-free thick-walled platinum nanotubes. The external surface of a tobamovirus was mineralized via a wet chemical process to generate a uniform and dense platinum nanoparticle layer. The virus template was subsequently removed using a controlled annealing process in air. The morphology of the platinum nanotubes was studied using a range of characterization techniques that show it to be free of biological template and consisting of domains of crystalline platinum metal. High-resolution 3D-TEM topography revealed that platinum nanotubes contained a central hollow channel of diameter ~13 nm running along their lengths and showed the metallic layer to be porous with voids of sizes up to 10 nm. This method for production of hollow tubular nanostructures could be useful for production of bespoke platinum catalysts and may be adaptable to different metal and metal oxides for use in conductive, catalytic and sensor applications.

Introduction

Metal and metal oxide nanotube structures have been the subject of considerable research over the last two decades due to their wide range of potential applications[1]. Development of new approaches for the synthesis of nanotubular structures with specific shape, size and surface morphology has led to materials which show potential in electrochemical catalytic activity, optical imaging, sensing, photochemical processes and therapeutic drug delivery[2]. At the same time, the use of biological molecules to build designed nanostructures has come of age[3] and bionano-structured templates have been exploited in the synthesis of complex nano-hybrid heterogeneous materials[4] and are being developed as next-generation therapeutics[5].

Platinum along with its alloys is a well known catalyst for reactions such as hydrogen oxidation and oxygen reduction, for example in fuel cells[6]. The high cost of platinum makes efficient use of the material necessary. This can be achieved for example, by using small particle sizes to maximize surface area. The activity of such micro- and nano-sized platinum catalysts are generally dependent upon their size, shape, stability and crystallinity. Hollow crystalline nano-composites show desirable properties such as high specific surface areas, high catalytic activities and low densities in comparison to solid non-crystalline counterparts[7].

Tobacco mosaic virus (TMV) is perhaps the most commonly used rod-shaped virus in bionanoscience and belongs to the *Tobamovirus* genus which includes tomato mosaic virus (ToMV). The two viruses are highly similar, indeed ToMV can be considered as a “natural mutant” of TMV[8, 9]. In this report we used unmodified ToMV which forms a robust nanotube 300 nm in length with an outer diameter of 18 nm and a 4 nm central cavity. It, like TMV, consists of ~2130 identical protein subunits self-assembled in a helical pattern around a 6.4 kb positive sense single strand genomic mRNA (Figure 1A)[10, 11]. The coat protein has surface-accessible, repeating functional groups, which are available for chemical[12] and genetic[13, 14] manipulation. TMV itself has been used in a wide variety of bionanoscience experiments[15] and gram-scale production from infected leaves is a quite feasible in the laboratory. These features give tobamoviruses advantages over other protein-based nanotubes and their use in templated production of nanometric structures may be a useful alternative to synthetic approaches[16].

The process of metal ion deposition (‘biomineralization’) on virus capsids is generally thought to occur via electrostatic interactions between charged metals or metal oxide ligands and accessible charged amino acid residues such as glutamate and aspartate on the capsid exterior[18], which provide nucleation points. Typically, mutations in capsid proteins have to be made in order to provide further functional groups enabling reduction of metals upon addition of reducing agents, as has been demonstrated beginning with early reports on TMV[16] as well as in other capsids such as Cowpea mosaic virus[17, 18]. Pt itself has previously been mineralized on the surface of TMV which was genetically modified to furnish it with surface-exposed cysteines to provide a binding site for platinum ions. This resulted in coverage of the virus with granular layer of platinum clusters[19]. The central channel of TMV has also been mineralized to produce nanowires[20, 21] and both the internal and external surfaces have been mineralized to produce dual-walled particles [22].

Using unmodified TMV has the advantage of not requiring time-consuming genetic manipulation steps and indeed, wild-type TMV has also been used as a template for mineralization by discrete platinum nanoparticles[23]. In the work presented here, a uniform platinum layer is produced on wild-type ToMV and, taking into account mineralization time, the Pt layer appears denser (i.e. a much smaller pore size) and thicker than in most previous reports. To the best of our knowledge, we have demonstrated for the first time a template-removal method to remove ToMV, a potential source of contamination for downstream applications, from the mineralized nanotube. Template removal utilizes a simple annealing process which avoids collapse of the tubular structure. Pt-mineralized ToMV (ToMV-Pt) and post-annealing platinum nanotube (Pt-NT) were characterized using transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), X-ray photoelectron spectroscopy (XPS) and 3D TEM topography.

Results and Discussion

Analysis of ToMV-Pt

ToMV prior to modification with Pt was initially viewed using TEM and shows the expected 300 nm long tubular capsids (Figure 1A). SEM images after Pt-mineralization (Figure 1B) show individual ToMV rods with a diameter of approximately 60 nm aligned end-to-end[22, 24] with a uniform platinum coating. In a small number of cases, some Pt nodules ranging from 25 to 50 nm in diameter were observed on the surface of the ToMV-Pt rods (Figure 1B) and are most likely mineralized coat protein (CP) disks, which are formed during the sonication process after the addition of platinum precursor (K_2PtCl_4). There is also the possibility of bulk platinum nano-cluster deposition on the outer surface of ToMV during the mineralization reaction. Separated rods could be visualized by dilution of the mineralized sample followed by a short sonication pulse (Figure S1).

TEM micrographs confirm that ToMV is coated with a dense platinum layer (Figure 1 C). Selected area electron diffraction (SAED) shows the diffraction ring pattern of crystalline platinum metal (Pt^0) (Figure 1C); *d*-spacings of 0.224, 0.194, 0.137, and 0.117 nm correspond to reflections 111, 200, 220, and 311, respectively. Higher magnification TEM images (Figure 1D) show that the layer consists of a dense coating of platinum nanoparticles with inter-fringe distances of 0.23 nm, equivalent to the Pt (111) plane of *fcc* platinum. For further analysis by XRD, see sputtering section. STEM, STEM-EDS and elemental color mapping (Figure 1 E-H) confirmed the presence of a thick, uniform platinum coating.

Analysis of Pt-NT

Thermal decomposition of mineralized TMV is known to occur from 180-430 °C [25]. In this study, Pt-NT was formed by removal of ToMV by controlled annealing in a furnace at 400 °C in air for 4 h on either a thermally stable silicon oxide wafer (for SEM) or silicon nitride (SiN) membrane (for subsequent use in TEM) followed by slow cooling to room temperature. Controls with ToMV alone confirmed that it was destroyed by such a heating step (Figure S2).

We compared samples pre and post-heating (Figure 2, Figure S3) Post heating, low magnification SEM images (Figure 2A) show a large number of Pt-NTs distributed across the wafer. Field emission scanning electron microscopy (FE-SEM) (Figure 2B) clearly showed that most of the Pt-NTs retained the characteristic tubular shape even after the annealing step. TEM images show that the outer surface of the Pt-NTs are notably smoother after the annealing step. In high-resolution FE-SEM (Figure 2C) a tube was visible apparently revealing a hollow interior and a broken Pt-NT shows a hollow cavity. We were also able to mechanically break Pt-NTs by snapping of the coated silicon wafer substrate and in many cases this resulted in holes at the end of the tubes also becoming visible (Figure 2D). These results suggest that annealing to remove viral template results in the production of hollow, Pt-NT structures.

We investigated the effects of low and high temperatures on the Pt-NT structures. FE-SEM images after rapid (~5 min) cooling from 300 °C to 25 °C in air appeared to show no visible damage to the Pt-NT (Figure S4). FE-SEM images after extended (overnight) heating in air at 400 °C (Figure S5) also showed no damage or deviation from the tubular morphology. After high temperature annealing in air for 4 h at 600 °C , the tubular morphology was still retained and the Pt-NTs showed smooth outer surfaces (Figure S6).

TEM analysis of the Pt-NTs produced after the annealing step (Figure 2E-H) was carried out. Compared to prior to annealing (Figure 1D), the overall size and shape of the tubes remained unchanged but external surfaces of individual Pt particles appeared smoother and voids were visible in the Pt layer. Voids in platinum nano composites have been observed after annealing at a temperature range of 250 ºC to 600 ºC[26]. Using HRTEM we were able to investigate the crystalline characteristics of the mineralized Pt post-annealing. Crystalline regions showed inter-lattice distances of approximately 0.23 nm that can be ascribed to the Pt(111) plane. The selected area electron diffraction (SAED) ring pattern (Figure 2) is consistent with *fcc* Pt^0 Pt-NTs that are crystalline along the Pt(111) plane as revealed by Fourier transforms.

High-angle annular bright field scanning transmission electron microscopy (HAABF-STEM) and high-angle annular dark field scanning transmission electron microscopy

(HAABF-STEM) (Figure 3) show a uniform Pt-NT with a central hollow channel of diameter approximately 13 nm remaining after ToMV removal. Numerous voids in the structure are also visible (see also Figures S6 and S7)

Energy dispersive X-ray spectroscopy (EDS) analysis across the Pt-NT showed a prominent Pt signal indicative of the L and M electronic shells of the platinum atoms (Figure 3C). Elemental color mapping showed that the nanotube predominantly consists of metallic platinum (Figure 3D). Energy-dispersive X-ray spectroscopy (EDS) line scanning of ToMV-Pt in STEM dark field mode, shows a well-correlated platinum signal across the ToMV-Pt surface, indicating platinum only was deposited during the mineralization processs (for more details see Figure S8). A similar signal is seen for the Pt-NT (For more details see Figure S9).

X-ray diffraction (XRD) patterns of both ToMV-Pt and Pt-NT exhibit peaks at (111), (200), (220), (311) and (222) corresponding to diffraction from the crystalline planes of the *fcc* platinum zero state[27] (Figure 4). Additionally, the sharper and taller peaks at 39.78 (111) and 46.25 (200) for Pt-NT in comparison with ToMV-Pt indicate annealing of Pt-NT causes it to become more crystalline. Broader peaks (111) and (200) for ToMV-Pt suggest that the size of constituent particles is smaller than in the annealed tube.

Sputtering

Sputtering was carried out in an attempt to remove possible contamination arising from the biological sample in solution which may be non-speficially attached to the mineralised tube surface. Removal of such a contaminating layer should maximise the pentration depth for XPS. The Ar^+ sputtered samples for both ToMV-Pt and Pt-NT were characterized by XRD (Figure 4). There is an evident increase in the relative peak intensities of Pt planes (111), (200) in contrast to (220), and (311) peaks in sputtered samples compared to non-sputtered samples. After Ar^+ sputtering for 40 s in a XPS chamber both samples were imaged by SEM (Figure S10) followed by XRD. The X-ray diffraction (XRD) and scanning electron microscopy (SEM) studies after sputtering of both ToMV-Pt and Pt-NT indicates the presence of the Pt *fcc* lattice.

During sputtering, samples were studied at time intervals of 5 s up to 40 s using XPS (Figure 5). XPS data for ToMV-Pt and Pt-NT were acquired in the Pt 4f region (Figure 5A, B). Due to the lower electric conductivity of ToMV-Pt from adsorbed proteins, the sample was charged up by photoemission and additional broad features were observed at the higher energy side. Such sample charging was also seen in other regions of XPS spectra (see below). The peaks of the lowest binding energy of the ToMV-Pt and Pt-NT appeared at 71.2 eV, respectively, which is assigned to Pt $4f_{7/2}$ peak of metallic platinum, 71.0 eV. This suggests that platinum particles are mostly in the metallic zero state (Pt^0). From the peak fitting analysis, an additional feature at 72.5 eV (Figure 5B) can be seen, which is assigned to Pt^{2+}. Similarly, the binding energy for Pt $4f_{5/2}$ can be seen at 74.8 eV and 76.8 eV (Figure 5B). Since these samples were exposed to air before loading to the XPS chamber, the sample surface of the tubes are expected to be oxidized.

After argon sputtering both Pt-ToMV and Pt-NT show a clear increase in the intensity of the Pt $4f_{7/2}$ peak at 71.2 eV, for the metallic platinum state (Pt^0)[28, 29] indicating reduction of platinum(II) oxide impurities, leaving behind metallic platinum (Figure 5C). ToMV-Pt was considered in more detail with measurements taken every 5 s (Figure 5D). Here the intensity of this peak after 40 s of sputtering is over five-fold that at the 0 s time-point. Sputtering causes a drastic change of the Pt4f spectra, probably due to a surface cleaning effect. The sharp Pt $4f_{7/2}$ peak at 71.2 eV increased with the sputtering time, suggesting that the surface adopted the metallic state due to ion bombardment. A similar effect is also observed with the Pt-NT sample although the increase (approx.1.5 times) is smaller (Figure 5C).

XPS also showed that the ToMV-Pt and Pt-binding energies of N1s , C1s and O1s, had main peaks located at ~401 eV , ~285 eV and ~532 eV respectively (Figures S11, S12).

XPS analysis is able to provide sensitive information at depths of approximately 1 nm-10 nm[30, 31]. This allows us to probe for the presence of the buried protein template via the N1s peak at 401 eV. Results indicate the presence of protonated amino groups in the case of the 40 s argon sputtered sample of ToMV-Pt which is absent in Pt-NT. Argon sputtered, N1s spectra for ToMV-Pt and Pt-NT are shown in Figures S13 and S14 respectively. The N peak would be expected to be absent in non-N containing materials. In the case of ToMV-Pt the increase in the intensity of the N1s and Pt $4f_{7/2}$ peaks after sputtering can be attributed to the decrease in the distance between the outer surface of the Pt particle and the central viroid coat protein core. A comparison of Pt $4f_{7/2}$ and N1s peaks areas between ToMV-Pt and Pt-NT (Figure S15) shows that for Pt-NT the difference before and after sputtering is less dramatic than for ToMV-Pt (Figure S15A). The non sputtered Pt-NT shows a greater N1s peak area but this decreases rapidly shortly after sputtering begins. We attribute this to the removal of protein-derived nitrogenous contamination from the exterior of the nanotube. In contrast, ToMV-Pt shows increasing N1s area as sputtering proceeds presumably due to the surface cleaning effect decreasing the distance between the nanotube surface and the buried protein core (Figure S15B).

3D analysis

Due to the limits of standard microscopy techniques for understanding the three-dimensional structure of the Pt-NTs, we analyzed them using three-dimensional TEM (3D-TEM). Images were acquired from -57.6° to +65° with 125 images generated for every 1° tilt. The volume-reconstructed Pt-NT topographical image (Figure 6 A) shows a tubular shaped Pt-NT with a central hollow channel. A large number of voids in the structure are also visible. Lateral and orthogonal slicing of the Pt-NT (Figure 6 B-C) shows the central hollow channel running along its length. Line profile measurements showed the outer and inner diameters of

Pt-NT to be 42 nm and 13 nm respectively (Figure 6D). The cross sectional image (Figure S16) shows a number of voids, some of which appear to be contiguous with the central cavity.

3D topographical movies of the results show overall structure of the Pt-NT to be straight with a thick coating of regular thickness with some surface roughness, the central cavity is clearly present and also does not appear to show large variation in diameter (Electronic Supporting Information M1). Numerous voids in the Pt layer are particularly clear when slices are taken through the tube structure orthogonal to and parallel to the long axis (Electronic Supporting Information M2 and M3 respectively).

Experimental Details

Platinum mineralization of tomato mosaic virus (ToMV-Pt):

100 µL of 0.5 mg/mL ToMV was dialyzed using a Slide-A-Lyzer mini dialysis tube with a 10,000 MWCO (Thermo Scientific) for 24 hours against milli-Q water followed by two changes of water. Dialyzed ToMV suspension in a 1.5 mL eppendorf tube was sonicated in a bench-top sonication bath (Branson 1510 DTH, 40 kHz) for 20 s before the addition of 10 mM potassium terachloroplatinate (II) (K_2PtCl_4; Aldrich chemicals, Japan). The Platinum mineralization reaction was carried in a 100 µL aliquot of dialyzed ToMV and 5 mM aqueous K_2PtCl_4. The suspension was mixed completely by vortexing for one min. and sonication for 20 s. The tube containing the suspension was wrapped in aluminum foil and incubated over night at 25 °C. The overnight-incubated reaction mixture was mixed by vortexing then sonicated for 30 s before addition of 2 µL of freshly prepared 10 mM dimethylamine borane (DMAB; Wako Chemicals, Japan). The reaction solution was gently mixed with a pipette for 5 min. Reduction of K_2PtCl_4 was ensured by incubation for a further 2 h at room temperature (25 °C) with gentle mixing applied every 30 min. A black precipitate of platinum mineralized ToMV (ToMV-Pt) settled on the bottom of the eppendorf tube (Figure S17).

Purification of platinum mineralization of tomato mosaic virus (ToMV-Pt): The black ToMV-Pt precipitate was centrifuged (Eppendorf-AG22331 minispin) at 2000 g for 2 min. The pellet was washed three times with 100 µL Milli-Q water and re-suspended in 100 µL of water. Unreacted platinum salts, reducing agent and other impurities were removed by dialysis using a Slide-A-Lyzer mini dialysis system (10,000 MWCO; Thermo Scientific) for 6 h, with Milli-Q water exchange every 2 h.

Synthesis of hollow, porous and thick walled platinum nanotube (Pt-NT): A 30 nm silicon nitride membrane (SiN) (0.1mm x 0.1mm window size; 200 µm substrate thickness: AGS171-1T from Agar Scientific) was subject to hydrophilic treatment (JEOL, HDT-400) for 300 s. A 4 µL drop of platinum mineralized ToMV (Figure 1B) suspension was placed on the SiN membrane, dried in air, and washed with 25 µL Milli-Q water. The SiN membrane was dried in air before imaging by TEM (JEOL JEM-2100F and JEOL JEM-1230). For removal of template ToMV, the same SiN membrane was heated in air with an initial 1 h heat step from 25 °C to 400 °C followed by holding for 4 h at 400 °C . The SiN membrane was then allowed to cool slowly to room temperature and used for further characterization.

Similarly, platinum nanotubes (Pt-NT) were synthesized on a thermally stable silicon oxide wafer (cut from a 4" x 0.50 mm, P-type wafer consisting a 300 nm SiO_2 layer on Si (100), 1SP R:0.01-0.05 Ω.cm (Item number SI-SO-Ba100D05C1-300 nm-1; MTI corporation, USA)). The wafers were treated for 30 min in an ultrasonicator (Branson 1510 DTH) in acetone, 2-propanol and water at 40 kHz. The wafer was cleaned in 150 mL water, 5 mL concentrated HCl heated up to 70 °C followed by slow additon of 5 mL H_2O_2 (30%). After 10 min the wafer was thoroughly washed with Milli-Q water and then dried in a nitrogen stream. Hydrophilization was achieved by a 300 s treatment in a hydrophilic treatment device (JEOL, HDT-400)]. A 5 µL droplet of platinum mineralized ToMV (Figure 1A) was deposited on a pretreated, 6x6 mm thermal oxide Si wafer and allowed to air-dry. The wafer surface was then washed with 1000 µL Milli-Q water and air dried, then imaged on scanning electron microscopy (SEM, JSM6330F). For ToMV removal, the same wafer was annealed in air at 400 °C in control temperature furnace for 4 h as mentioned above. The wafer containing (Pt-NT) was then imaged using a Hitachi S-4200 FE-SEM.

2D Transmission Electron microscopy (TEM): A 4 μL droplet of purified, platinum mineralized ToMV sample was placed on a silicon nitride membrane (Agar Scientific, 30 nm SiN on 200 μm, 0.5 mm x 0.5 mm), dried in air and washed with 25 μL Milli-Q water. The unstained dried SiN membrane was imaged before and after the annealing process using a TEM model JEOL JEM-1230. High-resolution images (HRTEM), STEM, SAED were recorded using a TEM model JEOL JEM-2100F.

3D TEM: Pt-NT sample on a SiN membrane was imaged using a JEM-2100F High Resolution TEM at JEOL Ltd (Akishima, Tokyo, Japan). The applied accelerating voltage was 200 kV and images were captured using a Gatan USC camera. The 3D TEM tomography tilt series data were acquired using data were software acquisition by recorder composer and visualize-kai software packages. Data was acquired for tilt angles from -57.6° to +68.0°.

Sputtering: We studied the effect of Argon (Ar^+) sputtering on ToMV-Pt and Pt-NT sample on silicon wafers using XPS (ThetaProbe, Thermo Fisher Scientific). Argon sputtering was carried out using an ion gun (EX-05) in a XPS instrument with a 1 μA beam current of 1 keV ions.

Conclusion

In this work we demonstrated a facile method for coating wild-type ToMV with a dense, regular layer of Pt of thickness ~20 nm followed by removal of the template via annealing at 400 ºC to thermally degrade biological material. Mineralization was confirmed by TEM and elemental analysis by EDS showed the presence of platinum metal. STEM and HRTEM showed a porous platinum layer present in both ToMV-Pt and Pt-NT which are crystalline in nature with lattice *d*-spacing of 0.23 nm. While the presence of the mineralised layer makes unambiguous demonstration of template removal difficult, our data point towards thermal degradation of ToMV in agreement with previous studies[20]. Thus the annealing step removes protein to create a central hollow channel ~13 nm in diameter as well as a large number of voids within the Pt layer itself. The XRD and XPS chemical component analysis of both ToMV-Pt and Pt-NT samples before and after argon sputtering confirmed the presence of diffraction peaks consistent with crystalline *fcc* metallic Pt. The 3D TEM results are, to the best of our knowledge, the first such analysis of a tobamovirus- templated nanotube and reveal a regular-shaped nanotubular structure. The hollow nature, porous surface morphology and presence of voids suggests that this thermally stable tube can offer high surface areas while using little material, properties which may prove useful for mass exchange and gas diffusion.

Acknowledgements

The authors are grateful to M. Kobayashi for gift of ToMV and to RIKEN, Center for Emergent Matter Science, Material Characterization Support Unit for TEM, EDS, SAED, SEM and XRD instrument facilities and for technical support. We are also grateful to Hye Ryung Byon for use of furnace equipment. Sachin Shah acknowledges this work was partly supported by a Wako-RIKEN, Presidential Grant Award, Japan for the year 2012-2013. Shama Shah was funded from RIKEN, Junior Research Associate (JRA) and Jonathan Gardiner Heddle and Sachin Shah were funded by RIKEN Initiative Research Funding awarded to Jonathan Gardiner Heddle.

Figure Legends

Figure 1. Analysis of ToMV: (A) TEM image of ToMV stained with 2% Phosphotungstic acid (PTA). (B) SEM image of purified platinum coated ToMVs; inset, SEM image of single end-to-end mineralized complex after a 200-fold dilution of the sample into Mill-Q water and sonication for two seconds. (C) TEM images of the ToMV-Pt on a SiN grid without negative

stain. Inset, SAED pattern of crystalline platinum nanoparticles on ToMV. (D) High-magnification TEM image shows ToMV in gray (white arrow) covered with a darker, high density platinum nanoparticle layer (black arrow). Pt particles are of approx. diameter 3-5 nm. Inset is a HRTEM image showing lattice fringes, demonstrating the crystalline nature of the platinum nanoparticles. (E) High-angle annular STEM bright field image of a single ToMV-Pt particle formed by end-to end assembly. (F) Dark field image showing ToMV (central black line) of approx. 16 nm diameter, covered with an approx. 35 nm platinum coating (light gray). (G) STEM-EDS analysis of the highlighted region in panel B showing standard platinum peaks with additional silicon peak arising from the SiN grid and copper from the TEM copper grid holder. (H) Elemental mapping confirmed presence of platinum metal (shown in red).

Figure 2: SEM images of unstained Pt-NTs after annealing in air at 400 °C for 4 h with slow cooling over 2 h to room temperature. (A) Low-magnification SEM image. (B) Higher magnification showing Pt-NTs of ~45 nm diameter and several 100 nm in length. (C) High-magnification SEM image showing apparent hole at the terminus of the tube (highlighted by yellow circle) and a broken tube (black rectangle); inset, zoom of the area in the black rectangle showing a Pt-NT apparently broken to reveal a 'hollow' interior. (D) Cross-sectional view of mechanically broken Pt-NTs; the holes at the end of tubes are highlighted by yellow circles; inset, a highly-magnified image of the end of a tube. Panels E-G show TEM images of unstained Pt-NT after annealing in air of the same areas of the samples shown in figure 1C and D respectively. (E) low magnification image showing a number of Pt-NTs. (F) A single Pt-NT of outer diameter approx. 40 nm shows mottled areas post-annealing at 400 °C likely due to the presence of voids. (G) The ToMV-Pt from figure 1D, after annealing in air displays a smooth outer surface with voids. Inset shows a HRTEM image of the highlighted square (white) showing lattice fringes with *d*-spacing 0.23 nm. (H) Selected area

electron diffraction patterns of the Pt-NT shows crystalline platinum morphology without any distortion. Inset, FFT image captured from HRTEM image shows that platinum nanoparticles in the Pt-NT demonstrate the (111) orientation of metallic platinum (Pt^0).

Figure 3. (A) High-angle annular bright field scanning transmission electron microscopy (HAABF-STEM) of Pt-NT showing a tube of approximately 60 nm diameter. (B) High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) reveals the central hollow channel of approximately 12 nm diameter (dark grey) as well as pores and voids ranging from 3 nm to 25 nm in diameter. (C) Characteristic platinum peaks recorded from a typical STEM-EDS scan of Pt-NT. Silicon peak is due to the SiN membrane. (D) Elemental mapping confirmed the tube consists of platinum metal (red). (Barium TEM holder used).

Figure 4. Representative XRD patterns of the solid samples. (A) Corresponds to platinum mineralized ToMV (blue line) with the same sample after sputtering for 40 s (red line). (B) As synthesized Pt-NT after annealing (green line) and followed by sputtering for 40 s (black line).

Figure 5. XPS spectra showing representative narrow range plots of the Pt 4f XPS spectra. (A) Shows as synthesized ToMV-Pt, (B) taken after annealing in air. (C) The effects of Argon (Ar^+) sputtering were studied after time 0 s (green), 20 s (magenta) and 40 s (cyan) for mineralized TOMV-Pt and after time 0 s (black), 20 s (red) and 40 s (blue) for Pt-NT. (D) Argon (Ar^+) sputtering of TOMV-Pt from 0 s to 40 s at 5 s time intervals.

Figure 6: Pt-NT topographical images showing 3D-TEM volume reconstruction. Pt-NT topographical images were acquired one per degree in the range -57.6° to +65°. (A) Pt-NT

showing Pt (red) with central black channel (white arrow) containing a number of voids (some of which are highlighted by yellow arrows). Inset is an enlarged image of the end of the tube showing the central cavity. (B) Cross section of the central channel (red arrow); hollow channel (white arrow) and the existences of nano-sized pores on the walls of the Pt-NT (yellow arrows). (C) Slices orthogonal to the long axis showing the central hollow channel (white arrow) and a large number of pores (blue arrows) along the length of the tube. (D) A single 2D TEM image of the Pt-NT from the tilt series (left panel). Line profile of the Pt-NT showing the outer and inner diameters to be ~42 nm and ~13 nm respectively. For movies of A-C see electronic Supporting materials (M1-M3).

Notes and references

* To whom correspondence should be addressed: E-mail: heddle@riken.jp; s.shah@riken.jp

[a] Heddle Initiative Research Unit, RIKEN 2-1, Hirosawa, Wako, Saitama 351-0198, Japan.

[b] Department of Life Science and Medical Bioscience, Waseda University, 2-2 Wakamatsu-cho, Shinjuku, Tokyo 162-8480, Japan.

[c] Functional Thin Films Team, Research Center for Photovoltaic Technologies, Advanced Industrial Science and Technology (AIST), Higashi 1-1-1, Tsukuba, Ibaraki 305-8565, Japan.

[#] These authors contributed equally

† Electronic Supplementary Information (ESI) available.

1. T. E. Kijima, *Inorganic and Metallic Nanotubular Materials*, Springer, Berlin.
2. J. Pérez-Juste, I. Pastoriza-Santos, L. M. Liz-Marzán and P. Mulvaney, *Coordin. Chem. Rev.*, 2005, **249**, 1870-1901.
3. J. G. Heddle, *Nanotechnology, Science and Applications*, 2008, **1**, 67-78.
4. J. K. Pokorski and N. F. Steinmetz, *Mol. Pharm.*, 2011, **8**, 29-43.
5. N. F. Steinmetz, *Nanomed-Nanotechnol.*, 2010, **6**, 634-641.
6. N. M. Markovic, in *Handbook of Fuel Cells – Fundamentals, Technology and Applications*, eds. W. Vielstich, A. Lamm and G. H. A., John Wiley & Sons Ltd, New York, 2003, vol. 2, p. 374.
7. S.-W. Kim, M. Kim, W. Y. Lee and T. Hyeon, *J. Am. Chem. Soc.*, 2002, **124**, 7642-7643.
8. A. J. Gibbs, J. S. Armstrong and M. J. Gibbs, *Arch. Virol.*, 2004, **149**, 1941-1954.

9. M. Kobayashi, M. Seki, H. Tabata, Y. Watanabe and I. Yamashita, *Nano Lett.*, 2010, **10**, 773-776.
10. K. Namba, R. Pattanayek and G. Stubbs, *J. Mol. Biol.*, 1989, **208**, 307-325.
11. K. Namba and G. Stubbs, *Science*, 1986, **231**, 1401-1406.
12. M. Knez, M. Sumser, A. M. Bittner, C. Wege, H. Jeske, T. P. Martin and K. Kern, *Adv. Funct. Mater.*, 2004, **14**, 116-124.
13. W. O. Dawson, D. L. Beck, D. A. Knorr and G. L. Grantham, *Proc. Natl. Acad. Sci. USA*, 1986, **83**, 1832-1836.
14. H. Yi, S. Nisar, S.-Y. Lee, M. A. Powers, W. E. Bentley, G. F. Payne, R. Ghodssi, G. W. Rubloff, M. T. Harris and J. N. Culver, *Nano Lett.*, 2005, **5**, 1931-1936.
15. X. Z. Fan, E. Pomerantseva, M. Gnerlich, A. Brown, K. Gerasopoulos, M. McCarthy, J. Culver and R. Ghodssi, *J. Vac. Sci. Technol. A*, 2013, **31**, 050815-050824.
16. W. Shenton, T. Douglas, M. Young, G. Stubbs and S. Mann, *Adv. Mater.*, 1999, **11**, 253-256.
17. S. N. Shah, N. F. Steinmetz, A. A. A. Aljabali, G. P. Lomonossoff and D. J. Evans, *Dalton T.*, 2009, 8479-8480.
18. N. F. Steinmetz, S. N. Shah, J. E. Barclay, G. Rallapalli, G. P. Lomonossoff and D. J. Evans, *Small*, 2009, **5**, 813-816.
19. S. Y. Lee, J. Choi, E. Royston, D. B. Janes, J. N. Culver and M. T. Harris, *J. Nanosci. Nanotechno.*, 2006, **6**, 974-981.
20. S. Balci, K. Hahn, P. Kopold, A. Kadri, C. Wege, K. Kern and A. M. Bittner, *Nanotechnology*, 2012, **23**, 045603.
21. R. Tsukamoto, M. Muraoka, M. Seki, H. Tabata and I. Yamashita, *Chem. Mater.*, 2007, **19**, 2389-2391.
22. M. Knez, A. M. Bittner, F. Boes, C. Wege, H. Jeske, E. Maib and K. Kern, *Nano Lett.*, 2003, **3**, 1079-1082.
23. M. Ł. Górzny, A. S. Walton and S. D. Evans, *Adv. Funct. Mater.*, 2010, **20**, 1295-1300.
24. Z. Niu, M. Bruckman, V. S. Kotakadi, J. He, T. Emrick, T. P. Russell, L. Yang and Q. Wang, *Chem. Comm.*, 2006, 3019-3021.
25. C. E. Fowler, W. Shenton, G. Stubbs and S. Mann, *Adv. Mater.*, 2001, **13**, 1266-1269.
26. S. L. Y. Chang, A. S. Barnard, C. Dwyer, T. W. Hansen, J. B. Wagner, R. E. Dunin-Borkowski, M. Weyland, H. Konishi and H. Xu, *J. Phys. Chem. Lett*, 2012, **3**, 1106-1110.
27. *Mineral Powder Diffraction File Data Book*, JCPDS International Centre for Diffraction Data, Swarthmore, PA, 1986.
28. J. S. Hammond and N. Winograd, *J. Electroanal. Chem.*, 1977, **78**, 55-69.
29. J. E. Castle, *Surf. Interface Anal.*, 1984, **6**, 302-302.
30. D. Briggs and M. P. Seah, *Practical Sur. Analysis*, Wiley, Chichester, 1990.
31. S. Hajati, Tougaard, S., *J. Surf. Anal*, 2009, **15**, 220-224.