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Fabrication of 3-nm Platinum Wires Using a Tobacco Mosaic Virus Template

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Fabrication of high aspect ratio 3-nm Pt wires was achieved by reducing K_2PtCl_4 with dimethylamine borane in the presence of a tube-shaped tobacco mosaic virus. The presence of a nonionic detergent, Tween 20 in the reaction mixture prevents aggregation of the virus, and isolated Pt wires can be readily transferred onto silicon surfaces. Our results provide a new chemical approach to fabricate and locate 3-nm Pt wires on a substrate, which could not be achieved using conventional lithography.

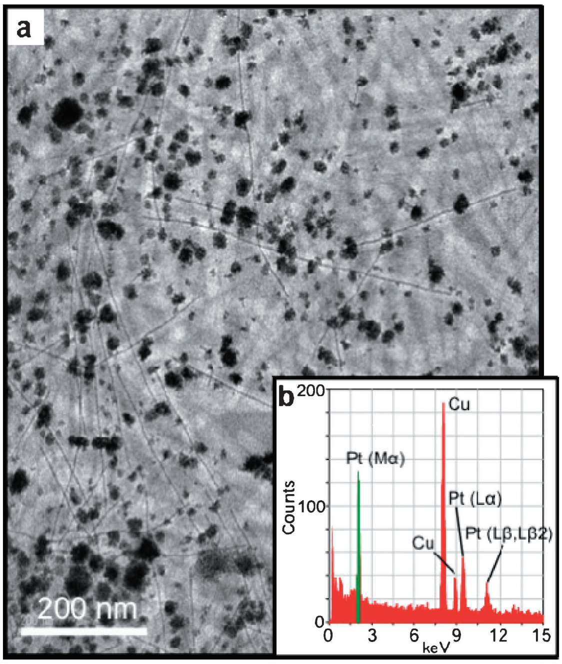

Figure 1. High aspect ratio 3-nm Pt wires were fabricated using a TMV template. (a) A 200 kV TEM image of platinum wires (black lines) inside TMVs (cloudy white rods surrounding black lines/the platinum wires). The sample was stained with 1% aurothioglucose. (b) Pt signals were detected by EDS analysis of a nonstained wire. Cu signals were derived from a TEM grid.

Biological molecules have been found to bring about unexpected chemical reactions. In some cases, a reaction proceeds preferably on a protein surface, resulting in metals or semiconducting materials molded in the shape of the template molecule. By choosing appropriate molecules or organisms, a desired shape that is conducive to a specific function can be fabricated.[1] Furthermore, it has been demonstrated that bio-templated nanoparticles are suitable for use in applications such as memory devices.[2,3] In addition to nanoparticles, wires with less than 10-nm diameters are indispensable building blocks for bottom-up fabrication of other nanometer-scaled devices.

Tobacco mosaic virus (TMV) has been favored among bio-template proteins for making nanowires (NWs), nanoparticles (NPs), and other nanostructures.[3,4] TMV is a tube-shaped plant virus that is 300 nm in length with outer and inner diameters of 18 and 4 nm, respectively.[5,6] Each virus particle is composed of a genomic single-stranded RNA and 2130 identical coat proteins. Using Pd as a catalyst, deposition of Ni, Co, and Cu in the central channel of TMV has been reported.[7] Using sonication to promote chemical reactions, magnetic Pt alloy wires of Fe/Pt and Co/Pt[6,8] have also been fabricated. However, sonication causes fragmentation of TMV, making it difficult or impossible to obtain 300-nm TMV. The average length was about 70 nm, which is much shorter than the length of TMV. In addition, it has been difficult to restrict the metal deposition to the inside of the central channel without aggregation of the virus.

Here we report the synthesis of isolated 3-nm Pt wires with a high aspect ratio using TMV.

First, 1 µL of TMV ($1\,mg\,mL^{-1}$ in water; ToMV species[6]) was dispersed into 65 µL of a 1 mM aqueous potassium tetrachloroplatinate (K_2PtCl_4: Wako Pure Chemical, Osaka) solution. The suspension was kept at 25 °C for 30 min. Next, 1 µL of freshly prepared 10 mM dimethylamine borane (DMAB: Wako Pure Chemical, Osaka) was added, and the resulting solution was incubated for another 30 min. The solution was put onto an elastic carbon-coated Cu grid and excess solution was removed by filter paper. The sample was stained with 1% aurothioglucose solution, which does not stain the central channel.[8] Transmission electron microscopy (TEM: JEM-2200FS, JEOL, Tokyo) observation revealed the formation of NWs inside the TMVs (Figure 1a). With this method, fragmentation of TMV was prevented, resulting in the formation of 300-nm or longer NWs. Some NWs longer than the length of TMV are formed probably because of head-to-tail connection of TMVs. Energy dispersive X-ray spectroscopy (EDS: JED-2200 analyzer, JEOL, Tokyo) confirmed that the wire was made of platinum (Figure 1b). Various duration times between 5 and 60 min gave similar results suggesting that sensitization by Pt proceeds very rapidly. As for reduction time, 15 min was found to be sufficient, leading us to speculate that Pt ions were inside the channel before the reduction started and were reduced when DMAB came into the channel. Although it is difficult to determine the exact diameter of the nanowire, it is between 3 and 4 nm, smaller than the dimension of the central channel of the TMV. This is reasonable because materials must be supplied from both ends of a tube in order to allow NWs to grow inside a tube-shaped template, and if full-width NWs were grown inside the channel, they would inhibit the source ion supply. However, the mechanism which causes NW growth to stop at around 3 nm is not clear. It is possible that the inner surface of the TMV hinders Pt crystallization. When K_2PtCl_4 was replaced with $KAuCl_4$ or $AgNO_3$ (Wako Pure Chemical, Osaka), many NPs were deposited on the outer surface of the TMV but no metal wire deposition was observed inside the cavity (Figure S1).[16] These results suggest that reduction of a given source ion does not necessarily allow NW formation inside the TMV even when the metal ion is reduced outside. One explanation is that the reduction of any metallic source ion results in tiny crystals, but only Pt NPs have NW-forming properties. Another possibility is that $PtCl_4^{2-}$ ions enter the central channel of TMV, but $AuCl_4^-$ or Ag^+ ions do not.

As described above, NWs with a high aspect ratio were fabricated inside TMV with high reproducibility. However, concurrent aggregation of TMV and deposition of large Pt particles outside TMV must be eliminated to meet the demands of future device application (Figure 1). The aggregation of TMV was not observed in the absence of $PtCl_4^{2-}$ ions (data not shown) suggesting that this aggregation was likely caused by the presence of $PtCl_4^{2-}$ ions. In fact, using EDS mapping analysis, Pt ion clusters were detected around TMVs in a K_2PtCl_4 solution (Figure S2).[16] A previous report also described that the reduction of Cu ions results in TMV aggregation.[9] These results indicate that aggregation of TMV could be mediated by metallic ions and that aggregation might be prevented if the outer surface of TMV were to become inaccessible to metallic ions. Therefore, we tried to coat the outer surface of TMV to prevent NP formation on the outer surface. There are several reports of coating TMV with inorganic or organic materials such as silica,[10] polyaniline,[11] and polypeptide.[4a] In particular, bovine serum albumin (BSA) has been reported to prevent TMV aggregation.[12] However, the presence of BSA (A0281, Sigma-Aldrich; in a particle ratio of BSA:TMV = 150:1)[12] did not prevent aggregation of TMV with Pt NWs, and a large amount of Pt deposition was observed on the outer surface of TMV (Figure S3).[16] Changing the concentration of BSA gave similar results (data not shown).

Next, we tried a nonionic detergent, Tween 20, which is commonly used to prevent undesired protein binding.[13] We found that the presence of 0.1–0.01% Tween 20 (MP Biomedicals, Germany) prevents TMV aggregation (Figure 2). Tween 20 is thought to cover the outer surface of TMV preventing the aggregation of the virus. Lower detergent concentration resulted in TMV aggregation while higher concentration (1%) of the detergent led to micelle formation (Figure S4).[16] Interestingly, in the presence of Tween 20, NW formation inside TMV was not affected and isolated TMVs were observed by high-resolution TEM (JEM-3100FEF, JEOL, Tokyo; Figure 3). The sample was stained with 3% phosphotungstic acid (PTA), which allows clearer visualization of proteins. PTA is known to stain the central channel of TMV as is evident in the faintly stained channel of the lower TMV in Figure 3. The NWs were confirmed to be made of Pt by EDS analysis (data not shown). The percentage of fabricated NWs longer than 100 nm was 5.5% (approximately one per 20 TMV), which was averaged from 600 TMVs observed on a single TEM grid.

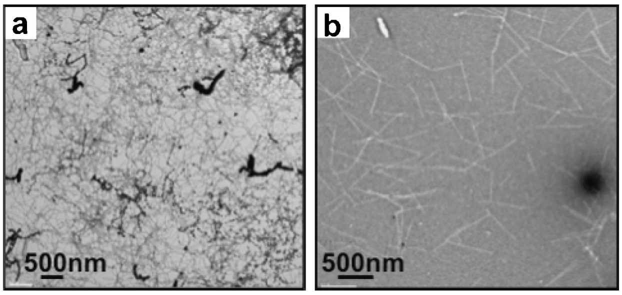

Figure 2. Aggregation of the virus is prevented by Tween 20, a nonionic detergent, in the reaction mixture. TEM images (200 kV) of TMVs after Pt deposition in the (a) absence or (b) presence of 0.01% Tween 20.

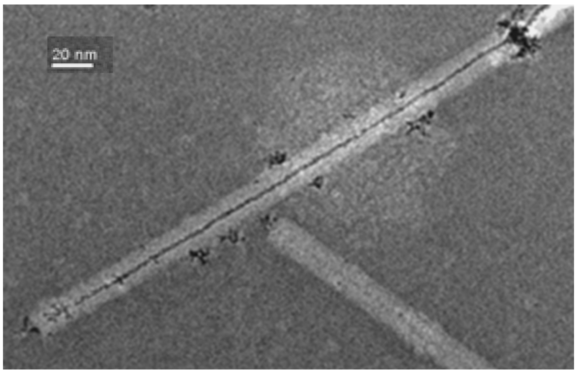

Figure 3. A 300 kV TEM image of 3-nm Pt wire (black line) inside TMV (cloudy white rods). The sample was stained with 3% phosphotungstic acid (PTA). The central channel of the lower TMV is faintly visible due to the presence of PTA.

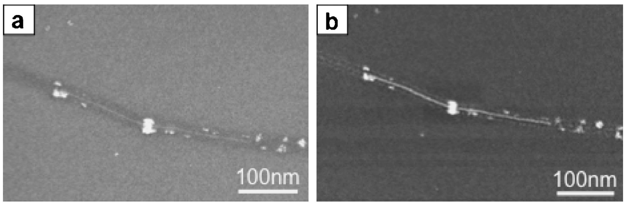

Figure 4. SEM observation of 3-nm wire fabricated and located on a silicon surface. (a) After spreading TMV/Pt wire onto a silicon surface. (b) A 3-nm line remains after UV/ozone treatment.

For future device applications, NWs formed inside TMV must be readily transferred onto silicon surfaces. To achieve this aim, a silicon substrate was first cleaned with UV/ozone (UV/ozone cleaner UV-1, SAMCO, Kyoto) at 110 °C with an oxygen gas flow rate of 0.5 $L\,min^{-1}$ for 10 min.[14] Next, 3 μL of TMV/Pt solution was applied and excess solution was removed by a spinner (1H-D2, MIKASA, Tokyo) at 12000 rpm for 20 s, followed by heating at 95 °C for 2 min.

Scanning electron microscopy (SEM; JSM-7400F, JEOL, Tokyo) observation revealed that TMV/Pt wires were dispersed onto the silicon substrate (Figures 4a and S5[16]) and after protein elimination, which was achieved by UV/ozone treatment for 30 min, a Pt NW was found at the same position with no migration or defect caused by the treatment (Figure 4b). Although UV/ozone treatment is commonly used to eliminate protein shells,[15] detailed analysis using X-ray photoelectron spectroscopy and atomic force microscopy may be necessary before fabricated NWs using a TMV template can be incorporated into nanometer-scaled devices.

In conclusion, we succeeded in fabricating and locating high aspect ratio 3-nm Pt wires on a silicon surface, which could not be achieved using conventional lithography. Utilizing the catalytic behavior of Pt, the possibility of fabricating other metal alloy NWs such as Co/Pt or Fe/Pt can now be explored as components for spintronics devices.

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16 TEM images in Figures S1, S2, S3, S4, and S5 are presented as Supporting Information which is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.