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Deposition of Platinum Clusters on Surface-Modified Tobacco Mosaic Virus

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Nanoscaled Pt conductors were prepared from genetically engineered *Tobacco mosaic virus* (TMV) templates through Pt cluster deposition on the outer surface of the TMV. Pt clusters were synthesized and deposited on the engineered TMV with surface-exposed cysteine via the *in situ* mineralization of hexachloroplatinate anions. This deposition was driven by the specific binding between thiols and the solid metal clusters. In addition, Pt-thiolate adducts are suggested to form on the engineered TMV in aqueous solutions that work as nucleation sites for the formation of the Pt clusters. The specific binding between Pt clusters and the engineered TMV template was investigated using UV/vis spectrophotometry and quartz crystal microbalance (QCM) analysis. The electric conductance of Pt-deposited TMV was greater than that of the uncoated TMV virion particles. This result suggests the application of metal cluster-deposited engineered TMV in future electrical devices such as rapid response sensors.

Keywords: Tobacco Mosaic Virus, Cysteine, Platinum, Conductance.

1. INTRODUCTION

Biomolecular templates are utilized in preparing complex-structured hybrid materials.^{1,2} Several characteristic properties of biomolecules such as self-assembly^{3–5} and biological recognition^{6,7} have been exploited in associating heterogeneous materials with biomolecules in a designed pattern. Recent progress in genetic engineering has increased the usefulness of biomolecules with techniques that modify their shapes and properties in a designed manner.^{5,8–12} The modified biotemplates are useful in synthesizing nanotubes and/or nanowires by hybridizing inorganic and metallic materials with them. The research on the hybridization of biomolecules with conducting materials is promising because of their potential use as conducting metal connections with smart recognition for nanoscale electrical devices. Various tubular and filamentous biomolecules such as DNA strands,^{13,14} actin filaments,¹⁵ amyloid fibers,⁵ protein tubules,¹⁶ and viruses^{8,17–20} are used as biotemplates in nanotube and nanowire synthesis.

Wild-type Tobacco mosaic virus (wt TMV) is a tubular plant virus that is used in nanotube synthesis.^{17–20} TMV has several advantages as a biotemplate. The

surface-exposed amine and carboxyl groups in the coat protein are useful in conjugating with other molecules or nanoparticles.¹⁷ The rigid tubular structure enables the TMV to be applied in various reactions without structural deformation. In addition, the well-studied genetic information on the amino acid sequence of the coat protein and cDNA cloning make it possible to modify the coat proteins with designed properties.^{21,22}

Several applications of wt TMV in inorganic nanotube synthesis and metal nanoparticle decoration have been reported. Electroless deposition of metal ions were applied to prepare metal nanoparticle-decorated wt TMV particles.^{18–20} In a previous study, Pt nanoparticles were deposited on the wt TMV template by the electroless deposition method, resulting in discrete Pt nanoparticle decoration along the TMV template. In performing the electroless deposition of anionic metal ion complexes, an acidic environment under the isoelectric point (pI) of wt TMV is used to associate the negatively charged metal ions with the positively charged wt TMV.¹⁸ Though the charge-charge attraction was used in attracting metal ions to the TMV template, the binding force of solid metal clusters on the wt TMV surface is unknown.²⁰ Thus, the metal nanoparticles were thought to be weakly bound non-specifically or electrostatically on the wt TMV surface.

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For the future use of metal nanoparticle-deposited TMV, the immobilization of nanoparticles through covalent binding is desired. Among the many specific binding possibilities available on the biomolecule, the covalent bond between the thiol and a solid metal surface is a well-known approach to immobilize the metal clusters on the surface of the biotemplate.

In this work, Pt conductors are prepared through the deposition of Pt clusters on the surface of the genetically engineered TMV containing surface-exposed cysteine residues. The genetically engineered TMV is used as a template for the Pt deposition that is accomplished via the *in situ* mineralization of Pt ions. The surface-exposed cysteine residues are expected to provide a dense array of binding sites for the metal ions and clusters. To confirm the role of cysteine residues in the specific binding of Pt clusters, UV/vis spectrophotometry and quartz crystal microbalance (QCM) analysis are performed with control experiments. Finally, the application of prepared Pt cluster-deposited TMV nanotubes as conductors is presented with its electrical conductance. To our knowledge, we are the first to report a study on the electrical conductance of the metal cluster-coated TMV particles derived from the engineered TMV.

2. EXPERIMENTAL DETAILS

2.1. Genetically Engineered TMV (TMV2cys)

Genetically engineered TMV, TMV2cys (2.1 mg/ml), stored in 0.01 M sodium phosphate buffer (pH 7.0) was prepared by a mutagenesis technique. The TMV2cys virion stock was chemically treated before Pt deposition in order to reduce any disulfide bonds between virion particles or coat proteins to individual thiol groups. The detailed procedures on the mutagenesis on TMV and the protocols of disulfide bond reduction are described elsewhere.^{23,24} Engineered TMV contains two additional cysteines at the position of 2 and 3 in coat protein sequence, resulting in an exposure of thiols to the outer surface. The exposed thiols per unit coat protein make a dense thiol array on the entire surface of TMV that makes it possible to form a dense metal cluster layer. The treated TMV2cys virions were suspended in deionized water to a concentration of 0.3 mg/ml for the Pt deposition.

2.2. Pt Cluster Deposition on TMV2cys Template

Two kinds of Pt chloride salt solutions in various pH were used in the Pt cluster deposition. Hydrogen hexachloroplatinate(IV) hydrate ($\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$, ACS grade, Aldrich, 0.1 mM) solutions at pH 2.2 and 3.8 were prepared for the deposition in acidic conditions. Potassium hexachloroplatinate(IV) (K_2PtCl_6 98%, Aldrich, 0.1 mM) solutions at pH 7.2 and 9.9 were used as the precursor solutions in neutral and basic conditions. The pH of the Pt precursor

solution was controlled by adding 2.0 M hydrochloric acid (HCl) and 0.1 M sodium hydroxide (NaOH), respectively. A volume of 25 μl of treated TMV2cys was mixed with 300 μl of each Pt salt solution and stored in the dark for 30 minutes at room temperature. The Pt ions were mineralized by adding 300 μl of the reducing agent, a dimethylamine borane (DMAB, 10 mM) solution. To investigate the specific binding property, post conjugation of Pt clusters with TMV2cys was carried out; Pt cluster suspension was prepared in the same way as above without the TMV template present, then TMV2cys stock added later to the Pt suspension. As a control experiment, Pt deposition on the wt TMV suspending in water with a concentration of 0.3 mg/ml was carried out using the same Pt precursor solution with pH 3.8 and reducing agent.

2.3. Characterization and Analysis

The Pt cluster-deposited TMV2cys (hereinafter referred as Pt-TMV2cys) particles were imaged using transmission electron microscopy (TEM, Philips CM10, 80 keV). An aliquot of 7 μl of the Pt-TMV2cys suspension was taken after 15 minutes of mineralization and positioned on the carbon coated copper grid for the TEM observation. All the samples were prepared without stain to prevent imaging artifacts. Electron dispersive spectroscopy (EDS, EDXA Dx4, 120 keV) were used in analyzing the metal composition. The UV/visible plasmon spectra were taken using a bench-top UV/vis spectrophotometer (Cary 100 Bio, Varian) and were used to observe the shifts of the absorbance peaks of the Pt clusters before/after conjugation with the TMV2cys. In UV/vis spectrophotometry study, the Pt cluster suspension was prepared by mixing equal volumes of the Pt precursor solution (0.1 mM) and DMAB solution (10 mM) without TMV template. The reduction of the Pt complex anion was carried out instantaneously as soon as the reducing agent was added. A volume of 20 μl of TMV2cys (concentration: 0.2 mg/ml) was added to 1 ml of Pt cluster suspension and the UV/vis plasmon absorbance spectra were monitored after ~ 2 minutes. For comparison, the wt TMV was added in a control experiment.

To investigate the association of Pt chloride ions to the TMV2cys, the mass change due to the association of Pt chloride ions on TMV2cys was monitored using a quartz crystal microbalance (QCM). QCM is based on the sensitivity of piezoelectric quartz detecting the change in the resonance frequency that is converted into the mass change in ng/cm^2 scale. QCM was applied in detection of the Pt complex anion on the tin-deposited gold substrate.²⁵ A temperature controlled QCM system (Qsense, model D300) with gold-deposited quartz crystal ($f = 5$ Mhz) was used in monitoring the Pt ion adsorption. A TMV2cys layer was formed on the gold-deposited quartz by continuous injection of a TMV2cys suspension in the 0.01 M sodium phosphate buffer (TMV2cys

concentration = 0.3 mg/ml, pH 7.3). The TMV2cys virions were covalently bound on the gold substrate to form TMV2cys layer on the gold coated quartz. The surface-exposed cysteine residues were used in anchoring TMV2cys covalently on the gold surface. Conversely, the wt TMV could not be fixed on the gold surface due to the lack of covalent binding, thus QCM test was not performed on the wt TMV samples. After TMV2cys layer formation, the sodium phosphate buffer and H_2PtCl_6 solutions (0.1 mM dissolved in 0.01 M sodium phosphate buffer, pH 7.3) were injected in sequence. The mass change was calculated from the frequency changes using Sauerbrey's equation.²⁶ The Sauerbrey constant of $17.7 \text{ ngHz}^{-1} \text{ cm}^{-2}$ was used in calculating the adsorbed mass from the frequency change. A control experiment was performed to investigate the Pt salt adsorption to the bare gold surface. Before injecting the Pt precursor solution, the bare gold-coated quartz was stabilized by flowing 0.01 M sodium phosphate buffer over the substrate. The frequency change of the QCM quartz after the injection of Pt precursor solution was monitored. In every QCM experiment, the pH of buffer and Pt precursor solutions was maintained at 7.3 to prevent frequency change from pH variations, and tests were performed at 25 °C. Fresh Pt precursor solutions were prepared and kept in dark to prevent to expose to the light, since the Pt complex anions can be reduced by the intense irradiation of light, specifically UV light. After the QCM test, the Pt precursor solution was investigated using TEM and dynamic light scattering system (Photocor) with a 20 mW He-Ne laser source ($\lambda = 633 \text{ nm}$) at room temperature.

2.4. Electrical Conductance Measurement

Gold electrodes with a gap size ca. 10 nm were constructed by the step junction technique.²⁷ Pt-TMV2cys particles bridged the gold electrodes after 25 μl of Pt-TMV2cys suspension was dropped between the electrodes. The remaining solution was wicked away, followed by washing with deionized water. The electrodes were air dried and kept under nitrogen until the measurement. Electrical conductance of the Pt-TMV2cys was measured using a micromanipulator probe station equipped with conductivity meter (semiconductor characterization system model 4200, Keithley) at room temperature. The image of the Pt-TMV2cys bridging electrodes was taken using atomic force microscopy (AFM, Nanoscope IIIa, Digital Instrument) in the tapping mode.

3. RESULTS AND DISCUSSION

Deposition of the Pt clusters on TMV2cys surface was achieved via *in situ* mineralization of the Pt precursor solutions. The *in situ* mineralization of $[\text{PtCl}_6]^{2-}$ ions is an effective method for the Pt cluster formation on the TMV template from the aqueous Pt precursors. To investigate

the effects of precursor solution pH on the solid cluster deposition on the TMV2cys template, acidic, neutral, and basic Pt precursor solutions were applied in the mineralization. TEM images of Pt-TMV2cys virions are shown in Figure 1. Pt cluster deposition was achieved in every sample regardless to the pH of the Pt precursor solution. A quasi-continuous deposition of granular Pt clusters was achieved using H_2PtCl_6 at pH 2.2 which is below the pI of the TMV2cys virion (Fig. 1a). A continuous Pt layer on the TMV template was achieved at pH 3.8, which is slightly higher than the pI of TMV2cys virion (Figs. 1c and 1d). The chemical composition of the deposited Pt layer was confirmed by EDS analysis (Fig. 1b), where the strong carbon and copper peaks are from the TEM grid. The quasi-continuous deposition of tiny Pt clusters was achieved even in neutral and basic conditions (Figs. 1e and 1f) where the pHs of precursor solutions are well above the pI of TMV2cys. The dense and continuous Pt layer on TMV2cys is clearly visible compared to the case of Pt cluster deposition on wt TMV virions (Fig. 1g) where discrete Pt cluster decoration is achieved at only some of the TMV templates. The sparse decoration of Pt clusters onto wt TMV virion is already reported,¹⁸ and it is clear that the engineered TMV with the modified surface has improved the Pt cluster deposition on the TMV templates.

It is notable that Pt deposition was achieved not only in the acidic conditions below the pI of TMV2cys template but also in basic conditions. Above the pI of the virion, specifically in basic conditions, the electrostatic interaction between $[\text{PtCl}_6]^{2-}$ (or its hydroxyl derivatives that are also negatively charged) and the negatively charged virion surface is repulsive so that Pt nanoparticles do not associate with wt TMV at pH 9.9.¹⁸ The poor association of $[\text{PtCl}_6]^{2-}$ with wt TMV at a pH below the pKa values of lysine (pKa = 10.8) and arginine (pKa = 12.5) strongly indicates that the sign of the overall surface charge of the virion template is the key factor in attracting $[\text{PtCl}_6]^{2-}$ anions electrostatically, and not the existence of positively charged amine groups on the coat protein surface. In other words, the attraction of positively charged amine groups is likely to be negligible compared to the repulsion of the abundant negatively charged carboxyl groups on the TMV surface. Since TMV2cys also has a pI value of 2.8 ~ 3.0, similar to that of wt TMV,²³ the electrostatic attraction of $[\text{Pt}_2\text{Cl}_6]^{2-}$ cannot explain the Pt coating at basic conditions. The successful Pt cluster coating on TMV2cys at pH 9.9 suggests that the binding of Pt clusters is mostly driven by the specific binding induced by thiol groups rather than the electrostatic attraction.

The thiol array on the TMV2cys surface is likely to associate with Pt in two ways; Firstly, the thiol array work as binding sites for the solid Pt clusters, which is a well-known covalent binding between the solid metal surface and thiol groups. Therefore, when TMV2cys is used as a template, the deposition of Pt cluster was achieved even at the basic condition in comparison to the wt TMV

Fig. 1. (a) TEM images of Pt-TMV2cys prepared from the H_2PtCl_6 precursor at pH 2.2. (under pI of TMV2cys, scale bar: 50 nm). (b) EDS analysis of Pt-TMV2cys. The strong Cu peaks come from the supporting copper grid. (c, d) TEM images of Pt-TMV2cys prepared from the H_2PtCl_6 precursor at pH 3.8 (over pI of TMV2cys) with low (c: scale bar 100 nm) and high (d: scale bar 50 nm) magnifications. (e, f) TEM images of Pt-TMV2cys prepared from K_2PtCl_6 solutions (e: at pH 7.2, f: at pH 9.9, scale bars: 50 nm). (g) Pt cluster-deposited wt TMV prepared at pH 3.8 (scale bar 100 nm). (h) Pt cluster-deposited TMV2cys virions prepared by post conjugation with solid Pt clusters (scale bar: 50 nm).

template.¹⁸ The TEM image of the Pt cluster deposited TMV2cys that was prepared by post conjugation supports the well-known role of the thiol for the solid metal cluster binding (Fig. 1h). Secondly, the surface-exposed thiol is expected to form Pt-thiolate adduct on the TMV2cys surface by associating with Pt chloride ions in the aqueous Pt precursor solution before mineralization. The Pt-thiolate adduct on the TMV2cys surface is likely to enhance the association of Pt ions with the TMV templates. This explains why the *in situ* mineralization resulted in a denser coating than the case of the post conjugation of Pt clusters with TMV2cys. A possible associated structure of $[\text{PtCl}_3\text{S-R}]^{2-}$ (R: alkyl group bound with thiol) is suggested when the $[\text{PtCl}_6]^{2-}$ anion encounters a thiol (R-SH) in an aqueous phase.^{28, 29} The Pt-thiolate adduct is expected to form

at the early stage of incubation of TMV and precursor solution mixture.

The dense array of Pt-thiolate adducts on TMV2cys is probably used as favored nucleation sites for the Pt deposition. Nucleation from the Pt-thiolate adduct is preferred and reacts faster than in the solution phase since thiol is a good donor ligand, enhancing the binding with metal ions and clusters. A molecular dynamics study on the selective Pt deposition on DNA strands has also suggested that the heterogeneous nucleation from Pt ions associated with donor ligands is preferred to nucleation in solution.³⁰ The donor ligand in the biomolecular structure facilitated nucleation, which results in selective deposition on the biotemplate.³¹ This explanation is analogous to the previous study on the nucleation of ligand stabilized

Fig. 2. The change of frequency difference during the adsorption of $[\text{PtCl}_6]^{2-}$ on the bare and TMV2cys layered QCM quartzes (red line: bare quartz, black line: TMV2cys layered).

metal precursor complex for noble metal nanocluster formation.³²

To investigate the association of Pt ions with thiols on the TMV2cys template, the change of mass after the association of Pt ion was monitored using QCM. In Figure 2, the variation of frequency difference (Δf) with the injection time of the buffer and Pt precursor solution is shown. The frequency changes containing TMV2cys layer showed a notable drop of frequency in comparison to the changes in the presence of bare quartz. The QCM study suggests the instant association of Pt ions with TMV2cys virions.

In preparing TMV2cys layer on the gold substrate, drastic frequency decrease observed when TMV2cys suspension in sodium phosphate buffer was introduced (data not shown). The drastic frequency change represents the binding of TMV2cys to the gold surface. After the initial drop of frequency, a continuous adsorption of TMV2cys to the gold-coated quartz resulted in a slight decrease of the frequency difference before injecting buffer solution (0 ~ 10 min). This slight decay is thought to represent the continuous association of TMV2cys as well as covalent binding on the gold surface. After the adsorption of TMV2cys layer, sodium phosphate buffer was injected in order to remove unbound TMV virions and to stabilize the system. Interestingly, no detectable change in the frequency was observed, which suggests that most of the TMV2cys virions were strongly bound and stabilized. Otherwise, an increase of frequency may be observed due to the washing of physisorbed TMV virions off from the surface of the quartz by the buffer injection.

A quick and notable change in frequency was observed when the Pt precursor solution was introduced to the TMV2cys bound quartz plate. Considering that the only difference between buffer and Pt solution is the existence of Pt ions, the change of frequency difference is obviously due to the association of Pt ions with thiols. The quick response to the Pt ions is rationalized considering the fast reaction constant and chemical stability of Pt-thiolate

adduct. The reported values of the reaction constant in the Pt-thiolate formation is on the order of $10^{-1} [\text{M}^{-1} \cdot \text{s}^{-1}]$, with a stability constant of $10^3 [\text{M}^{-1}]$.²⁹ The large stability constant suggests that the Pt-thiolate adduct is chemically stable and the dissociation of Pt ions from the adduct is negligible. The frequency continued to decrease slowly with time, suggesting a continuing association of Pt ions with the TMV2cys.

The specific binding of Pt ions to TMV2cys virion was supported from the control experiment of Pt ion adsorption to the QCM quartz. Without the TMV2cys layer, the frequency difference dropped slowly to ~9 Hz after injection of the Pt precursor solution, which is due to the direct adsorption of Pt ions to the gold surface. However, the frequency difference changes rapidly when the Pt ions were initially injected in the TMV2cys layer. These indicate that most of the Pt ions were associated instantaneously with the thiol groups of the TMV2cys virions. The frequency difference continuously decayed with time suggesting the continuous association of Pt ions to the TMV2cys virions. After ~25 minutes from the injection of Pt solution, the frequency difference between bare and TMV-layered quartzes was ~38 Hz, corresponding to a mass difference of ~224 ng/cm².

After the QCM test, the Pt precursor solution was investigated using dynamic light scattering and TEM to check nanoparticles formation in the bulk precursor solution. Some tiny dots (approximately ~1 nm) having weak electron scattering were observed in the TEM images. However, this observation does not confirm the Pt nanoparticle formation since the tiny dots can be made during the drying of the Pt precursor solution in the TEM sample preparation (data not shown). The existence of particles was not detected by dynamic light scattering. Considering the dynamic light scattering result and the use of fresh Pt precursors, the possibility of Pt nanoparticle formation in the bulk solution is thought to be very low.

Biological recognition of TMV2cys to the solid Pt clusters was confirmed from the UV/vis plasmon absorbance band shift. The characteristic maximum plasmon peak for Pt clusters, observed at 524 nm (solid black lines in Fig. 3), was shifted to 547 nm and broadened after the association with TMV2cys (Fig. 3a, broken red line). Considering the stable, well-dispersed Pt nanoparticles containing stabilizer will not show any peak in the visible wavelength,³³ the peak appearance at the 524 nm is probably due to the aggregation of the Pt clusters resulting in the scattering of visible light. Since no stabilizer was added to the Pt cluster sol, the aggregation of Pt clusters may happen. The aggregation of Pt clusters was confirmed in the further TEM study; even tens of nanometer-sized aggregates were found as well as nanoscaled Pt particles (data not shown). The peak broadened a little more after the additional injection of TMV2cys stock without shift of the maximum peak position (Fig. 3a, dotted blue line). Considering that the cysteine does not have any specific peak appearance in

Fig. 3. UV/vis plasmon absorbance spectra. (a) Red shift of characteristic Pt clusters after the addition of TMV2cys. (b) Absorbance changes after the addition of wt TMV. (Black solid line: spectrum of Pt clusters without the TMV template, red broken line: after addition of 20 μ l of TMV2cys/wt TMV stock, blue dotted line: after addition of extra 20 μ l of TMV2cys/wt TMV stocks to each sample, green dash-dot line: TMV2cys/wt TMV, 0.1 mg/ml and 0.3 mg/ml respectively).

the range of 500 ~ 550 nm and TMV has a characteristic peak only at ~290 nm (green dash-dot line), the peak shift is caused by the Pt cluster immobilization on the TMV2cys template via specific binding. The UV/vis spectra of TMV2cys and wt TMV does not show a peak or shoulder in the range between 400 and 700 nm and were compared with those of the Pt clusters. It is obvious that the peak shift was not caused by overlapping of spectra of Pt clusters and TMV templates.

The shift and broadening of the UV/vis plasmon peak is caused by the decrease in the distance between particles and by the particle aggregation, respectively.^{34,35} Aggregation and binding of Pt clusters on the TMV2cys surface may happen, thus the distance between the Pt clusters is most likely decreased. The addition of more TMV2cys seems to promote further Pt cluster aggregation on the TMV2cys templates. The specific binding of Pt clusters is supported in the control experiment where wt TMV is added. Compared to the results of the TMV2cys, no shift of the maximum peak was observed after the addition of wt TMV to the Pt cluster suspension. The center of the characteristic peak for the Pt clusters at 524 nm

remained constant. After the addition of more wt TMV, the position of the plasmon absorbance peak remained constant (Fig. 3b). This specific binding of Pt clusters to the TMV2cys virion is also supported from the pH value of pre-formed Pt nanoparticle suspension, 8.1 ± 0.4 . The basic synthesized Pt nanoparticle suspension prevents the electrostatic association of Pt clusters with wt TMV templates. These plasmon absorbance shift and basic Pt nanoparticle suspension indicate the specific binding of Pt clusters to TMV2cys which does not exist in the wt TMV template.

An application of Pt-TMV2cys particles as conducting nanowires is presented in Figure 4a. Pt-TMV2cys particles prepared from a H_2PtCl_6 precursor were positioned between gold electrodes with a ~10 nm spacing. The Pt-TMV2cys showed enhanced electrical conductance with a resistance of $52.3 \pm 7.4 \text{ G}\Omega$ as compared to the uncoated TMV2cys which showed no conductance. The electrical conductance is likely due to the Pt layer deposited on the TMV2cys surface. Interestingly, the Pt-TMV2cys demonstrates hysteresis in the conductivity measurement. The reason for the hysteresis is thought a result of the capacitive charging effects. The gate oxide layer under the gold electrodes works as a capacitor in measuring the current

Fig. 4. (a) I - V curve of the Pt-TMV2cys. The I - V curve of the uncoated TMV2cys is represented by white dots. (b) AFM image of Pt-TMV2cys bridging gold electrodes. The black arrow indicates a Pt-2cys particle bridging electrodes (scan size: 268 nm).

resulting in offset currents at zero voltage. The resistance of Pt-TMV2cys is much higher compared to previous studies on nanowires.^{5,15} The main reason for the high resistance of Pt-TMV2cys is due to the very thin conducting layer of the Pt clusters. The thickness of Pt layer on Pt-TMV2cys is smaller than 3 nm, which is much thinner than the conducting layers of 70 ~ 200 nm used in previous studies.

The conductance measurement of the nanowires is still under debate because too many factors (such as water vapor, salt film, and other uncontrollable artifacts that are chemisorbed or physisorbed between electrodes) affect the electrical conductance. In addition, the junction between the nanowires and electrodes affects the conductance measurements. For the exact conductance measurement of a single Pt nanowire, the segregation and alignment of a single Pt-TMV2cys nanotube in a controlled environment is being investigated.

Pt-TMV2cys and uncoated TMV2cys particles bridging the electrodes were visualized using tapping mode AFM. Only 3 or 4 Pt-TMV2cys were found to bridge the electrodes (Fig. 4b). Considering the low nanotube concentration and the small width of electrodes of ~1 μm , the small number of bridging Pt-TMV2cys is not surprising. The measured height of Pt-TMV2cys from the section analysis is approximately 12 nm, which is similar to the apparent height of wt TMV on a gold[111] substrate.³⁶

4. CONCLUSION

In this work, genetically engineered Tobacco mosaic virus, which has biological recognition to the noble metal compounds, was applied to prepare Pt conductors via a template technique. The cysteine residues on the engineered TMV resulted in immobilization of Pt clusters by forming a Pt-thiolate adduct in the aqueous solution as well as covalent binding with solid clusters. The Pt-thiolate adducts appear to be nucleation sites which are effective in coating a dense Pt cluster layer on the biomolecular surfaces. The immobilized Pt clusters on the engineered TMV was experimentally confirmed via various analysis techniques. This interdisciplinary work of mutagenesis and electrochemical techniques provides a reliable method for the preparation of nanomaterials from engineered biotemplates, possibly leading to the fabrication of nano-scaled devices and sensors in a reliable manner.

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