Direct growth of ultra-long platinum nanolawns on a semiconductor photocatalyst

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Abstract

A template- and surfactant-free process, thermally assisted photoreduction, is developed to prepare vertically grown ultra-long Pt nanowires (NWs) (about 30-40 nm in diameter, 5-6 μm in length, and up to 80 NWs/100 μm² in the wire density) on TiO₂ coated substrates, including Si wafers and carbon fibers, with the assistance of the photocatalytic ability and semiconductor characteristics of TiO₂. A remarkable aspect ratio of up to 200 can be achieved. TEM analytical results suggest that the Pt NWs are single-crystalline with a preferred 〈111〉 growth direction. The precursor adopted and the heat treatment conditions are crucial for the yield of NWs. The photoelectrons supplied by TiO₂ gives rise to the formation of nano-sized Pt nuclei from salt melt or solution. The subsequent growth of NWs is supported by the thermal electrons which also generated from TiO₂ during the post thermal treatment. The interactions between the ions and the electrons in the Pt/TiO₂ junction are discussed in this study.

Introduction

Platinum has become a crucial material due to its outstanding catalytic characters in fuel-cell technology, hydrogenation reaction, three-way automobile catalytic conversion and gas sensing [1-4]. A great deal of effort has been devoted to the synthesis of one-dimensional Pt nanostructures, however, it still remains a grand challenge to synthesize long and oriented single-crystalline Pt nanowires (NWs). Table 1 summarizes the relevant reports concerning template-free chemical means for preparing Pt NWs. Xia et al. [5-7] have demonstrated the synthesis of single crystalline Pt NWs on polymeric, ceramic or metallic substrate by a polyol process, combined with a trace addition of an iron species (Fe²⁺ or Fe³⁺) and poly(vinylpyrrolidone) (PVP) as the surfactant. Cetyltrimethylammonium bromide (CTAB) has also been applied to the photoreduction of Pt ions to Pt NWs [8,9]. Moreover, using neither templates nor surfactants, HCOOH [10-13] and vitamin B₂ [14] have been suggested, respectively, to act as the reductant agents in the chemical routes for the synthesis of Pt NWs. Through the aforementioned processes, the Pt NWs produced are extremely fine (<10 nm in diameter) but exhibit a limit in length of about 200 nm so that their aspect ratios do not exceed 50.

It is well known that TiO₂ is an excellent photocatalyst under exposure to ultraviolet (UV) light. According to the Honda-Fujishima effect [15], electrons and holes on the surface of TiO₂ films can be activated by UV light, which enables the reduction of metallic ions from the solution. The photoreduction process of metallic ions (M⁺) can be expressed briefly as follows,

$$\text{TiO}_2 \xrightarrow{hv} h^+ + e^-$$

$$M^+ + e^- \rightarrow M^0$$

Based on this, a recently developed process, thermally assisted photoreduction (TAP), has been applied to prepare metallic NWs via the photoreduction of metallic ions on the surface of thin-film TiO₂ under certain irradiating and heating conditions [16,17]. However, it has so far not been possible to produce Pt NWs with the commonly used precursor, H₂PtCl₆, which was ascribed to the high charge number of Pt ions.

By extending the selection of the precursors, a modified route for the synthesis of Pt NWs is proposed in this study. In addition to Si wafers, carbon cloths are also chosen as the substrate for investigation, since nanostructured Pt-TiO₂ on carbon fibers or nanotubes...
has been suggested as excellent electrocatalysts for
direct ethanol fuel cells [18,19]. Considering the
mechanism for forming the NWs was still elusive, this
study also discusses the growth of Pt NWs from the
view points of the transfer of ions and electrons, as well
as their interactions.

Experimental details
Thin film preparation
To make a gel coating film, TiO2 was deposited by dip-
ping Si wafers and carbon cloths into the sol and then
only the wafers were spun at 1000 rpm for 30 s. The
solution used was prepared with isopropyl alcohol (IPA):
titanium isopropoxide (TTIP):hydrogen chloride (HCl)
with a volume ratio of 170:12:0.4 and stirred for 10 min
before aging at room temperature (20°C) for 2 days. The
as-synthesized TiO2 films were annealed at 500°C for 8
h in an oxygen atmosphere to obtain well-crystallized
anatase TiO2 (step 1 in Figure 1), which could be identi-
fied by the grazing-angle X-ray diffraction (XRD) pat-
tern shown in Figure 2.

| Method                      | Orientation | Surfactant (S) or reductant (R) | Diameter (nm) | Length       | Crystallization     | Precursor     | Authors                                                                 |
|-----------------------------|-------------|---------------------------------|---------------|--------------|---------------------|---------------|-------------------------------------------------------------------------|
| Chemical reduction          | {111}       | PVP (S)                          | ~5            | ~200 nm      | Single-crystalline  | H2PtCl6       | Xia et al. [5-7]                                                        |
| Chemical reduction          | -           | CTAB (S)                         | 2.2           | Networks     | Polycrystalline     | K2PtCl4       | Song et al. [8]                                                         |
| Photochemical reduction     | {111}       | CTAB (S)                         | 3-4           | 20-60 nm     | Single-crystalline  | K2PtCl4       | Krishnaswamy et al. [9]                                                 |
| Chemical reduction          | {111}       | HCOOH (R)                        | 4             | 100-200 nm   | Single-crystalline  | H2PtCl6       | Sun et al. [10-13]                                                      |
| Chemical reduction          | -           | Vitamin B2 (R)                   | 10            | Several tens of nm | Polycrystalline | Pt metal salt | Nadagouda et al. [14]                                                   |
| Thermal-assisted photo reduc-
   tion                       | {111}       | -                                | 32            | 6 μm         | Single-crystalline  | Na2Pt(OH)6   | Our group                                                               |

PVP (poly(vinylpyrrolidone)), CTAB (cetyltrimethylammonium bromide).

NWs synthesis
As indicated by the step 2 in Figure 1, Na2Pt(OH)6 was
selected as the precursor. Fifteen microliter of 0.05 M
aqueous salt solution was dropped on the TiO2 coated
substrates. Afterward the samples were isothermally
heated at 300°C for 3 h in air by an infrared (IR) furnace
(the same heating conditions as adopted in previous stu-
dies [16,17]), followed by a furnace-cooling to the ambi-
etent temperature (namely the post thermal treatment,
step 3 in Figure 1). For comparison, the commonly used
precursor, H2PtCl6, was also adopted. To clarify how the
state of the precursor affects the yield of NWs, the pre-
cursor was also applied in the form of powders.

NWs characterizations
The structure and phase of the NWs were characterized
using a transmission electron microscope (FEI-TEM, Philips Technai G2) with an accelerating voltage of 200
kV and also an grazing incidence X-ray diffraction

![Figure 1 Schematic illusion of the main steps for forming Pt NWs by TAP.](image1.png)

![Figure 2 XRD pattern of the TiO2 thin film annealed at 500°C for 8 h.](image2.png)
meter (GIXRD, Rigaku D/MAX2500) (incidence angle of 0.5°) with graphite monochromatic Cu Kα radiation (λ = 0.15418 nm) at a scanning rate of 2° per minute from 20° to 50°. The yield (i.e. the wire number per 100 μm²) and dimensions of NWs were measured using a scanning electron microscope (SEM, JEOL JSM-6700) and Scion Image 4.0.2 image analysis software. Each data was the average of 100 observations.

Results and discussion
After heating the salt solutions at 300°C for 3 h, the SEM image shown in Figure 3a illustrates that the commonly used precursor, H₂PtCl₆, still remained untransformed and was with nodular or worm-like appearance. For Na₂Pt(OH)₆ (Figure 3b), all the Pt salt was transformed into Pt NWs in large quantities, with an average diameter of 34 nm and remarkable length of about 6 μm (a superb aspect ratio of up to 200, which is the greatest value reported so far, among Pt NWs synthesized by various template-less and surfactant-free methods), grew vertically on the TiO₂ coated Si substrate. No byproducts were found and thus no purificatory procedures are needed. Ultra-long Pt NWs can also be prepared on other substrate materials coated with TiO₂. Figure 3c displays Pt NWs grown radially on carbon fibers. The above results manifest that the selection of the precursor was crucial. Given that the melting point of H₂PtCl₆ is 60°C [20], it can be deduced that H₂PtCl₆ melted and re-solidified during the thermal treatment. The transformation of Na₂Pt(OH)₆ into Pt NWs was associated with the relatively lower electronegativity of the OH group (3.02) [21] compared to Cl (3.16), which may cause the metal ions to be reduced easily, thus allow the growth of NWs.

The XRD pattern and EDS spectrum (Figure 4a,b) demonstrate that the NWs thus produced were pure Pt with an FCC structure without any detectable impurity. For a better understanding of the structure of Pt NWs, a high-resolution transmission electron microscope (HRTEM) image recorded from a Pt NW (Figure 4c) depicts the lattice spacing between the {111} planes of 0.23 nm, which was in agreement with the value in a bulk Pt crystal, suggesting the growth direction of the Pt NWs was along {111} axes. The inserted electron diffraction pattern constructed by fast Fourier transform (FFT) also verifies this preferred growth direction.

To clarify how the state of the precursor affects the yield of NWs, Na₂Pt(OH)₆ powders and aqueous solution were placed or dropped on the TiO₂ coated Si wafers, respectively, and isothermally treated at chosen temperatures for 3 h in air by an IR furnace. According to the melting point of Na₂Pt(OH)₆, 150°C [20], the thermal treatment was held at 140°C to keep the salt in solid state or 160°C to turn it into liquid. The SEM images in Figure 5 show the morphologies of the samples after the TAP routes. For the solution samples after being thermal-treated at 140°C for 3 h (Figure 5a), chunky Na₂Pt(OH)₆ nodules and very few Pt NWs located in between them could be observed. Interestingly, when the holding temperature was raised to 160°C, the Pt salt solution was transformed into a plenty of Pt NWs with the average diameter of 40.9 nm and length of about 5.2 μm (Figures 5b and 6a,b), which
were slightly shorter and thicker than those synthesized at 300°C. Similar results were observed if the aqueous solution was replaced by powders. As illustrated in Figure 5c, the powders of Na₂Pt(OH)₆ remained without forming any NWs subsequent to the post thermal treatment at 140°C. Remarkably, after isothermal heating at 160°C, Na₂Pt(OH)₆ powders were transformed to Pt nanolawns, with average wire diameter and length of 44.6 nm and 5.8 μm, respectively (Figures 5d and 6a,b).

Quantitative data given in Figure 6c reveal that a large yield of NWs of up to 80 NWs/100 μm² could be obtained for both solution and powder samples subjected to thermal treatment at 160°C, i.e. 10°C higher than the melting point of Na₂Pt(OH)₆. Heating at 140°C, NWs were barely observed in the Na₂Pt(OH)₆ aqueous solution samples; and further, they were absent in the powder samples. The XRD patterns shown in Figure 7 support the above observations.

The state of Pt salts indeed caused a great difference in the NW yield. With respect to the solution samples at 140°C, water soon evaporized upon heating and thus Na₂Pt(OH)₆ re-precipitated as massive nodules. The evidence that a very small number of Pt NWs could be found in the solution samples heated at 140°C implies that dissociated Na₂Pt(OH)₆ in water was still capable of forming NWs, however, the reaction time was quite limited because water vaporized and depleted fast. At 160°C, Na₂Pt(OH)₆ in both solution and powder samples melted and transformed into NWs effectively. Accordingly, it is reasonable to infer that free ions in an electrolyte, especially the molten salt, are important for the resultant yield of Pt NWs.

It has been demonstrated that metallic ions can be reduced to form nano-sized nuclei on the surface of photocatalytic TiO₂ [22]. In our case, once the Pt⁴⁺ ions gained photoelectrons and the elemental Pt started to precipitate on the surface of TiO₂, a Schottky barrier formed since the work function of Pt (5.65 eV) [23] is larger than TiO₂ (4.2 eV) [24], a n-type semiconductor according to the results of Hall measurement listed in Table 2. As sketched in Figure 8, in order to align Fermi levels for the metal (E_Fm) and semiconductor (E_FS) at equilibrium, electrons move to the metal and then the positive charge due to ionized donor ions within W, the depletion region adjacent to the junction, matches the negative charge on the metal [25]. The equilibrium contact potential V₀ (so-called built-in potential barrier, the difference in work functions between Pt and TiO₂) prevents further net electron diffusion from the semiconductor conduction band into the metal. On the other side of the junction, Φ_B is the potential barrier for backward electron flow from the metal to the semiconductor.

It is suggested that during the subsequent thermal treatment, thermal electrons generated in TiO₂ can supply the follow-up reduction of Pt ions to grow NWs from the nano-sized nuclei. The formula for calculating
Figure 5 The reaction products on the TiO₂ coated substrate subjected to TAP process: (a) the solution samples heated at 140°C, (b) the solution samples heated at 160°C, (c) the powder samples heated at 140°C and (d) the powder samples heated at 160°C.

Figure 6 Histograms of the quantitative data of Pt NWs under different growth conditions: (a) diameter, (b) wire length and (c) wire density (the yield of NWs).
the number of thermal electrons \(n\) in a semiconductor as a function of temperature is shown below [26]:

\[
n = 2 \left( \frac{kT}{2\pi\hbar^2} \right)^{3/2} \left( m_em_h \right)^{3/4} \exp \left( -E_g/2kT \right)
\]

where \(k\) is Boltzmann’s constant, \(h\) is Planck’s constant, \(m_e\) and \(m_h\) are the effective mass of electron and hole, \(T\) is calculated in Kelvin and \(E_g\) is the band gap. It can be deduced that the great standard reduction potential of Pt\(^{4+}\) (1.15 V) can overcome the potential barrier, \(V_o\), and gave rise to a net electron flow for further reduction of the metallic ions. In order to maintain the charge neutrality at the Pt/TiO\(_2\) interface, hydroxide ions (OH\(^-\)) in the salt melt or aqueous solution were able to balance the positive charge on the TiO\(_2\) side, as illustrated in Figure 8. As a result, the thermal electrons attracted by Pt\(^{4+}\) were allowed to cross the interface and diffuse to the growing front of Pt nuclei. Consequently, the reduced Pt atoms accumulated and stacked on the closest packed facet to form \(\langle 111 \rangle\) -oriented one-dimensional nanostructure.

### Conclusions

By means of the TAP process, vertically grown ultra-long Pt NWs with the remarkable aspect ratio of up to 200 can be obtained on the TiO\(_2\) coated substrate in large quantities, without the additional assistance of surfactants, templates and seeding. The Pt NWs are single-crystalline with preferred growth direction along \(\langle 111 \rangle\). The selection and the state of the precursor are crucial for the yield of NWs. The nucleation and the growth of NWs are, respectively, supported by the photoelectrons and thermal electrons subsequently excited from TiO\(_2\). A model describing the interactions between the ions (Pt\(^{4+}\) and OH\(^-\)) and the electrons (photo- and thermal electrons) in the Pt/TiO\(_2\) junction was proposed and can be adopted to design the template-less fabrication process of ultra-long metallic NWs for further application.

### Abbreviations

CTAB: cetyltrimethylammonium bromide; FFT: fast Fourier transform; HRTEM: high-resolution transmission electron microscope; HCl: hydrogen chloride; IPA: isopropylalcohol; IR: infrared; NWs: nanowires; PVP: poly(vinylpyrrolidone); TAP: thermally assisted photoreduction; TTIP: titanium isopropoxide; TEM: transmission electron microscope; UV: ultraviolet; XRD: X-ray diffraction.

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