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

Yu-Lin Shen¹, Shih-Yun Chen², Jenn-Ming Song^{3*}, Tzu-Kang Chin³, Chu-Hsuan Lin⁴ and In-Gann Chen⁵

Abstract

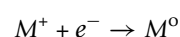
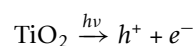
A template- and surfactant-free process, thermally assisted photoreduction, is developed to prepare vertically grown ultra-long Pt nanowires (NWs) (about 30–40 nm in diameter, 5–6 μm in length, and up to 80 NWs/100 μm² in the wire density) on TiO₂ coated substrates, including Si wafers and carbon fibers, 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 in the reduction 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,



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

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Table 1 A summary of prior works on the template-less synthesis of Pt NWs

Method	Orientation	Surfactant (S) or reductant (R)	Diameter (nm)	Length	Crystallization	Precursor	Authors
Chemical reduction	$\langle 111 \rangle$	PVP (S)	~5	~200 nm	Single-crystalline	H_2PtCl_6	Xia et al. [5-7]
Chemical reduction	-	CTAB (S)	2.2	Networks	Polycrystalline	K_2PtCl_4	Song et al. [8]
Photochemical reduction	$\langle 111 \rangle$	CTAB (S)	3-4	20-60 nm	Single-crystalline	K_2PtCl_4	Krishnaswamy et al. [9]
Chemical reduction	$\langle 111 \rangle$	HCOOH (R)	4	100-200 nm	Single-crystalline	H_2PtCl_6	Sun et al. [10-13]
Chemical reduction	-	Vitamin B ₂ (R)	10	Several tens of nm	Polycrystalline	Pt metal salt	Nadagouda et al. [14]
Thermal-assisted photoreduction	$\langle 111 \rangle$	-	32	6 μ m	Single-crystalline	$Na_2Pt(OH)_6$	Our group

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

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, TiO_2 was deposited by dipping 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 isopropylalcohol (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 TiO_2 films were annealed at 500°C for 8 h in an oxygen atmosphere to obtain well-crystallized anatase TiO_2 (step 1 in Figure 1), which could be identified by the grazing-angle X-ray diffraction (XRD) pattern shown in Figure 2.

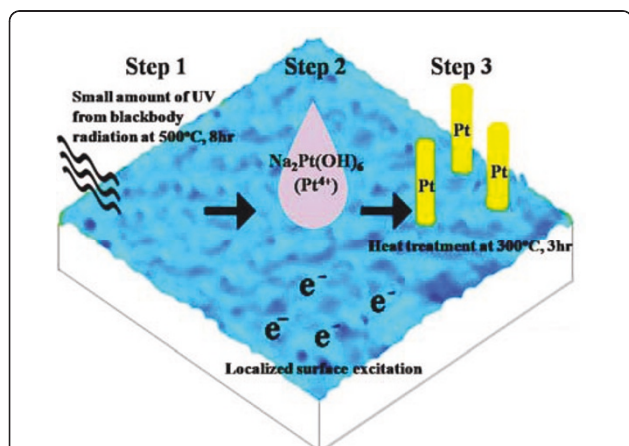


Figure 1 Schematic illusion of the main steps for forming Pt NWs by TAP.

NWs synthesis

As indicated by the step 2 in Figure 1, $Na_2Pt(OH)_6$ was selected as the precursor. Fifteen microliter of 0.05 M aqueous salt solution was dropped on the TiO_2 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 studies [16,17]), followed by a furnace-cooling to the ambient temperature (namely the post thermal treatment, step 3 in Figure 1). For comparison, the commonly used precursor, H_2PtCl_6 , was also adopted. To clarify how the state of the precursor affects the yield of NWs, the precursor 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

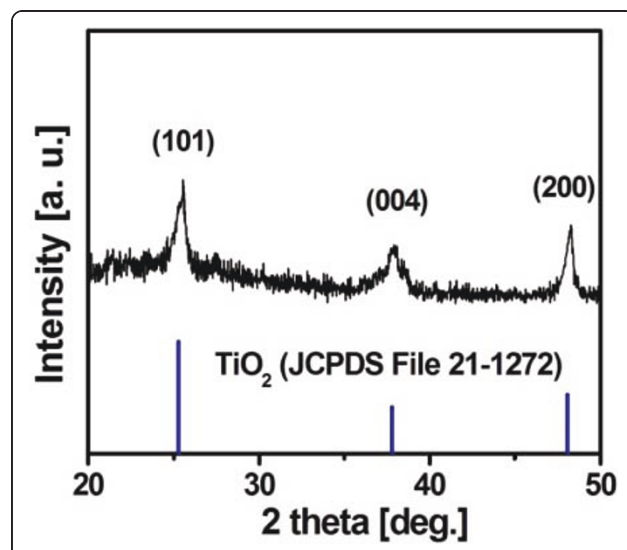


Figure 2 XRD pattern of the TiO_2 thin film annealed at 500°C for 8 h.

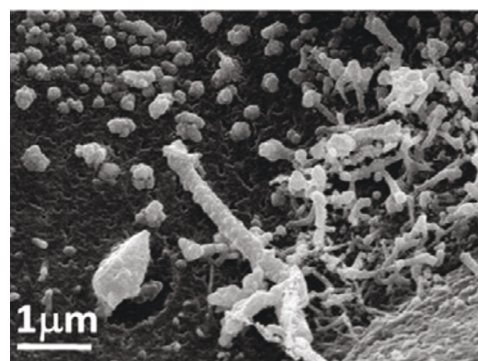
meter (GIXRD, Rigaku D/MAX2500) (incidence angle of 0.5°) with graphite monochromatic Cu $K\alpha$ radiation ($\lambda = 0.15418$ nm) at a scanning rate of 2° per minute from 20° to 50° . The yield (i.e. the wire number per $100 \mu\text{m}^2$) and dimensions of NWs were measured using a scanning electron 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

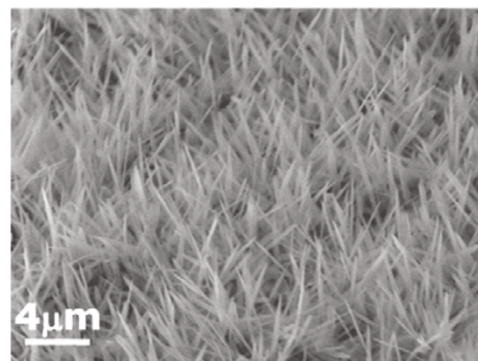
After heating the salt solutions at 300°C for 3 h, the SEM image shown in Figure 3a illustrates that the commonly used precursor, H_2PtCl_6 , still remained untransformed and was with nodular or worm-like appearance. For $\text{Na}_2\text{Pt}(\text{OH})_6$ (Figure 3b), all the Pt salt was transformed into Pt NWs in large quantities, with an average diameter of 34 nm and remarkable length of about $6 \mu\text{m}$ (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 TiO_2 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 TiO_2 . 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 H_2PtCl_6 is 60°C [20], it can be deduced that H_2PtCl_6 melted and re-solidified during the thermal treatment. The transformation of $\text{Na}_2\text{Pt}(\text{OH})_6$ 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 $\langle 111 \rangle$ axes. The inserted electron diffraction pattern constructed by fast Fourier transform (FFT) also verifies this preferred growth direction.

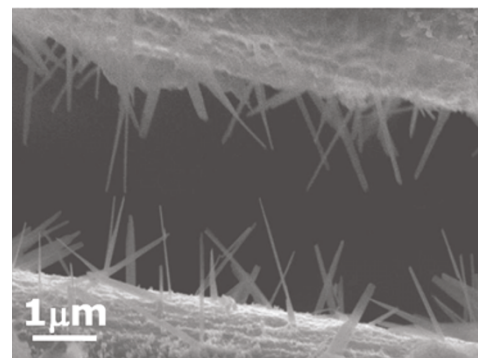
To clarify how the state of the precursor affects the yield of NWs, $\text{Na}_2\text{Pt}(\text{OH})_6$ powders and aqueous solution were placed or dropped on the TiO_2 coated Si wafers, respectively, and isothermally treated at chosen temperatures for 3 h in air by an IR furnace. According to the melting point of $\text{Na}_2\text{Pt}(\text{OH})_6$, 150°C [20], the thermal treatment was held at 140°C to keep the



(a)



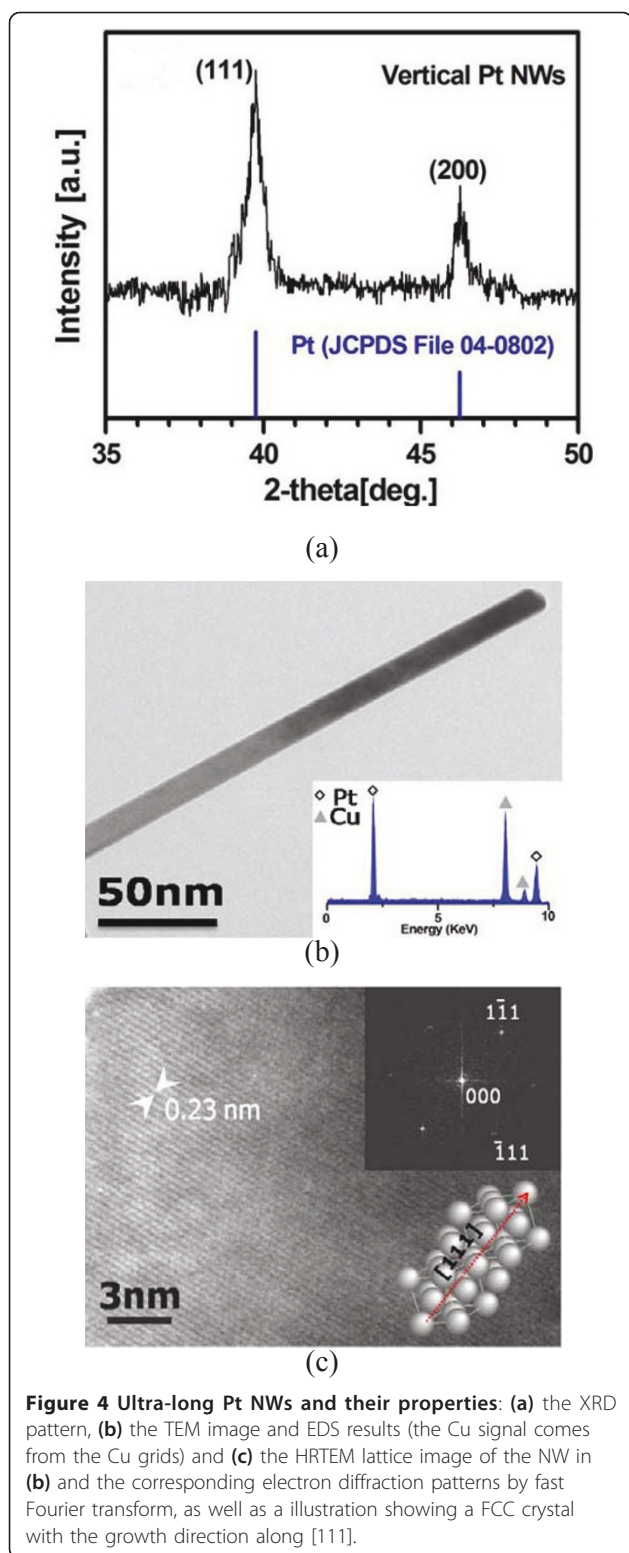
(b)



(c)

Figure 3 Nano- or micron-structures obtained from different Pt salts on TiO_2 coated substrates subjected to heating at 300°C : (a) H_2PtCl_6 on Si wafer, (b) $\text{Na}_2\text{Pt}(\text{OH})_6$ on Si wafer and (c) $\text{Na}_2\text{Pt}(\text{OH})_6$ on carbon fibers.

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 $\text{Na}_2\text{Pt}(\text{OH})_6$ 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 $5.2 \mu\text{m}$ (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 $\text{Na}_2\text{Pt}(\text{OH})_6$

remained without forming any NWs subsequent to the post thermal treatment at 140°C. Remarkably, after isothermal heating at 160°C, $\text{Na}_2\text{Pt}(\text{OH})_6$ 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/ $100 \mu\text{m}^2$ 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 $\text{Na}_2\text{Pt}(\text{OH})_6$. Heating at 140°C, NWs were barely observed in the $\text{Na}_2\text{Pt}(\text{OH})_6$ 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 $\text{Na}_2\text{Pt}(\text{OH})_6$ 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 $\text{Na}_2\text{Pt}(\text{OH})_6$ in water was still capable of forming NWs, however, the reaction time was quite limited because water vaporized and depleted fast. At 160°C, $\text{Na}_2\text{Pt}(\text{OH})_6$ 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 TiO_2 [22]. In our case, once the Pt^{4+} ions gained photoelectrons and the elemental Pt started to precipitate on the surface of TiO_2 , a Schottky barrier formed since the work function of Pt (5.65 eV) [23] is larger than TiO_2 (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 V_0 (so-called built-in potential barrier, the difference in work functions between Pt and TiO_2) 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 TiO_2 can supply the follow-up reduction of Pt ions to grow NWs from the nano-sized nuclei. The formula for calculating

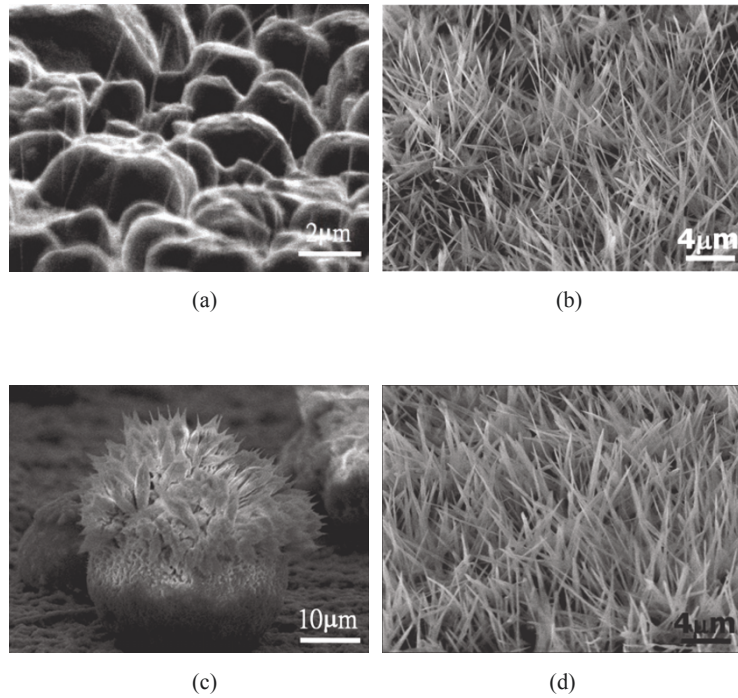


Figure 5 The reaction products on the TiO₂ coated substrate subjected to TAP process: (a) the solution samples heated at 140°C, (b) the solution samples heated at 160°C, (c) the powder samples heated at 140°C and (d) the powder samples heated at 160°C.

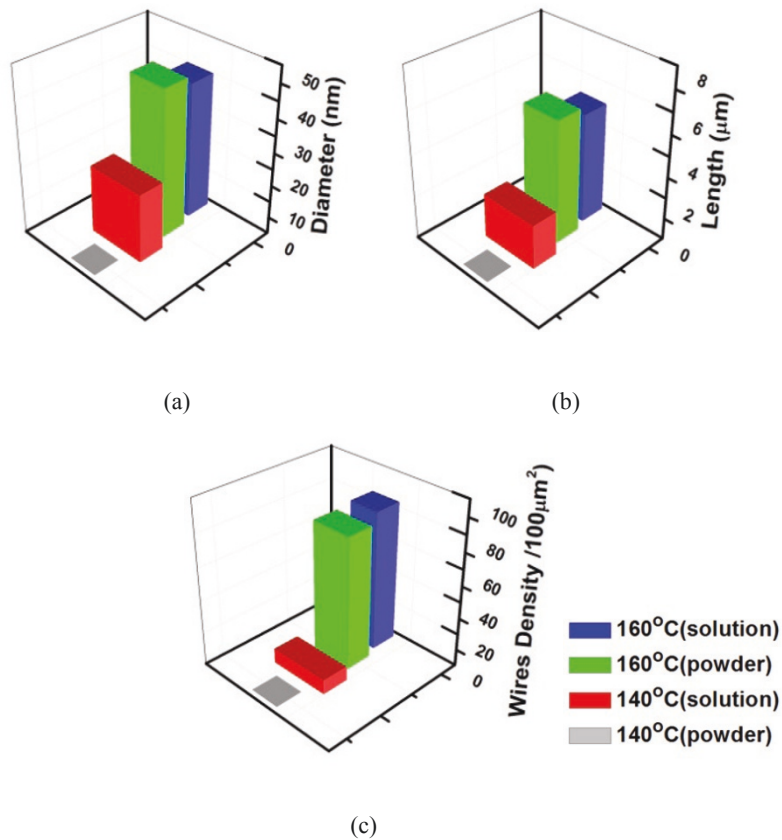
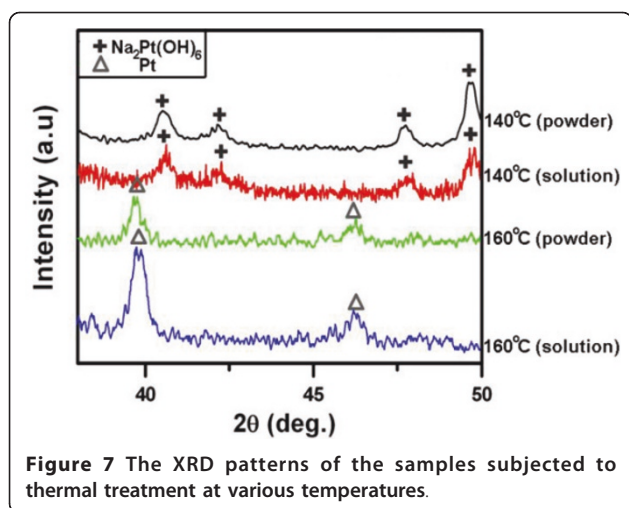


Figure 6 Histograms of the quantitative data of Pt NWs under different growth conditions: (a) diameter, (b) wire length and (c) wire density (the yield of NWs).



the number of thermal electrons (n) in a semiconductor as a function of temperature is shown below [26]:

$$n = 2 \left(\frac{kT}{2\pi h^2} \right)^{3/2} (m_e m_h)^{3/4} \exp(-E_g/2kT)$$

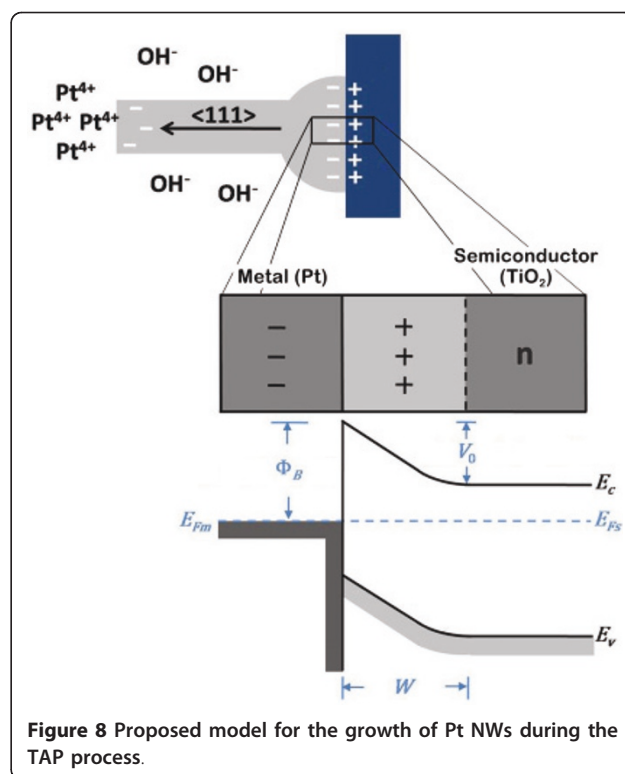
where k is Boltzmann's constant, h is Planck's constant, m_e and m_h are the effective mass of electron and hole, T is calculated in Kelvin and E_g is the band gap. It can be deduced that the great standard reduction potential of Pt^{4+} (1.15 V) can overcome the potential barrier, V_o , and gave rise to a net electron flow for further reduction of the metallic ions. In order to maintain the charge neutrality at the Pt/TiO₂ interface, hydroxide ions (OH^-) in the salt melt or aqueous solution were able to balance the positive charge on the TiO₂ 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 TiO₂ 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

Table 2 Electrical properties of TiO₂ obtained from the Hall measurement

Type	Carrier concentration (cm ⁻³)	Mobility (cm ² /V s)	Resistivity (Ω cm)
n	1.89×10^{17}	53	6.23×10^{-1}



$\langle 111 \rangle$. 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 TiO₂. A model describing the interactions between the ions (Pt^{4+} and OH^-) and the electrons (photo- and thermal electrons) in the Pt/TiO₂ 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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Authors' contributions

YLS carried out the main part of synthetic and analytical works, participated in the sequence alignment and drafted the manuscript. TKC participated in the synthetic experiments. SYC and CHL participated in the discussion of the growth mechanism. JMS participated in the design of the study, draft preparation and coordination. IGC conceived of the study and participated in its design. All authors read and approved the final manuscript.

Competing interests

The authors declare that they have no competing interests.

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