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Keywords: photocatalysts; titania nanotube; site-selective deposition of Pt nanoparticles; decomposition of acetaldehyde

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Graphical abstract

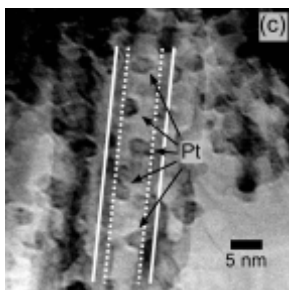
Title: Development of a titania nanotube (TNT) loaded site-selectively with Pt nanoparticles and their photocatalytic activities

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Summary:

We investigated site-selective deposition of Pt nanoparticles on the inside surface of TNT in order to improve the photocatalytic activity of the TNT. TNT loaded site-selectively with Pt nanoparticles by UV-irradiation under ethanol vapor showed the highest photocatalytic activity because the transfer rates of electrons were fastest and the active sites on TNT surface were not covered by Pt nanoparticles.



Development of a titania nanotube (TNT) loaded site-selectively with Pt nanoparticles
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Abstract

Site-selective deposition of Pt nanoparticles on a titania nanotube (TNT) was investigated in order to improve **the** photocatalytic activity of a TNT. TEM images showed that Pt nanoparticles were deposited site-selectively on the inside surface of the TNT by two methods. TNT powder loaded with Pt nanoparticles by UV irradiation under ethanol atmosphere exhibited the highest photocatalytic activity for oxidation of acetaldehyde. When Pt nanoparticles were deposited on only the inside surface of the TNT by UV irradiation, active sites on the TNT were not covered by Pt nanoparticles, resulting in an increase in its photocatalytic activity for oxidation of acetaldehyde.

Keywords: photocatalysts; titania nanotube; site-selective deposition of Pt nanoparticles; decomposition of acetaldehyde

1. Introduction

Titanium(IV) oxide (TiO_2) is known to have excellent photocatalytic activity and has been applied to **relieve** environmental pollution and destruction on a global

scale [1]. In addition, TiO_2 has been generically used a catalyst because of its optical and electronic properties, low cost, high level of photocatalytic activity, chemical stability and non-toxicity [2].

Nanosized materials derived from TiO_2 have been extensively investigated for various applications, including solar cells/batteries, electrode materials and photocatalysis, owing to their unique chemical and physical behaviors [3-6]. Moreover, since the discovery of a carbon nanotube [7], there have been many studies on one-dimensional nanostructures, such as nanotubes, nanorods and nanowires. TiO_2 -based nanotubes with a highly specific surface area, ion-exchangeable ability and photocatalytic ability have been considered for extensive applications [5, 6, 8]. However, unfortunately, this nanotube itself does not have a high level of photocatalytic ability. In order to improve the photocatalytic activity of TiO_2 , one generally loads platinum on the TiO_2 surface. Platinum loaded on a TiO_2 surface easily traps photoexcited electrons, resulting in an increase in efficiency of charge separation between electrons and holes [9, 10]. Therefore, the addition of metal to these nanotubes is expected to lead to improvement in their photocatalytic properties.

In this study, we successfully developed a TNT on which Pt nanoparticles were deposited site-selectively. The TNT with Pt nanoparticles, deposited through UV irradiation under an ethanol atmosphere, showed enhanced photocatalytic activity for oxidation of acetaldehyde.

2. Experimental

2.1. Materials and instruments

The TNT was kindly supplied by Catalysts & Chemicals Ind. Co., Ltd. The TNT was used after calcination at 350 °C for 3 hours in order to improve the crystallinity of the TNT. The relative surface areas of the TNT before and after calcination were 130 m² g⁻¹ and 110 m² g⁻¹, respectively. Hydrogen hexachloroplatinate (IV) hexahydrate (H₂PtCl₆•6H₂O), ethanol, and acetaldehyde were obtained from Wako Pure Chemical Industry. Other chemicals were obtained from commercial sources as guaranteed reagents and were used without further purification. The relative surface areas of the powders were determined by using a surface area analyzer (Micromeritics, FlowSorb II 2300). TEM observations were performed by using a HITACHI

H-9000NAR. X-ray photoelectron spectra (XPS) of the TNT loaded with Pt nanoparticles were measured using a JEOL JPS90SX photoelectron spectrometer with an MgK α source (1253.6 eV). The shift of binding energy due to relative surface charging was corrected using the C 1s level at 284.6 eV as an internal standard. The XPS peaks were assumed to have Gaussian line shapes and were resolved into components by a non-linear least-squares procedure after proper subtraction of the baseline.

2.2. Random deposition of Pt nanoparticles on the TNT surface

TNT powder was randomly loaded with platinum by means of the photo-deposition method using H₂PtCl₆•6H₂O as a platinum source and ethanol as a sacrificial electron donor as follows [11, 12]. Two g of TNT powder was added to 90 mL of deionized water, 10 mL of ethanol and 0.5 wt% of TiO₂ of H₂PtCl₆•6H₂O in a 300 mL flask. Nitrogen gas was passed through the suspension for 30 minutes to degas **any** oxygen dissolved in **the** water. After nitrogen bubbling, the reaction was carried out under weak UV-irradiation (1.0 mW cm⁻²) using a high-pressure mercury lamp

(WACOM Co. Ltd., BMS-251 SW) for 3 hours. Then the solution was stirred for 24 hours in the dark. After the platinum deposition, the powder was washed with deionized water and dried under vacuum at 60 °C for 3 hours. The TNT loaded with Pt nanoparticles by photodeposition is abbreviated as Pt-TNT-A.

2.3. Site-selective deposition of Pt nanoparticles on the TNT surface

Site-selective deposition of Pt nanoparticles on the TNT surface was performed as follows. First, 0.5 wt% of TiO_2 of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ was dissolved in 100 mL of deionized water, and then 2 g of pure TNT was suspended in the Pt^{4+} ions aqueous solution. The suspension was stirred for 24 hours. After filtration, the powder was washed with deionized water in order to remove all Pt^{4+} ions adsorbed on the outside surface of TNT. The powder was dried under reduced pressure at 60 °C for 3 hours. After Pt^{4+} ions had been adsorbed on the TNT, we used two methods for reduction of Pt^{4+} to metal Pt nanoparticles as follows.

(1): Reduction of Pt^{4+} ions adsorbed on the TNT was carried out under an H_2 atmosphere at 350 °C for 3 hours. The relative surface area of the TNT after the heat

treatment was $100 \text{ m}^2 \text{ g}^{-1}$. The TNT loaded with Pt nanoparticles by this method is abbreviated as Pt-TNT-B.

(2): Reduction of Pt^{4+} ions adsorbed on the TNT was carried out by irradiating light using a Xe lamp as a light source (XFL-300L) under a flow of ethanol-nitrogen gas. The intensity of the incident light and irradiation time were about 50 mW cm^{-2} and 24 hours, respectively. The TNT loaded with Pt nanoparticles by this method is abbreviated as Pt-TNT-C.

2.4. Photocatalytic degradation of acetaldehyde on TNT in gas phase

Photocatalytic activities of the TNT powders were evaluated by measuring the change in concentrations of acetaldehyde and evolved CO_2 as a function of irradiation time. A Tedlar bag (AS ONE Co. Ltd.) was used as the photo-reactor vessel with a volume of 125 cm^3 . One hundred mg of TNT powder was spread evenly on the bottom of a glass dish (area: $9.6 \text{ cm}^2 =$ irradiation area), and the glass dish was placed in the reaction vessel described above.

Five hundred ppm of acetaldehyde was prepared in the vessel by injection of

saturated gaseous acetaldehyde. The irradiations were conducted at room temperature after equilibrium between the gaseous and adsorbed acetaldehyde had been reached, which was ascertained by monitoring the concentration by a gas chromatograph about every 30 min. A 500 W Xe lamp (USHIO Co. Ltd., SX-UI501XQ) was used as a light source. Fine stainless meshes were used as neutral density filters to adjust the irradiation intensity (12.7 mW cm^{-2}). After starting the irradiation, we measured the decrease in acetaldehyde concentration using a gas chromatograph (Shimadzu Model GC-8A, FID detector) equipped with an FEG-20M 20% Celite 545 packed glass column using a CR-8A CHROMATOPAC for data processing. At the same time, the amount of gaseous carbon dioxide evolved was analyzed using a gas chromatograph (Shimadzu Model GC-9A, FID detector) equipped with a TCP 20% Uniport R packed column and a methanizer (GL Sciences, MT-221) operated at a temperature of $375 \text{ }^{\circ}\text{C}$ and using CR-8A CHROMATOPAC for data processing.

2.5. PA spectra measurement

In order to analyze the role of Pt nanoparticles loaded on the TNT, we

measured the PA spectra of a pure TNT sample and of platinized TNT. PA spectra were measured as previously reported [13]. A flow-type PA cell in which the atmosphere was controlled by the flow of 2-propanol-vapor containing nitrogen was used for time-resolved measurements. TNT powder was placed in the cell. The 2-propanol-nitrogen gas was injected into the PA cell for 30 minutes. TNT powder was photoirradiated using a light-emitting diode (Nichia NCCU033) emitting light at 365 nm for excitation of the TNT. An LED (Luxeon LXHL-ND98) emitting light at 625 nm as a probe light source was used, and its output intensity was modulated by a digital function generator (NF DF1905) at 80 Hz. The PA signal acquired by a condenser microphone buried in the cell was amplified and monitored by a digital lock-in amplifier (NF LI 5640).

3. Results and discussion

3.1. XPS spectra of the TNT loaded with Pt nanoparticles

Oxidation states of Pt atoms loaded on the TNT were determined by XPS analysis. Figure 1 shows Pt 4f spectra of TNTs loaded with Pt by various treatments. Pt

4f spectra of the TNT impregnated with Pt⁴⁺ ions aqueous solution (Fig. 1 (a)) showed peaks at 79.4 eV (Pt 4f_{5/2}) and 76.2 eV (Pt 4f_{7/2}). These peaks are assigned to Pt⁴⁺ ions [9, 10, 14]. In Pt 4f spectra of Pt-TNT-A (Fig. 1 (b)), Pt-TNT-B (Fig. 1 (d)) and Pt-TNT-C (Fig. 1 (c)), positions of the two peaks due to Pt⁴⁺ ions were shifted to a lower binding energy region around 74.5 eV and 71.6 eV. These peaks are assigned to Pt⁰ metal [9, 10, 14]. This suggested that Pt⁴⁺ ions adsorbed on the TNT surface were reduced to Pt metal by heat treatment under a hydrogen atmosphere or by photoexcited electrons.

3.2. TEM images of site-selectively platinized TNT

Figure 2 shows TEM images of Pt-TNT-A (Fig. 2 (a)), Pt-TNT-B (Fig. 2 (b)) and Pt-TNT-C (Fig. 2 (c)). The structure of the TNT was maintained after heat treatment at 350 °C for 3 hours as shown in Figure 2. The outer diameter of the nanotube was about 10 nm and the inner diameter was about 5 nm. Figure 2 (a) shows TEM image of Pt-TNT-A. Pt nanoparticles were deposited on the inside and outside surfaces of TNT. The size distribution of Pt-TNT-A was 1.4 – 5.7 nm. The average size of Pt

nanoparticles of Pt-TNT-A was 3.8 nm. TEM images of Pt-TNT-B (Figure 2 (b)) and Pt-TNT-C (Figure 2 (c)) indicated that Pt nanoparticles were loaded on the inside surface of TNT. Diameters of Pt nanoparticles loaded on Pt-TNT-B were 3.0 – 3.5 nm. The average size of Pt particles on Pt-TNT-B was 3.3 nm. On the other hand, diameters of Pt nanoparticles loaded on Pt-TNT-C were 2.1 – 3.5 nm and the average size of that was 2.9 nm. The Pt nanoparticles loaded on Pt-TNT-C were smaller than the Pt nanoparticles loaded on Pt-TNT-B. Pt nanoparticles loaded on Pt-TNT-B were thought to have been sintered due to heat treatment at 350 °C under a hydrogen atmosphere.

3.3. PA spectra of TNT powders

Figure 3 shows PA spectra of pure TNT and platinized TNT powders. PA intensity indicates that amount of Ti^{3+} ions generated by photoexcited electrons. If the photoexcited electrons do not transfer to molecules adsorbed on surface, the photoelectrons reduce Ti^{4+} ions in TiO_2 bulk or surface, resulting in increase in PA intensity. In the case of platinized TNT, PA intensity is supposed to decrease as a compared to pure TNT because photoexcited electrons transfer to Pt metal on TNT. The

PA intensity of pure TNT increased gradually under UV irradiation (365 nm). Few photoexcited electrons transferred to oxygen and they accumulated in TNT particles, resulting in an increase in the amount of Ti^{3+} ions. On the other hand, the PA intensity of platinized TNT was remarkably decreased. The rate of transfer of photoexcited electrons to oxygen is improved due to deposition of Pt nanoparticles on the TNT. PA spectra of Pt-TNT-A, Pt-TNT-B and Pt-TNT-C were similar. PA spectra of Pt-TNT-A and Pt-TNT-C were completely superimposed, although the amount of Pt nanoparticles loaded on Pt-TNT-C was smaller than the amount of Pt nanoparticles loaded on Pt-TNT-A. Pt nanoparticles loaded on the outside surface of the TNT were thought not to play a role as co-catalyst for electron transfer. The PA intensity of Pt-TNT-B was slightly higher than that of the other platinized TNT at the initial stage of UV light irradiation. The transfer rate of photoexcited electrons of Pt-TNT-B is thought to be slightly slower than that of the other platinized TNT due to aggregation of Pt nanoparticles by heat treatment.

3.4. Photocatalytic activities of site-selectively platinized TNT for acetaldehyde

oxidation

Figure 4 shows the amount of CO₂ evolved by oxidation of acetaldehyde as a function of irradiation time. Photocatalytic activity of Pt-TNT-A was slightly higher than that of pure TNT. We assume that oxidation of acetaldehyde is mainly carried out on the outside TNT surface because diffusion of acetaldehyde to **the** inside of the TNT was restrained. In the case of random Pt deposition, Pt nanoparticles loaded on the outside of the TNT covered active sites on the TNT surface, resulting in a decrease in photocatalytic activity.

The photocatalytic activity of Pt-TNT-B was remarkably decreased. In the process of deposition with hydrogen, the TNT was calcined at 350 °C for 3 hours in order to reduce Pt⁴⁺ ions to Pt⁰ metal. Under these conditions, the size of Pt particles was increased (Fig.2 (a)) because of sintering. Larger Pt particles might reduce the electron transfer rate of Pt-TNT-B (Fig.3) because the number of O₂ **molecules** adsorbed on larger Pt particles prepared by heat treatment under hydrogen is smaller than that on smaller Pt particles prepared by deposition under UV irradiation in the presence of ethanol vapor due to a decrease in **the** surface area of Pt particles. Therefore, **the**

photocatalytic activity of Pt-TNT-B decreased. Alternatively, the diffusion of oxygen inside the nanotube was thought to be restrained by packing larger Pt nanoparticles inside TNT. In the case of Pt-TNT-C, the photocatalytic activity of Pt-TNT-C was remarkably improved as compared with those of Pt-TNT-A and Pt-TNT-B due to overcome these problems. However, further investigations are needed in order to clarify the mechanism of improvement in photocatalytic activity.

4. Conclusion

We investigated site-selectively deposited Pt nanoparticles on a TNT surface. Pt nanoparticles were loaded on the inside surface of the TNT by heat treatment under hydrogen and by UV irradiation under ethanol-nitrogen gas. The Pt nanoparticles loaded on Pt-TNT-C were smaller than those loaded on Pt-TNT-B. Pt-TNT-C showed the highest photocatalytic activity. The electron transfer rate of Pt-TNT-C was faster than that of Pt-TNT-B because the Pt nanoparticles loaded on Pt-TNT-C were smaller than those on Pt-TNT-B. In addition, active sites on outside TNT surface were not covered by Pt nanoparticles. On the other hand, the photocatalytic activity of Pt-TNT-A

decreased as compared to Pt-TNT-C because Pt nanoparticles loaded on the outside surface of the nanotube did not contribute to charge separation (Figure 3) and prevented acetaldehyde from adsorbing on active sites of TNT and prevented TNT particles from absorbing irradiation light.

Acknowledgement

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Figure captions

Figure 1 XPS spectra of Pt atoms loaded on TNTs obtained by various reduction treatments: (a) without reduction treatment, (b) Pt-TNT-A, (c) Pt-TNT-C and (d) Pt-TNT-B.

Figure 2 TEM images of Pt-TNT-A (a), Pt-TNT-B (b) and Pt-TNT-C (c).

Figure 3 PA spectra of pure TNT, Pt-TNT-A, Pt-TNT-B and Pt-TNT-C.

Figure 4 Amount of evolved CO₂ on TNT loaded with Pt nanoparticles ((a) pure TNT, (b) Pt-TNT-A, (c) Pt-TNT-B and (d) Pt-TNT-C) as a function of irradiation time.

Figure 1

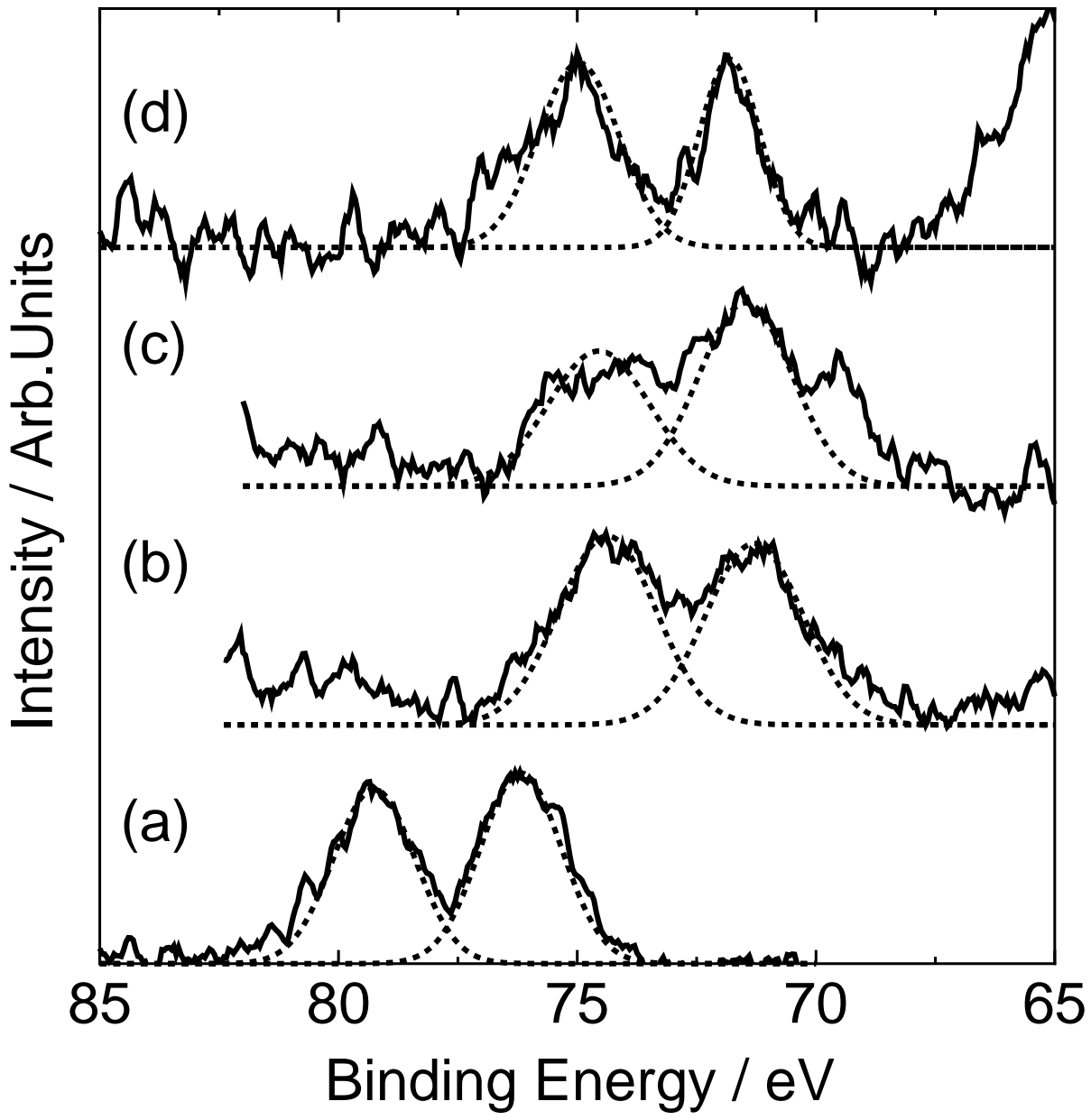


Figure 2 (a)
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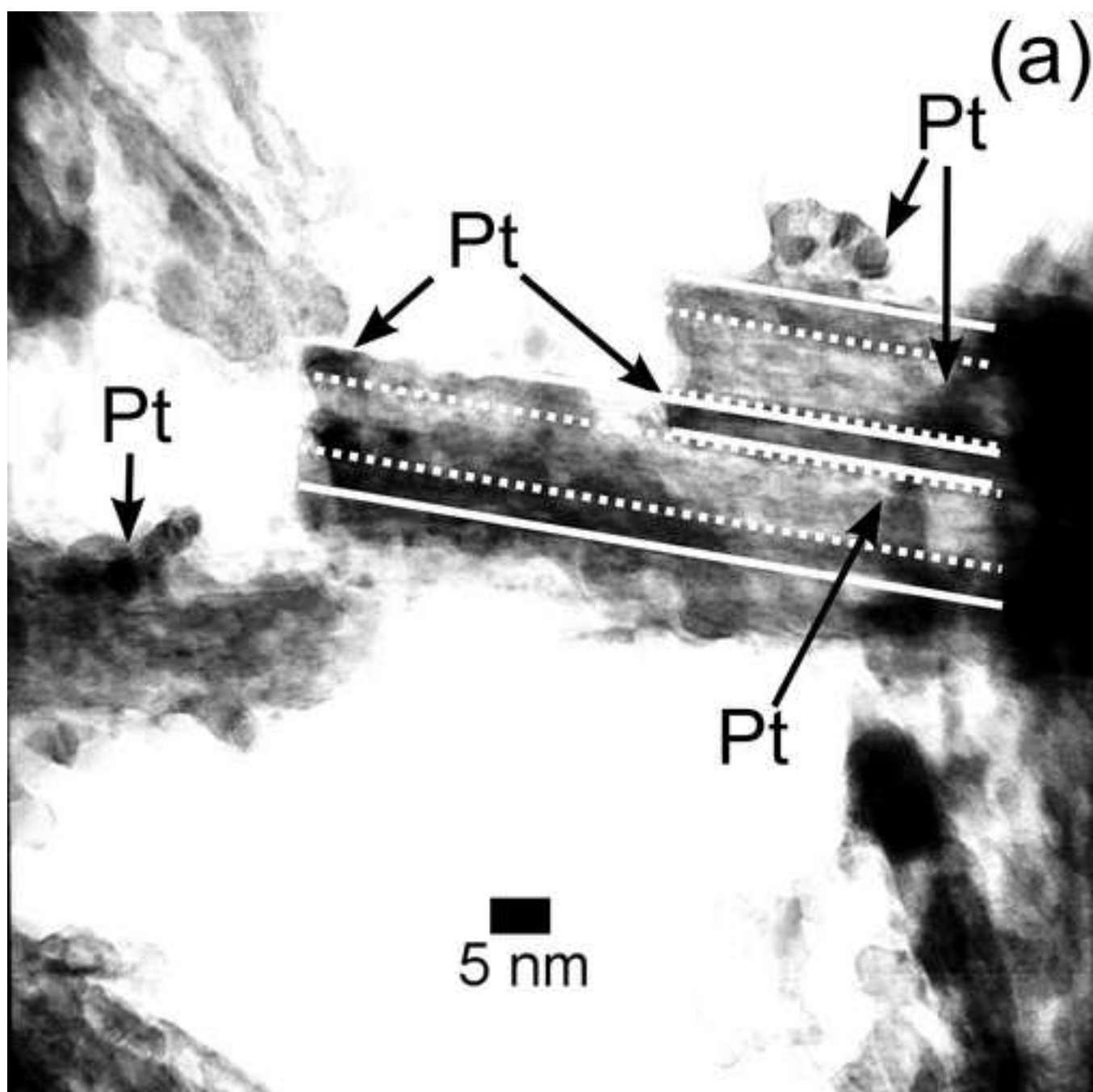


Figure 2 (b)
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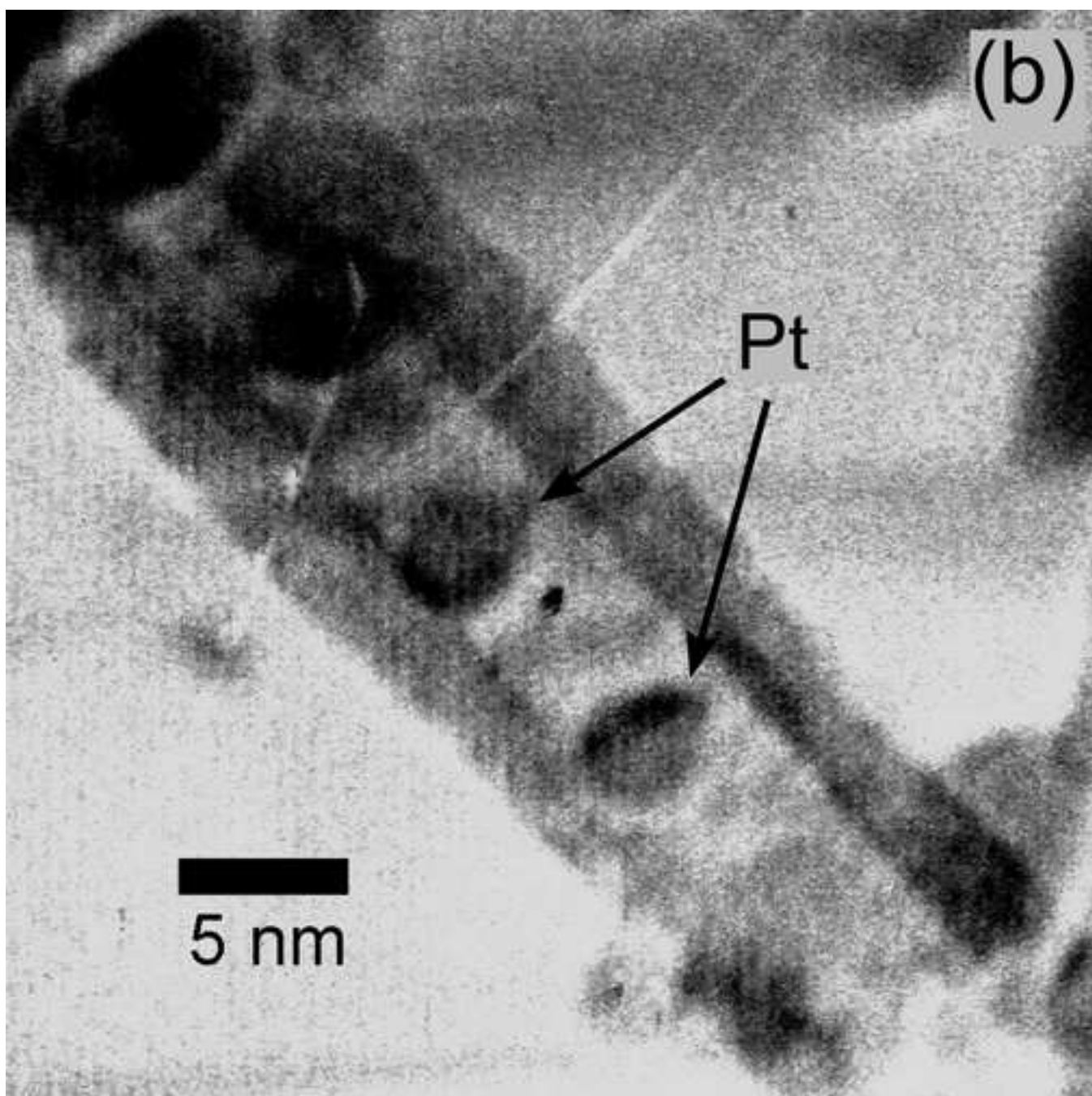


Figure 2 (c)
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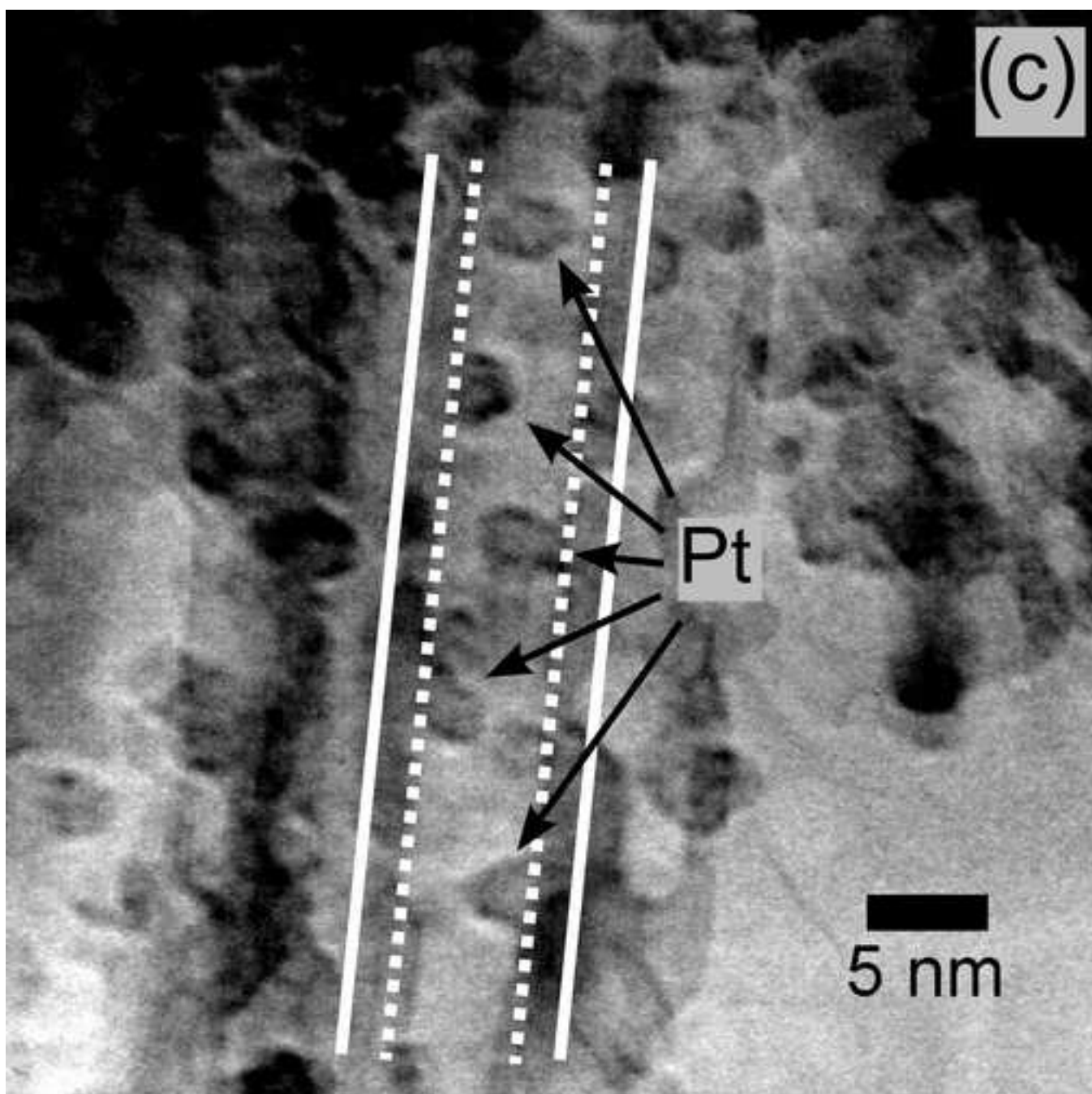


Figure 3

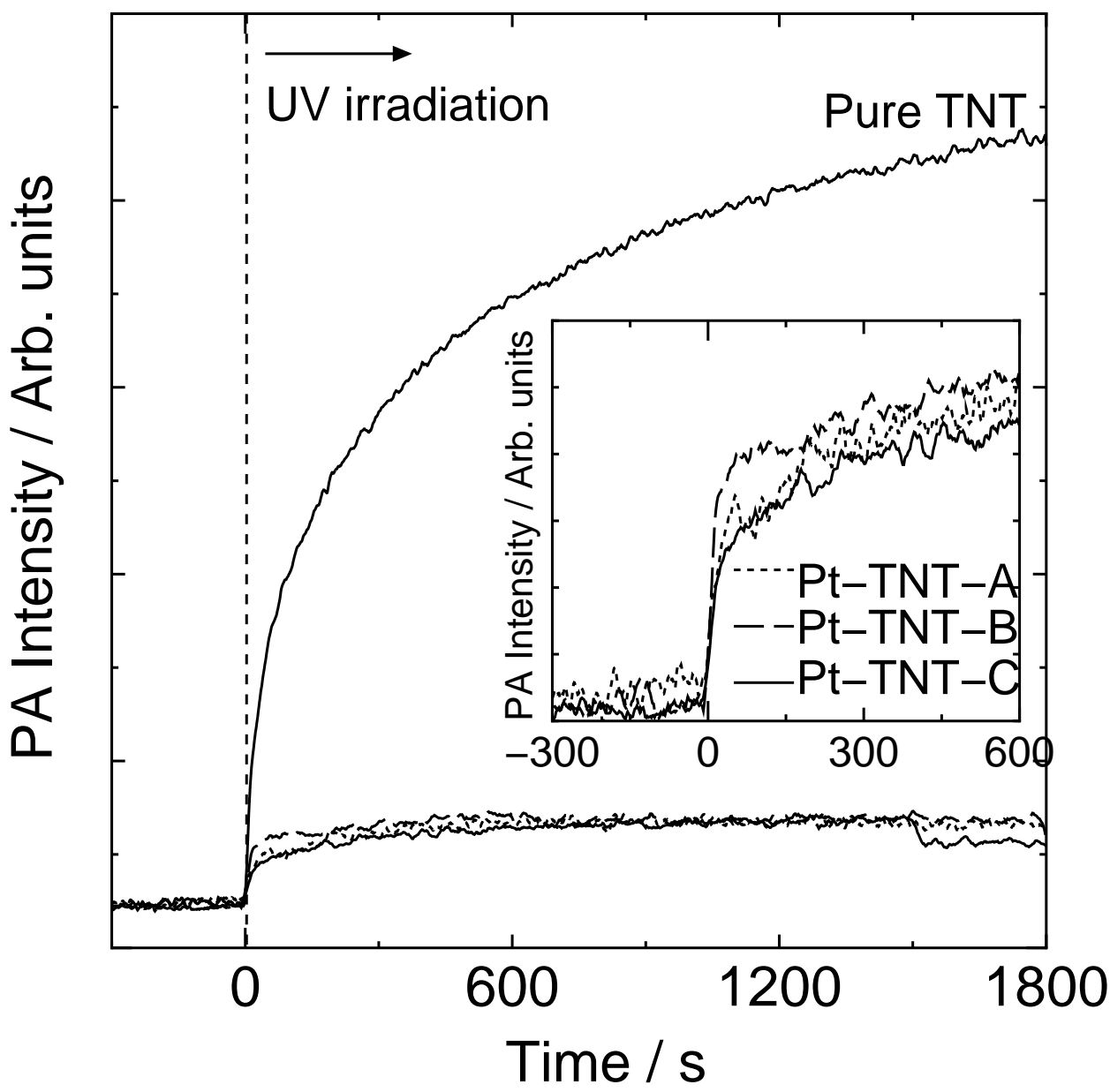


Figure 4

