

Improvement of photocatalytic activity of brookite titanium dioxide nanorods by surface modification using chemical etching

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Abstract

Surface morphology of brookite titanium dioxide (TiO_2) nanorods was modified by chemical etching with aqueous hydrogen (H_2O_2)-ammonia (NH_3) or sulfuric acid (H_2SO_4) solution. The brookite nanorods after chemical etching were characterized by TEM, SAED, FE-SEM, XRD and specific surface area measurements. Brookite nanorods after chemical etching with H_2O_2 - NH_3 solution exposed new crystal faces in the tips, and nanorods with sharper tips were observed. On the other hand, etching with H_2SO_4 at 200 °C induced morphological changes in the tip faces and broadened the angle between tip faces as a result of dissolution along the [001] direction, though brookite nanorods were only slightly etched after etching with H_2SO_4 at room temperature. Photocatalytic activity of brookite nanorods was tested by toluene decomposition in gas phase under ultraviolet irradiation. Brookite nanorods etched with H_2O_2 - NH_3 solution showed higher photocatalytic activity than that of brookite nanorods before etching. In the case of H_2SO_4 etching at 200 °C, brookite nanorods after etching exhibited lower photocatalytic activity. One reason for this may be that the formation of newly exposed crystal faces by H_2O_2 - NH_3 etching improved separation of redox sites due to their strong oxidation ability.

Keywords: Surface modification, Brookite nanorods, Chemical etching, Redox site, Photocatalytic activity.

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1. Introduction

Titanium dioxide (TiO_2) has been intensively studied as a semiconductor photocatalyst for various applications owing to its high activity, chemical stability and nontoxicity [1, 2]. In nature, TiO_2 exists in three kinds of crystal phases: anatase, rutile and brookite. Each phase displays different physical and chemical properties due to the difference in structure. Brookite is the rarest natural TiO_2 crystal phase, and it had been difficult to prepare single-phase brookite due to its thermodynamic metastability. Recently, single-phase brookite has been successfully prepared by hydrothermal treatment of a titanium complex, such as titanium glycolate complex [3, 4] or titanium bis (ammonium lactate) [5], and its photocatalytic activity has been discussed.

A semiconductor photocatalyst is activated by photogeneration of charge carriers, i.e., electrons in the conduction band (CB) and positive holes in the valence band (VB), which can be exploited to promote reduction and oxidation processes on the surface. Abilities for reduction and oxidation are greatly influenced by potential positions of the CB and VB, which are determined by the constituent elemental atom and crystal structure. Brookite TiO_2 possesses the most negative CB potential among TiO_2 crystals [5]. This is preferable for a TiO_2 photocatalyst because oxygen (O_2) reduction, which is the counterpart reaction of oxidation, of organic compounds is a rate-limiting step. Therefore, application of brookite to photocatalytic decomposition of organic compounds may be reasonable because of its strong ability for O_2 reduction.

Modification of surface morphology is another strategy for improvement of photocatalytic reaction. Our group proposed that exposed crystal faces on the surface of TiO_2 induced separation of redox sites as a result of predominant reaction on each face [6, 7]. This means that properties of exposed crystal faces can greatly influence both reduction and oxidation processes. So far, exposed crystal faces have been controlled by utilizing a shape-control reagent in sample preparation [8] or by modifying with a chemical etching reagent such as hydrofluoric acid (HF) or sulfuric acid (H_2SO_4) solution [9, 10].

Recently, our group has reported improvement of photocatalytic activity of rutile nanorods by chemical etching with aqueous hydrogen (H_2O_2)-ammonia (NH_3) solution [11]. Newly exposed crystal faces exhibited superior oxidation ability, resulting in enhancement of photocatalytic activity for toluene decomposition [11]. In the present study, surface morphology of brookite nanorods with exposed crystal faces was modified by chemical etching. We firstly discuss the relation between surface morphology and photocatalytic activity for brookite nanorods.

2. Experimental

2.1. Chemicals

All chemical materials were commercial products and were used without further treatment. Titanium (IV) ethoxide, H_2O_2 , NH_3 , glycolic acid, H_2SO_4 , 2-propanol, hexachloroplatinic acid, lead nitrate, nitric acid and toluene were purchased from Wako Pure Chemical Industries. Commercial TiO_2 P-25 (Evonik Industries) with a specific surface area of $47 \text{ m}^2 \text{ g}^{-1}$ was used as a reference TiO_2 photocatalyst. Throughout the paper, samples are referred to as shown in Table 1.

2.2. Synthesis of brookite nanorods

Brookite nanorods were prepared by the reported procedure [3, 4]. Ten grams of titanium (IV) ethoxide was added to 50 ml of ethanol solution, and then three milliliters of deionized water was added to the solution. The solution was stirred for 30 minutes and then centrifugally separated. Amorphous TiO_2 was obtained by drying the specimens in a vacuum oven.

Four grams of amorphous titania was dispersed in a water-cooled solution containing 40 ml 30% H_2O_2 and 10 ml 28% NH_3 . After stirring the mixture for 2 h, two grams glycolic acid was added. The color of the mixture changed from yellow to red. After stirring for 24 h to eliminate excess H_2O_2 and NH_3 (aq), a titanium glycolated complex solution was obtained. The pH and volume of the complex solution were adjusted to 10 and 50 ml by addition of NH_3 and deionized water. The solution was placed in a sealed Teflon-lined autoclave reactor. The reactor was heated in an oven at 200°C for 25 h. The substrate was centrifuged, washed with deionized water several times, and dried in a vacuum oven.

2.3. Chemical etching with H_2O_2 - NH_3 or H_2SO_4 solution [11]

In the case of H_2O_2 - NH_3 etching, three hundred milligrams of brookite particles obtained by hydrothermal synthesis was added to a solution containing 15 mL of 10% H_2O_2 and 1 mL of 25% NH_3 . The mixture was stirred for 0.5-3 h at room temperature. After the treatment, brookite particles were separated by centrifugation, washed, and dried at 70°C in a vacuum.

Concentrated H_2SO_4 solution was used for H_2SO_4 etching. Five hundred milligrams of brookite particles was added to 10 mL of H_2SO_4 solution at room temperature. The mixture was stirred for 1 week at room temperature or for 30 min at 200°C . After the treatment, brookite particles were filtered and washed with 1% NH_3 solution. Then brookite particles were washed with deionized water until ionic conductivity of the solution was below 10 S cm^{-1} . Finally, the

brookite particles were dried at 70 °C in a vacuum oven.

2.4. Characterization

Crystal phase identification was performed by using an X-ray diffract meter (XRD; Rigaku, Min Flex II) with Cu K α radiation ($\lambda=1.5405$ Å). The surface morphology of the samples was observed by a field emission scanning electron microscope (FE-SEM; JEOL, JSM-6701FONO) and transmission electron microscope (TEM; Hitachi, H-9000NAR). The specific surface area was determined with a surface area analyzer (Quanta-chrome, NOVA 4200e) by using the Brunauer-Emmett-Teller equation. Diffuse reflectance (DR) spectra were measured by using a UV-Vis spectrophotometer (Shimadzu, UV-2500) equipped with an integrating sphere unit (Shimadzu, ISR-240A). X-ray photoelectron spectra (XPS) of the samples were measured using a photoelectron spectrometer (Shimadzu, KRATOS AXIS-NOVA).

2.5. Photocatalytic activity test

Photocatalytic activity of brookite TiO₂ nanorods was evaluated by decomposition of toluene under UV-Vis irradiation. A Tedlar bag (AS ONE) was used as the reactor vessel. After 150 mg of TiO₂ powder had been spread on the bottom of a glass dish, the dish was put into a reaction vessel with a volume of 125 ml mixed air (79% nitrogen (N₂), 21% O₂, < 0.1 ppm of carbon dioxide (CO₂), 100 ppm of toluene). After an adsorption equilibrium had been reached in the dark, light irradiation was conducted at room temperature. A 500 W Xe-lamp (Ushio Co. Ltd. SX-UI501XQ) was used as the light, source and light wavelengths shorter than 350 nm were cut off with a UV-35 filter (AGC Techno glass). Fine stainless meshes were used as neutral density filters to adjust the irradiation intensity (5 mW cm⁻²). During irradiation, the amount of toluene concentration and evolved CO₂ as a function of irradiation time was analyzed by a gas chromatograph (Shimadzu GC-1700 and GC-8A).

2.6. Determination of redox sites by photocatalytic deposition of platinum (Pt) and lead dioxide (PbO₂) on brookite nanorods

Photocatalytic deposition of Pt and PbO₂ on brookite nanorods was performed by the following procedure [6, 7]. One hundred milligrams of brookite nanorods was added to 50 ml of mixed solution containing 0.52 mol L⁻¹ 2-propanol and 1 mmol L⁻¹ hexachloroplatinic acid. N₂ gas was purged into the suspension to remove the oxygen. The mixed solution was irradiated by

UV-LED (Nichia, NCCU033, λ =ca. 365 nm, 1 mW cm⁻²) for 24 h. After irradiation, the color of the particles changed from white to silver. This indicates that Pt was deposited by the procedure. The suspension was centrifuged and washed with deionized water. The obtained particles were dried at 70 °C in vacuum oven for 4 h.

For PbO₂ deposition, Pt-deposited brookite particles were used as the starting material. Sixty milligrams of Pt-deposited brookite TiO₂ nanorods was dispersed in 30 ml of a solution containing 0.1 mol L⁻¹ PbNO₃, and pH of the suspension was adjusted to 1.0 by addition of nitric acid solution. The suspension was irradiated by a mercury lamp (Ushio Co. Ltd. SX-UI501HQ) with a light intensity of 100 mW cm⁻² for 24 h. After the photoreaction, the color of the particles changed from silver to brown. This indicates that PbO₂ was photodeposited on the Pt-deposited brookite nanorods.

3. Results and discussion

3.1. Characterization of brookite nanorods after etching with H₂O₂-NH₃ solution

Figure 1 shows XRD patterns of brookite nanorods before and after chemical etching with H₂O₂-NH₃ solution. In the XRD patterns, all of the peaks agreed with those of brookite TiO₂ phase and other crystal phases, i.e., rutile and anatase were not detected. In addition, the crystal structure of brookite TiO₂ was retained after etching with H₂O₂-NH₃ solution. However, the diffraction peaks attributed to brookite TiO₂ became broader after etching. This indicates that brookite nanorods become smaller by etching. The average crystallite size of the sample was calculated by Scherrer's equation from the peak attributed to brookite {211} (Table 1). The crystal size of brookite nanorods decreased with an increase in etching time. This decrease of particle size agreed with the specific surface area (Table 1).

Figure 2 shows TEM and SEM images of brookite nanorods before and after chemical etching with H₂O₂-NH₃ solution. Brookite nanorods before etching showed a rod-like shape with specific exposed crystal faces (Fig. 2a). SEAD patterns suggest that exposed crystal faces on the side and tip were attributed to {210} and {212} faces and that the rod evolved along the [001] direction. Surfaces of brookite nanorods were selectively etched from the tip by H₂O₂-NH₃ etching, and the angle between tip faces became sharper with increase in etching time. The newly exposed crystal faces on the tip of the brookite nanorods after etching for 30 min were attributable to {21n_b} (n_b < 2) faces (Fig. 2b). With an increase in etching time up to 1 h, the tips of the brookite nanorods became sharper and newly exposed crystal faces {21n_c} (n_c < n_b) were observed (Fig. 2c). After etching for 3 h, side exposed crystal faces {210} were also etched and nanorods without specific exposed crystal faces were observed. Similar

morphological changes have been reported in the case of rutile nanorods etched by $\text{H}_2\text{O}_2\text{-NH}_3$ solution, and thus rutile nanorods were mainly etched from the tips and formed newly exposed crystal faces [11].

During etching with $\text{H}_2\text{O}_2\text{-NH}_3$ solution, the color of the mixed suspension became yellow. Ohtani et al. reported that the yellow color of the suspension, which was generated by $\text{H}_2\text{O}_2\text{-NH}_3$ etching of commercial TiO_2 P-25, originated to in the formation of a $\text{Ti}^{4+}\text{-H}_2\text{O}_2$ complex and that the rate of dissolution of rutile was faster than that of anatase [12, 13]. Judging from the color change and obtained amount of brookite, the dissolution rate of brookite was also faster. Brookite nanorods were completely dissolved in $\text{H}_2\text{O}_2\text{-NH}_3$ solution with longer etching time (> 6 h).

3.2. Characterization of brookite nanorods after chemical etching with H_2SO_4 solution

Figure 3 shows XRD patterns of brookite nanorods before and after chemical etching with H_2SO_4 solution. Etching at room temperature for 1 week induced only a small difference in the XRD patterns. The average crystallite size of brookite nanorods was only slightly increased after etching at room temperature for 1 week (Table 1). One plausible reason is that the etching rate of small brookite particles was faster than that of large particles and small brookite particles were preferentially dissolved in H_2SO_4 solution. On the other hand, an appreciable difference was observed between XRD patterns of the samples before and after etching with H_2SO_4 at 200°C . The average crystallite size decreased after etching with H_2SO_4 at 200°C , and changes in specific surface area also supported these results. Therefore, brookite nanorods were greatly dissolved in H_2SO_4 at 200°C (Table 1).

Figure 4 shows TEM and SEM images of brookite nanorods before and after etching with H_2SO_4 solution. Appreciable changes in morphology of brookite nanorods were not observed after etching with H_2SO_4 at room temperature for 1 week (Fig. 4b). However, brookite nanorods after etching with H_2SO_4 at 200°C were etched along the $[001]$ direction and newly exposed crystal faces $\{21n_s\}$ ($n_s > 2$) were observed (Fig. 4c). This shape evolution of brookite was similar to that of rutile nanorods, though rutile was etched in H_2SO_4 at room temperature [11]. This indicates that brookite is very stable against H_2SO_4 solution compared to rutile crystal.

3.3. Photocatalytic activity for toluene decomposition

Figure 5a shows the time course of CO_2 evolution for toluene decomposition over brookite nanorods before and after etching with $\text{H}_2\text{O}_2\text{-NH}_3$ solution. All brookite nanorods exhibited higher photocatalytic activities than that of commercial TiO_2 P-25. This may imply that more

negative potential of the CB potential induced efficient O₂ reduction, resulting in higher activity. Brookite nanorods after H₂O₂-NH₃ etching showed higher activity than that before etching, and the brookite nanorods after 1 h of etching exhibited the highest photocatalytic activity among the samples. However, all samples had similar specific surface areas (Table 1). These results suggest that specific surface area does not play a dominant factor in photocatalytic activity for decomposition of toluene.

It has been reported that TiO₂ particles after H₂O₂ treatment increase the absorption range up to visible light due to generation of surface peroxide species [14]. This color change from white to yellow was observed during H₂O₂-NH₃ etching, but the color of the sample was recovered to white by the washing procedure after H₂O₂-NH₃ etching. Moreover, an appreciable difference in DR spectra was not observed among brookite nanorods before and after H₂O₂-NH₃ etching (data not shown). Therefore, changes in photoabsorption were not the reason for increase in photocatalytic activity. In addition, it is possible that formation of surface peroxide species influence toluene adsorption. However, a difference in the concentrations of toluene adsorption was not observed in this study (Table 1). Therefore, we consider that evolution of exposed crystal faces in the tip induced activity changes ($\{212\} \rightarrow \{21n_b\} \rightarrow \{21n_c\}$, $n_c < n_b < 2$). This will be discussed in section 3.4. In contrast, the decrease in photocatalytic activity of brookite nanorods after 3 h of etching may be explained by poorly-defined faces on the side face, which decreased separation efficiency of redox sites.

Figure 5b shows the time course of CO₂ evolution for toluene decomposition over brookite nanorods before and after etching with H₂SO₄. Brookite nanorods after etching with H₂SO₄ at room temperature showed activity similar to that before etching. This is reasonable since only a slight difference was observed among these samples. However, brookite nanorods after etching with H₂SO₄ at 200 °C showed an appreciable decrease in photocatalytic activity, though it has been suggested that H₂SO₄ treatment increases photocatalytic activity of rutile due to an increase in the number of acid sites [15]. Therefore, adsorption species of SO₄²⁻ on the surfaces of brookite nanorods is thought to have an influence on photocatalytic activity. However, sulfur atoms were not observed on the surfaces of brookite nanorods by XPS analysis (data not shown). Thus, morphological change may be another plausible reason. Brookite rod length was shortened after H₂SO₄ etching at 200 °C, resulting in the formation of newly exposed crystal faces $\{21n_s\}$ ($n_s > 2$) and decrease in surface area of $\{210\}$ side crystal faces. This might be due to deterioration of the balance between redox reactions. This will be discussed in section 3.4.

3.4. Determination of redox sites by photodeposition of Pt and PbO₂

In order to clarify the photocatalytic reaction properties, we determined redox sites of

brookite nanorods by photodeposition of Pt and PbO₂. Figure 6 shows TEM and SEM images of brookite nanorods after photodeposition of Pt and PbO₂. Small particles with a size of ca. 3 nm were observed on side faces of brookite nanorods (Fig. 6a, c). These small particles were attributed to photodeposited Pt, judging from the results of EDX analysis (Fig. 6e) and change in color from white to silver. This indicates that reduction of Pt⁴⁺ to Pt by excited electrons mainly proceed in side faces {210}, and side exposed crystal faces {210} provide reduction sites. In the case of PbO₂ deposition, particles with a size of ca. 10 nm were observed on the tip surfaces of brookite nanorods (Fig. 6b, d). These particles were attributable to PbO₂, judging from the results of TEM-EDX analysis (Fig. 6f) and change in color to brown. These results indicate that Pb²⁺ was oxidized to PbO₂ mainly on the tip surface {212} and that the tip surfaces {212} provide oxidation sites. Therefore, the reason for the high activity of brookite nanorods was not only CB potential but also the separation of redox sites (oxidation on the tip faces and reduction on the side faces).

Chemical etching is thought to have an influence on efficiency of redox separation because surface morphology can be modified by chemical etching. In the case of H₂O₂-NH₃ etching, tip faces {212} attributed to oxidation sites were greatly modified, and new tip faces with sharper angles between tip faces were formed (Fig. 2). These morphological changes increased photocatalytic activity. On the other hand, shortened rod length and broadened angle between tip faces induced by H₂SO₄ etching at 200 °C decreased photocatalytic activity (Fig. 4). Thus, changes in the ratio of surface area between reduction (S_{red}) and oxidation (S_{ox}) might influence photocatalytic activity as a result of changes in the balance between redox reactions. However, the same tendency for decrease in $S_{\text{red}}/S_{\text{ox}}$ was observed in samples etched by H₂O₂-NH₃ and samples etched by H₂SO₄, though the photocatalytic activities showed an inverse tendency. This means that change in $S_{\text{red}}/S_{\text{ox}}$ is not the predominant reason for improvement of photocatalytic activity. Another reason might be that the activity of oxidation sites was changed by newly exposed crystal faces. Similar changes were observed in chemical-etched rutile nanorods, which showed changes of activity by morphological modification of oxidation sites [11]. As a result, change in oxidation activity of faces influenced photocatalytic activity, and {21n} ($n < 2$) faces showed high oxidation activity, while {21n} ($n > 2$) faces showed low activity, compared to {212} faces.

4. Conclusions

In the present study, we firstly investigated the relation between surface morphological changes induced by chemical etching and photocatalytic activity for brookite nanorods. Etching rate of brookite nanorods with H₂O₂-NH₃ was fast. After etching, morphology was modified

from the tip faces and newly exposed crystal faces $\{21n\}$ ($n < 2$) were observed. On the other hand, H_2SO_4 etching induced small changes at room temperature, but brookite nanorods were dissolved along the $[001]$ direction in H_2SO_4 at $200\text{ }^\circ\text{C}$. Increase of photocatalytic activity was observed only in brookite nanorods after $\text{H}_2\text{O}_2\text{-NH}_3$ etching. The reason for this might be that the newly exposed faces formed by $\text{H}_2\text{O}_2\text{-NH}_3$ etching can improve oxidation ability as a result of highly active faces working as oxidation sites.

Figure captions

Figure 1. XRD patterns of brookite nanorods before and after chemical etching with $\text{H}_2\text{O}_2\text{-NH}_3$ solution.

Figure 2. TEM and SEM images and SEAD patterns of brookite nanorods (a) before etching and after (b) 30 min, (c) 1 h, and (d) 3 h of $\text{H}_2\text{O}_2\text{-NH}_3$ etching.

Figure 3. XRD patterns of brookite nanorods before and after chemical etching with H_2SO_4 solution.

Figure 4. TEM and SEM images and SEAD patterns of brookite nanorods (a) before etching, (b) after 1 week of H_2SO_4 etching at room temperature, and (c) after 30 min of H_2SO_4 etching at $200\text{ }^\circ\text{C}$.

Figure 5. Time profiles of CO_2 evolution of toluene decomposition over commercial and prepared TiO_2 particles before and after chemical etching with (a) $\text{H}_2\text{O}_2\text{-NH}_3$ solution and (b) H_2SO_4 solution.

Figure 6. (a) TEM and (c) SEM images of brookite nanorods after photodeposition of Pt. EDX analysis (e) was carried out for small particles on side faces of rods during TEM measurements. (d) TEM and (d) SEM images of Pt-deposited brookite nanorods after photodeposition of PbO_2 . EDX analysis (f) was carried out for small particles on tip faces of rods during TEM measurements.

Table 1. Physical and chemical properties of commercial TiO_2 and prepared brookite nanorods.

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Figure 1
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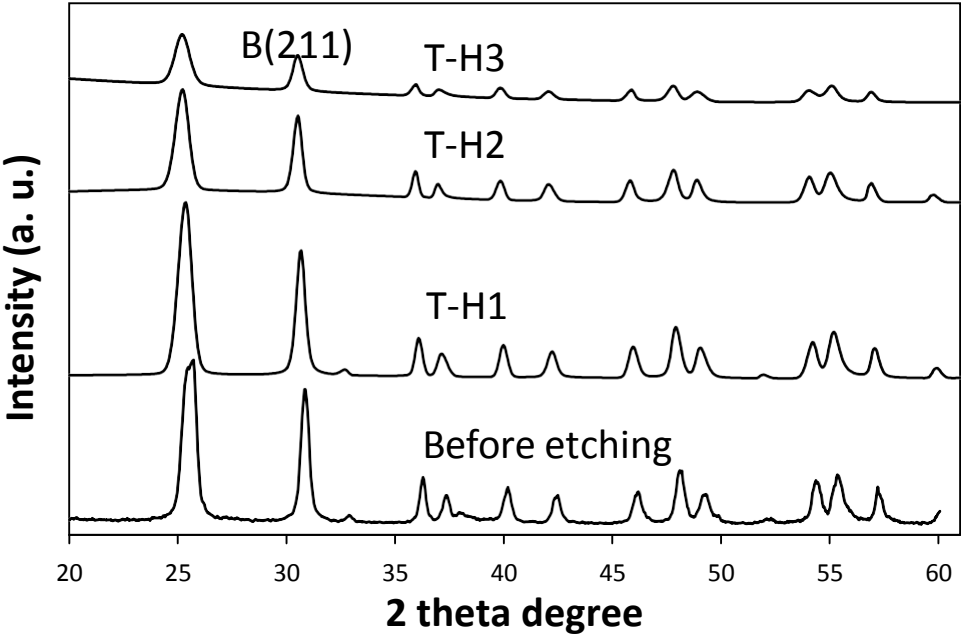


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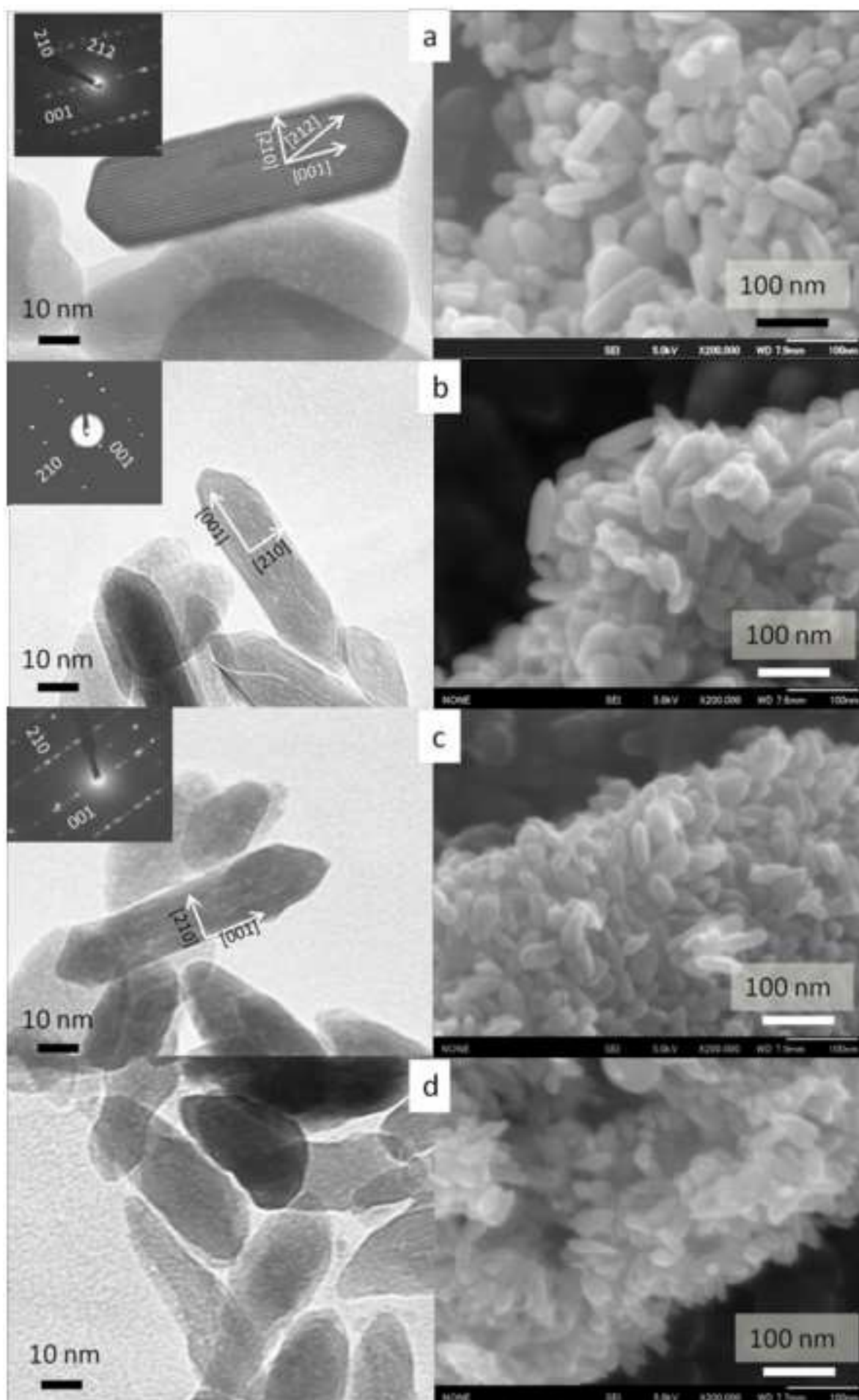


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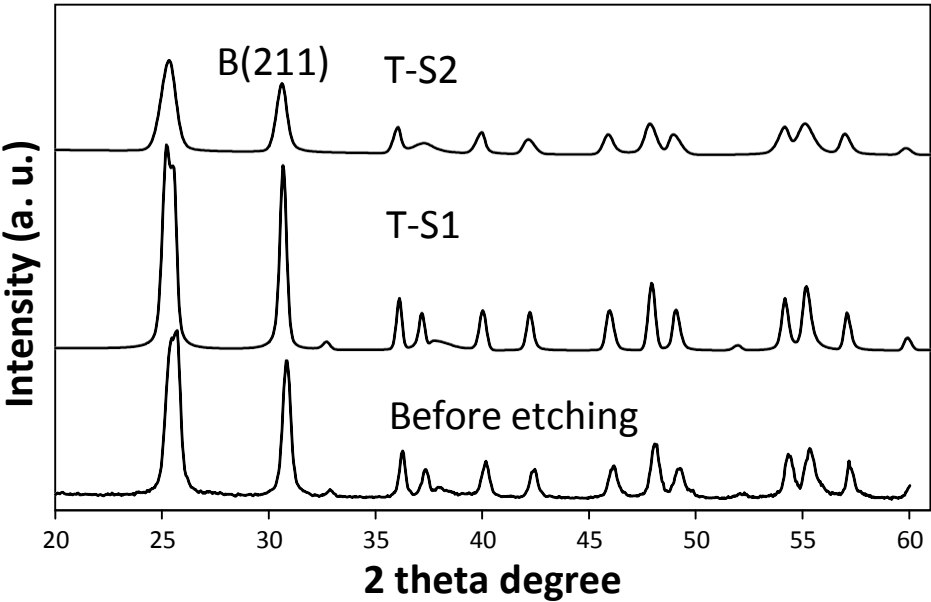


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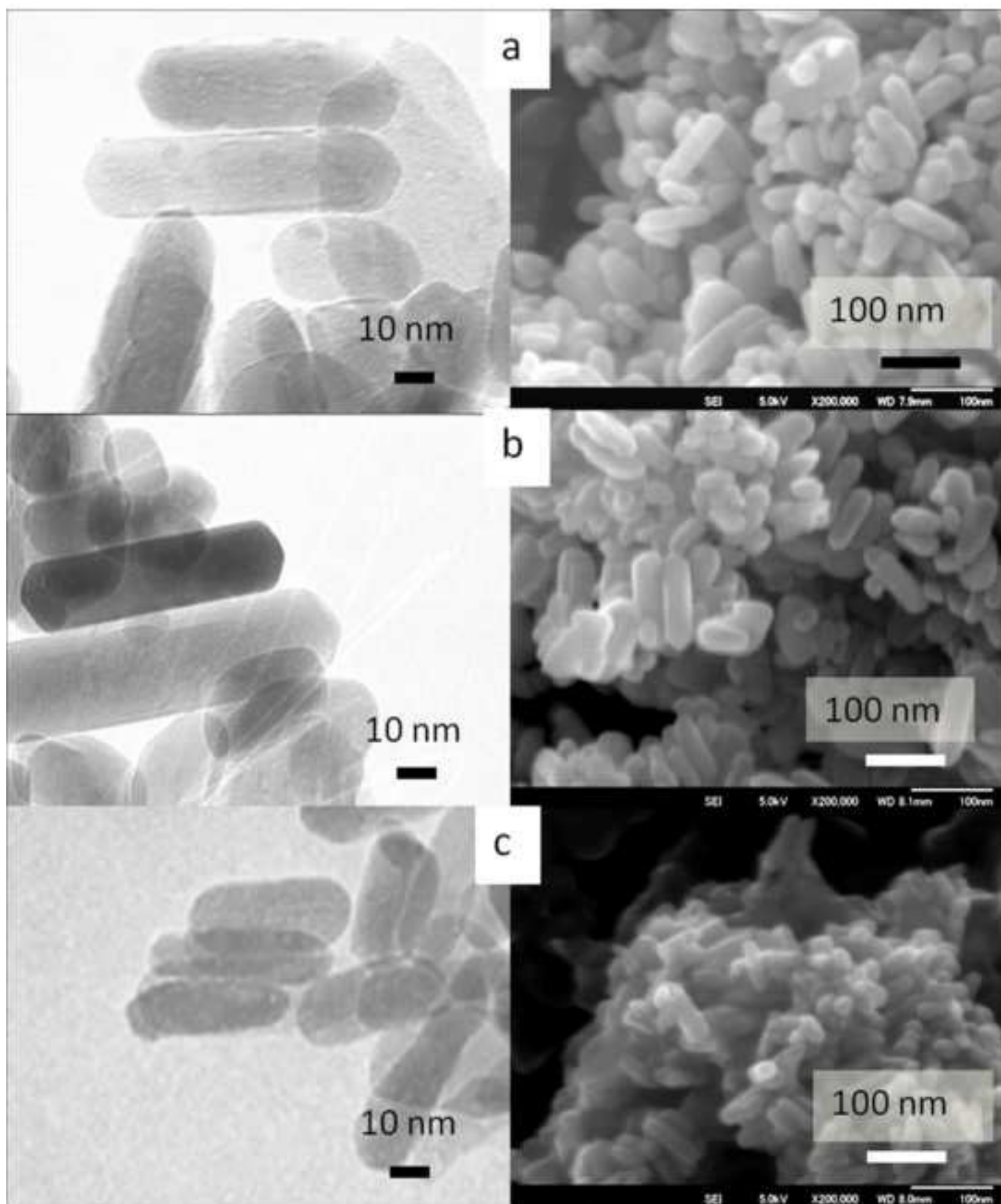


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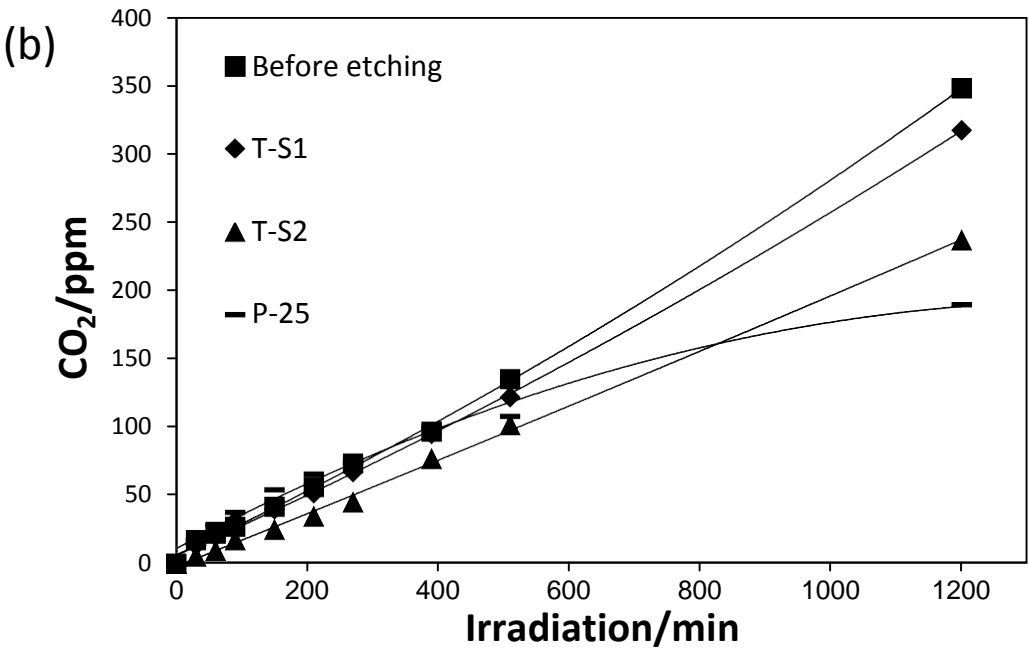
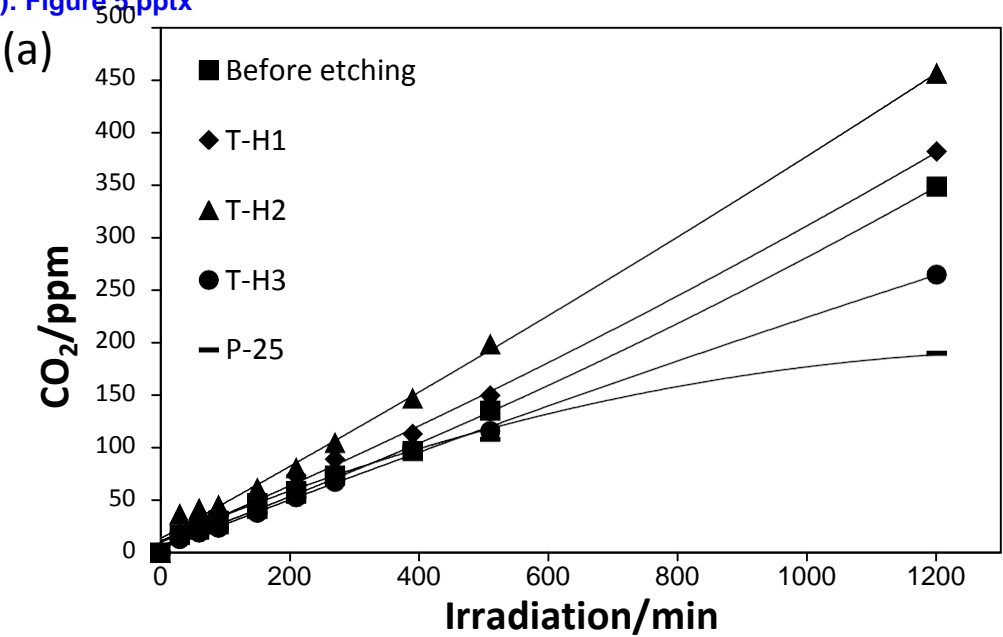


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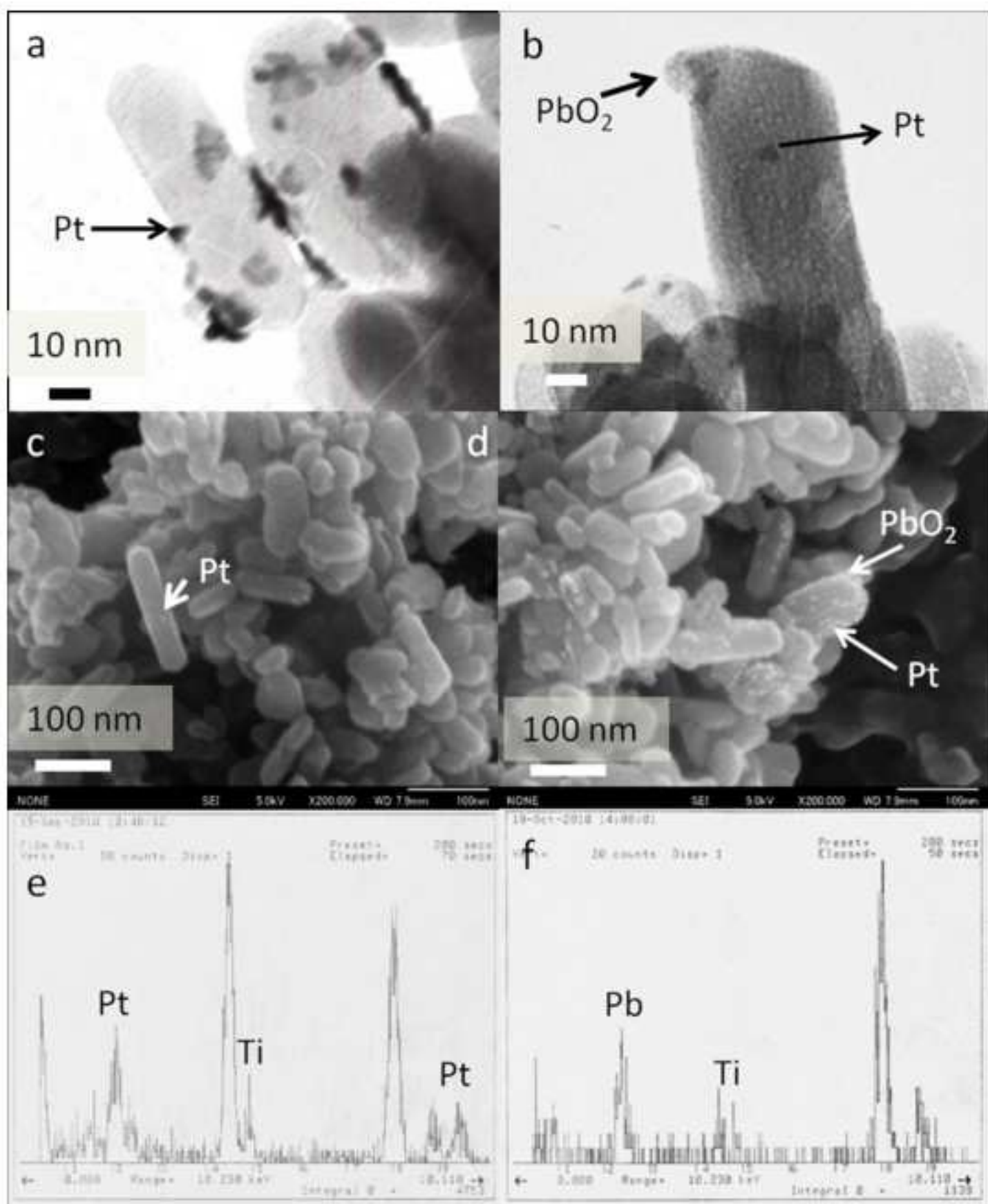


Table 1

Sample name	Etching condition	Etching time	Mean crystallite size (nm)	BET surface area (m ² g ⁻¹)	Toluene adsorbance balance in dark (ppm)
P-25				47	32.2
Before etching			20.4	53	25.8
T-H1	H ₂ O ₂ -NH ₃	30 min	18.48	57	25.5
T-H2	H ₂ O ₂ -NH ₃	1 h	17.79	58	26
T-H3	H ₂ O ₂ -NH ₃	3 h	16.53	62	25.9
T-S1	H ₂ SO ₄ -25°C	1 week	24.24	48	24.6
T-S2	H ₂ SO ₄ -200°C	30 min	15.21	79	26.1