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Synthesis of titanium(IV) oxide of ultra-high photocatalytic activity: high-temperature hydrolysis of titanium alkoxides with water liberated homogeneously from solvent alcohols

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Abstract

Thermal treatment of titanium(IV) alkoxides dissolved in alcohols at temperature of 523-573 K under autogenous pressure yielded microcrystalline anatase titanium(IV) oxide (TiO_2) with diameter of 11-31 nm and surface area of 42-138 m^2g^{-1}. Similar treatment in hydrocarbons such as toluene gave no solid products, indicating that both hydrolysis of alkoxides with water liberated homogeneously from solvent alcohols and crystallization of anatase phase occurred simultaneously. These TiO_2's were thermally stable, e.g., BET surface area of TiO_2 synthesized at 573 K, 63 m^2 g^{-1}, was reduced only 30% (45 m^2g^{-1}) even by calcination at 973 K.

Their photocatalytic activity was examined in mineralization of acetic acid in aqueous solutions under aerated conditions and dehydrogenation of 2-propanol under deaerated conditions; almost all the samples showed the activity more than twice higher than those of representative active photocatalysts, Degussa P-25 and Ishihara ST-01. The superior activity of the present TiO_2 photocatalysts was attributable to compatibility of high crystallinity and large surface area owing to the newly developed synthetic procedure.

Keywords: Titanium(IV) oxide; Anatase; Photocatalyst; Thermal stability; Crystallization; Organic solvent; Titanium alkoxide; Hydrolysis

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1. Introduction

Titanium(IV) oxide (TiO_2) has attracted much attention mainly in expectation of being applied to environmental photocatalytic processes such as deodorization, prevention of stains, sterilization [1], and removal of pollutants from air and water.[2-4] For the realization of their practical application, development of highly active TiO_2 photocatalyst is keenly desired. Based on the kinetic investigation of photocatalytic reactions, one of authors (B.O.) has pointed out that TiO_2 particles having both large surface area and high crystallinity must exhibit higher photocatalytic activity [5]. The former property should increase the amount of surface-adsorbed substrate(s) to enhance the capture of photogenerated electron (e^-) and positive hole (h^+), and the latter, i.e., less defects acting as the recombination center, should suppress mutual e^--h^+ recombination.

In the course of study on inorganic syntheses in organic media [6-9], we have found that microcrystalline TiO_2 powders having an average diameter of ca. 10 nm could be synthesized by thermal decomposition (TD) of titanium(IV) tert-butoxide (TTB) in inert organic solvents such as

toluene under autoclaving conditions [8]. Due to the small solubility of TiO_2 in organic solvents, these TD-TiO_2 powders consisted of the agglomerates of nano-sized single crystals of anatase and exhibits the characteristic properties, large surface area, high crystallinity, and high thermal stability. As expected from these properties, TD-TiO_2 showed the activity more than twice higher than those of commercially available active TiO_2 powders for photocatalytic mineralization, i.e., complete decomposition, of acetic acid in aqueous solutions under aerated conditions [8].

In the TiO_2 synthesis by the TD method, structure of alkyl groups in titanium alkoxide was found to be an important factor; at 473 K, TTB was decomposed while primary and secondary alkoxides were not decomposed even at 573 K [8]. Difference in thermal stability of the C-O bond in each alkoxide was attributable to these results. On the other hand, when water was fed in the autoclave separately from the organic solvent, the alkoxide was hydrolyzed at high temperature with water dissolved in the organic solvent from gas phase and thereby microcrystalline TiO_2 was produced [6]. In this HyCOM (Hydrothermal Crystallization in Organic Media) method, the structure of the alkyl group was not a decisive factor for the TiO_2 formation. The resulting highly-crystallized nanoparticles also exhibited the highest, as far as we examined, photocatalytic activity in several reaction systems [10-12].

In the present paper, we intended to hydrolyze titanium alkoxide more homogeneously in organic solvents at high temperatures and developed a novel method, i.e., hydrolysis of titanium alkoxides with water homogeneously formed from alcohols used as the solvent. Here we show the synthesis of nano-sized crystalline TiO_2 powders and their ultra-high activity in some photocatalytic reaction systems.

2. Experiments

Titanium(IV) alkoxides, 10 g, was dissolved in a 70 cm^3 portion of an alcohol in a test tube which was then set in a 200 cm^3 autoclave. An additional 30 cm^3 of the alcohol was placed in the gap between the test tube and the autoclave wall. The autoclave was thoroughly purged with nitrogen, heated to desired temperature (523-573 K) at a rate of 2.7 deg min^{-1}, and kept at that temperature for 2 h. After the autoclave treatment, the resulting powders were washed repeatedly with acetone and dried in air. In the present paper, the TiO_2 samples prepared by this method is called THyCA (Transfer Hydrolytic Crystallization in Alcohols) TiO_2. A part of the THyCA-TiO_2 powders was calcined in a box furnace for 1 h in air.

Powder X-ray diffraction (XRD) (RINT 2500, Rigaku, Tokyo, Japan) was measured using Cu*K*α radiation and a carbon monochromator. Morphologies of the particles were observed with a transmission electron microscope (TEM) (JEM-3010, JEOL, Tokyo, Japan) operated at 300 kV.

Photocatalytic activity of TiO_2 for mineralization of acetic acid in aerated aqueous suspension was determined according to the previous papers [8,11]. Prior to the photocatalytic reaction, pre-treatment was carried out in order to decompose contaminated organic moieties on the TiO_2 surface; TiO_2 (50 mg) was suspended in 5 cm^3 of water and photoirradiated at wavelength at > 300 nm by a high-pressure mercury arc (100 W) under oxygen with magnetic stirring until carbon dioxide (CO_2) was not liberated any more. After the pre-treatment, air was bubbled into the suspension for 15 min, and then acetic acid (175 μmol) was injected through a rubber septum. The resulting aerated aqueous suspension was irradiated again at room temperature. Amount of CO_2 in the gas phase was measured at every 1 h by a Shimadzu GC-8A gas chromatograph equipped with a Porapak QS column. Photocatalytic dehydrogenation of 2-propanol (500 μmol) in aqueous solution (5 cm^3) was also examined as another model system under deaerated conditions; the TiO_2 powders were calcined, platinized (0.5 wt%) by photodeposition method [13], and then used for the photocatalytic reaction where a 400-W mercury arc was used. The details of photoirradiation and product analyses were reported

elsewhere [14].

3. Results and Discussion

3.1. General features of THyCA-TiO_2

(Fig. 1)

(Fig. 2)

An XRD pattern of THyCA-TiO_2 prepared from titanium n-butoxide (TNB) in 2-butanol at 573 K is depicted in Fig. 1(a), which shows that anatase was formed without contamination of any other phases such as rutile or brookite. Addition of water to the supernatant after the autoclaving gave no precipitates, indicating that TNB was completely hydrolyzed during the thermal treatment. Judging from the fact that, as mentioned previously, the treatment of TNB in toluene at the same temperature yielded no product, the source of water for the hydrolysis was that generated from 2-butanol. The crystallite size of this sample was calculated to be 19 nm from the line-broadening of the 101 diffraction peak of anatase. TEM observation (Fig. 2) revealed that the sample consisted of the agglomerates of primary particles of an average diameter of 20 nm, which was in good agreement with the crystallite size estimated from the XRD pattern. Therefore, each particle observed in TEM should be a single anatase crystal. This sample possessed sufficient surface area of 63 m^2g^{-1}, which was slightly smaller than that (78 m^2g^{-1}) calculated from the average particle size (20 nm) by assuming the density of anatase to be 3.84 g cm^{-3} [15]. Agglomeration of TiO_2 crystals is attributed to this, i.e., a part of the surface of the primary particles is not accessible for nitrogen molecules so that the BET surface area was smaller than that expected from the particle size. Thermal gravimetric analysis (TG) revealed that this sample showed gradual weight loss of 2.42% from 373 to 1273 K and only a

very weak exothermic peak at 560 K was observed in a DTA (differential thermal analysis) curve due to combustion of a small amount of remaining organic moieties. Absence of sharp exothermic peak due to crystallization of anatase at around 673-773 K suggests that the product contains a negligible amount of amorphous-like phase, which is well consistent with the results of XRD and TEM.

3.2. Effect of synthesis conditions on the physical properties of THyCA-TiO_2

Several physical properties of the THyCA-TiO_2 synthesized under various conditions are summarized in Table 1. Reactions in other 2-alkanols, 1-alkanols except ethanol, and *tert*-alkanol yielded also microcrystalline anatase TiO_2 as in the case of 2-butanol, showing that all alcohols except ethanol used in this work undergo dehydration to liberate water under the autoclaving conditions. The use of alkoxides having other type of alkyl chains also resulted in the anatase formation. The amount of water formed from alcohol seems to be different and, as shown in Table 1, the autogenous pressure during the reaction depended on the kind of alcohol. Therefore, anatase particles of various crystallite size (11-31 nm) and surface areas (42-138 m^2g^{-1}) could be synthesized.

(Table 1)

Effects of reaction temperature was examined for the TNB-2-propanol system (Table 1). Microcrystalline TiO_2 was formed at 548 K while reaction at 523 K gave no solid product, indicating that dehydration of 2-propanol requires temperature higher than 523 K. When titanium isopropoxide (TIP) was dissolved in a mixed solvent of 7 vol% 2-propanol in toluene, TIP was completely hydrolyzed to give anatase as observed in 100% 2-propanol. The amount of water required for complete hydrolysis of TIP is calculated to be 0.14 mol. Assuming that 2-propanol in toluene is completely dehydrated, the amount of water formed from the mixed solvent is estimated to be 0.064 mol, which is smaller than that necessary for the complete

hydrolysis of TIP. Two possibilities might account for this; 2-propanol formed by hydrolysis of TIP was dehydrated to yield water which was then used for the hydrolysis, and/or water generated by dehydration of hydrated TiO_2 was used again to hydrolyze TIP. In both processes water was recycled.

3.3. Thermal stability of THyCA-TiO_2

Effect of calcination on THyCA-TiO_2 prepared in the TNB-2-butanol system is also depicted in Table 1. Post-calcination at <= 973 K reduced the BET surface area slightly. This is consistent with the result that the XRD pattern of the TiO_2 sample calcined at 823 K was almost identical to that before calcination, as shown in Fig. 1(b). Even after calcination at 973 K, the THyCA-TiO_2 was composed of small anatase crystallite of 26 nm diameter (Fig. 1(c)) and still possessed sufficient surface area of 45 m^2g^{-1}. Calcination at 1173 K induced partial transformation into the rutile, but the sample still predominantly consisted of the anatase crystallite (Fig. 1(d)). The high thermal stability of THyCA-TiO_2 is interpreted by assuming that the as-prepared THyCA TiO_2 consists of single crystals and contains negligible amount of amorphous-like phase to be crystallized into anatase and to induce sintering of crystallites upon calcination.

3.4. Photocatalytic activity of THyCA-TiO_2 for mineralization of acetic acid in aqueous solution under aerated conditions

This reaction has been found to be less sensitive to the conditions, e.g., concentration of acetic acid, and stoichiometric decomposition ($CH_3COOH + 2O_2 = 2CO_2 + 2H_2O$) proceeds by TiO_2 photocatalysts with fairly good reproducibility [8,11]. Time dependence of CO_2 yield from acetic acid in aqueous suspension of THyCA-TiO_2, synthesized in the TNB-2-propanol

system at 573 K without further calcination, is shown in Fig. 3. The molar amount of CO_2 increased linearly with photoirradiation time, indicating a pseudo-zero-order kinetics on the acetic acid concentration.

(Fig. 3)

The rate of photocatalytic CO_2 formation by uncalcined THyCA-TiO_2 powders prepared under various conditions is shown in Table 1. For comparison, results for a laboratory-made and some commercial TiO_2 powders are also listed. As clearly seen, most of THyCA-TiO_2 samples exhibited the rates relatively larger than the commercial TiO_2 samples, ST-01 and P-25, which have been known to show high photocatalytic activity. Since the THyCA-TiO_2 powders satisfied the basic requirements for active TiO_2 photocatalyst, i.e., both large surface area and sufficient crystallinity, the present results can be reasonably accepted. An amorphous hydrated TiO_2 of quite large surface area prepared by hydrolysis under atmospheric conditions showed negligible activity (<1 μmol h^{-1}), due to large recombination probability of photogenerated e^- and h^+ at large number of surface defects.

Photocatalytic activity of THyCA-TiO_2 strongly depended on the alcohols used in the synthesis procedure. Although relation between the physical properties and photocatalytic activities of THyCA-TiO_2 was ambiguous, TiO_2 samples prepared in alcohols of smaller carbon numbers tended to exhibit higher activity. Among the butanols, the activity of THyCA-TiO_2 increased in the following order (the structure of butanols):

$$primary < secondary \simeq tertiary$$

As shown in Table 1, autogenous pressure during the synthesis increased with the decrease in the carbon number of alcohols and with the change in the structure of alcohol from primary to tertiary. The higher pressure seems to improve the crystallinity of anatase, leading the decrease in the surface defects and thereby the increase in photocatalytic activity. As clearly seen in Table 1, calcination of THyCA-TiO_2 powders decreased their photocatalytic activities but the rate was still larger than those of the commercial powders or the sample obtained by

calcination of the hydrated TiO_2.

3.5. Photocatalytic activity of THyCA-TiO_2 for dehydrogenation of 2-propanol in aqueous solution under deaerated conditions

This reaction ($CH_3CHOHCH_3 = H_2 + CH_3COCH_3$) has been used as the model system under deaerated conditions. THyCA-TiO_2 powders synthesized in the TNB-2-butanol system at 573 K and the samples obtained by calcination of the as-prepared powders at 823, 973 and 1173 K exhibited the rates for photocatalytic H_2 formation of 89, 147, 200 and 27 $\mu molh^{-1}$, respectively whereas P-25 showed the rate of 100 $\mu molh^{-1}$. Thus the THyCA-TiO_2 calcined at 973 K has been shown to be ultra-highly active compared with P-25 which is one of the most active photocatalyst. Effect of calcination temperature on the activity was similar to that for HyCOM-TiO_2's and this is consistent with our proposal that for the 2-propanol dehydrogenation the crystallinity predominantly influences the activity rather than surface area [16].

4. Conclusion

The THyCA-TiO_2 powders showed remarkably higher activities for reactions under both aerated and deaerated conditions as has been observed with HyCOM- and TD-TiO_2's, because the THyCA process might allow the compatibility of large surface area and high crystallinity of resulting anatase nanoparticles.

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Footnotes

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Fig. 1 XRD patterns of (a) TiO_2 prepared by the thermal treatment of titanium n-butoxide in 2-butanol at 573 K, and (b), (c), and (d) the samples obtained by calcination of (a) at 823, 973 and 1173 K, respectively. Peaks indicated by closed circle and closed square are assigned to the anatase and rutile, respectively.

Fig. 2 A TEM photograph of the THyCA-TiO_2 whose XRD pattern is shown in Fig. 1(a).

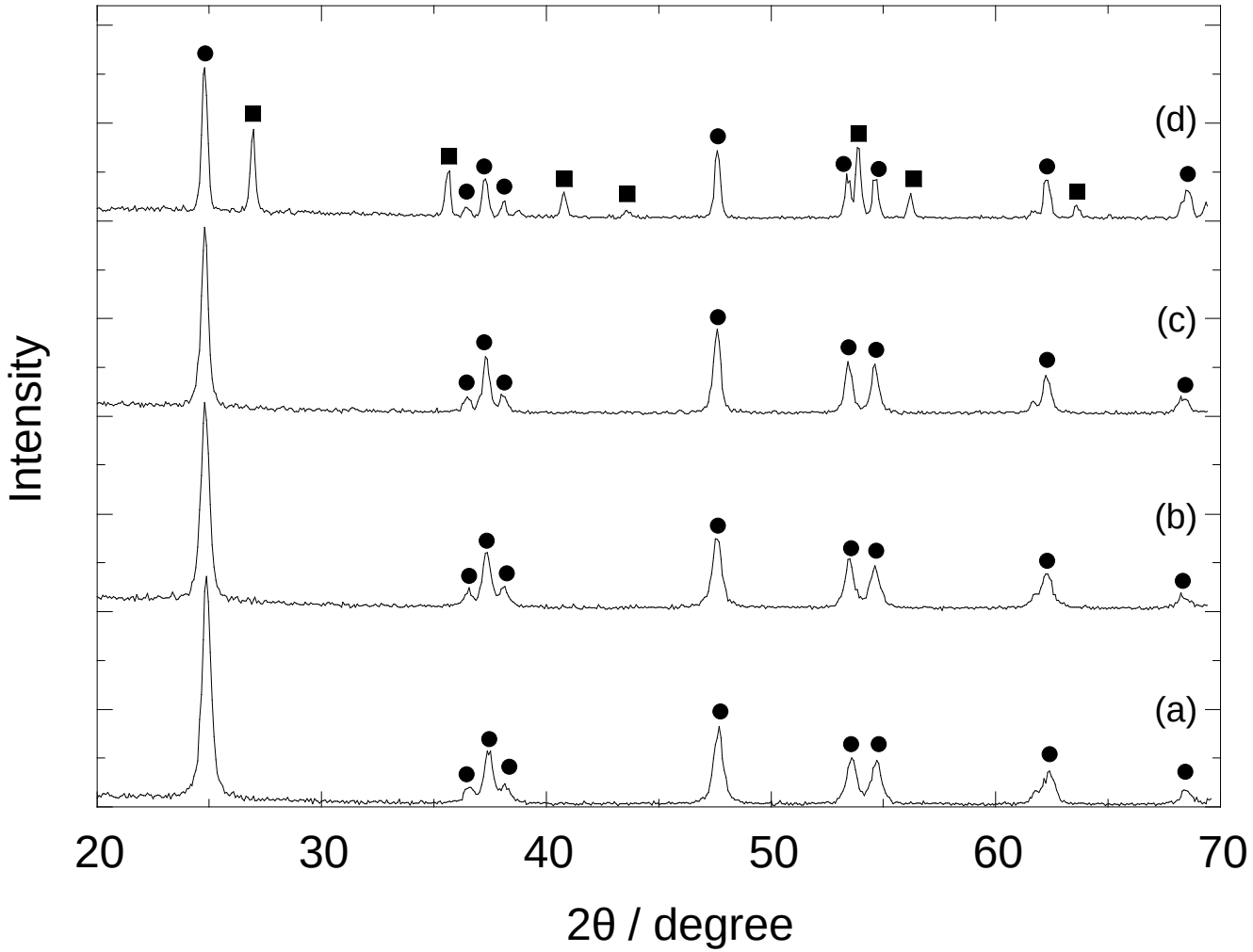
Fig. 3 Time course of photocatalytic CO_2 formation from an aqueous acetic acid solution by suspended THyCA-TiO_2. The photocatalyst was prepared by the thermal treatment of titanium n-butoxide in 2-propanol at 573 K.

Table 1 Some physical properties of TiO_2 powders prepared by various reaction conditions and their photocatalytic activities for mineralization of acetic acid in aqueous solutions

alko-xides[a]	alcohols	T_{syn}[b] /K	P_{syn}[c] /MPa	T_{cal}[d] /K	phase by X-ray[e]	d_{101}[f] /nm	S_{BET} /m^2g^{-1}	CO_2[g] /μmol h^{-1}
TNB	ethanol	573	12	No reaction				
TNB	1-propanol	573	8	—	A	16	75	22.1
TNB	2-propanol	573	11	—	A	25	52	29.5
TNB	1-butanol	573	4	—	A	12	107	17.4
TNB	2-butanol	573	15	—	A	19	63	21.3
TNB	2-butanol	573	15	823	A	20	56	13.8
TNB	2-butanol	573	15	973	A	26	45	11.1
TNB	2-butanol	573	15	1173	A,R	ND	7.3	2.8
TNB	t-butanol	573	19	—	A	14	81	22.0
TNB	2-hexanol	573	4	—	A	15	86	9.6
TNB	cyclohexanol	573	1	—	A	15	98	11.1
TNB	1-octanol	573	1	—	A	11	138	12.9
TNB	2-octanol	573	2	—	A	27	60	14.3
TNB	2-propanol	548	8	—	A	23	62	17.4
TNB	2-propanol	523	6	No reaction				
TTB	2-propanol	573	11	—	A	19	84	10.5
TIP	2-propanol	573	13	—	A	31	42	16.7
TE	2-propanol	573	12	—	A	26	75	16.1
TIP	2-propanol[h]	573	4	—	A	26	62	21.3
(P-25)[i]			—		A,R	24	50[j]	8.5
(ST-01)[i]				—	A	7[j]	320[j]	11.6
TNB	(ethanol)[k]	r.t	—	—	AM	—	452	<1
TNB	(ethanol)[k]	r.t	—	823	A	18	29	2.6

[a]TNB; titanium n-butoxide, TTB; tert-butoxide, TIP; isopropoxide, TE, ethoxide.
[b]synthesis temperature. [c]autogenous pressure during autoclaving.
[d]calcination temperature. [e]A; anatase, R; rutile, AM; amorphous.

f)crystallite size calculated from the 101 diffraction peak of anatase.
g)rate of photocatalytic CO_2 production from acetic acid (175 µmol) in aqueous suspension (5 cm^3) of THyCA-TiO_2 (50 mg). h)7vol% 2-propanol in toluene.
i)P-25; Degussa, ST-01; Ishihara. j) Data reported by the suppliers.
k)Alkoxide was hydrolyzed in ethanolic solution under atmospheric pressure.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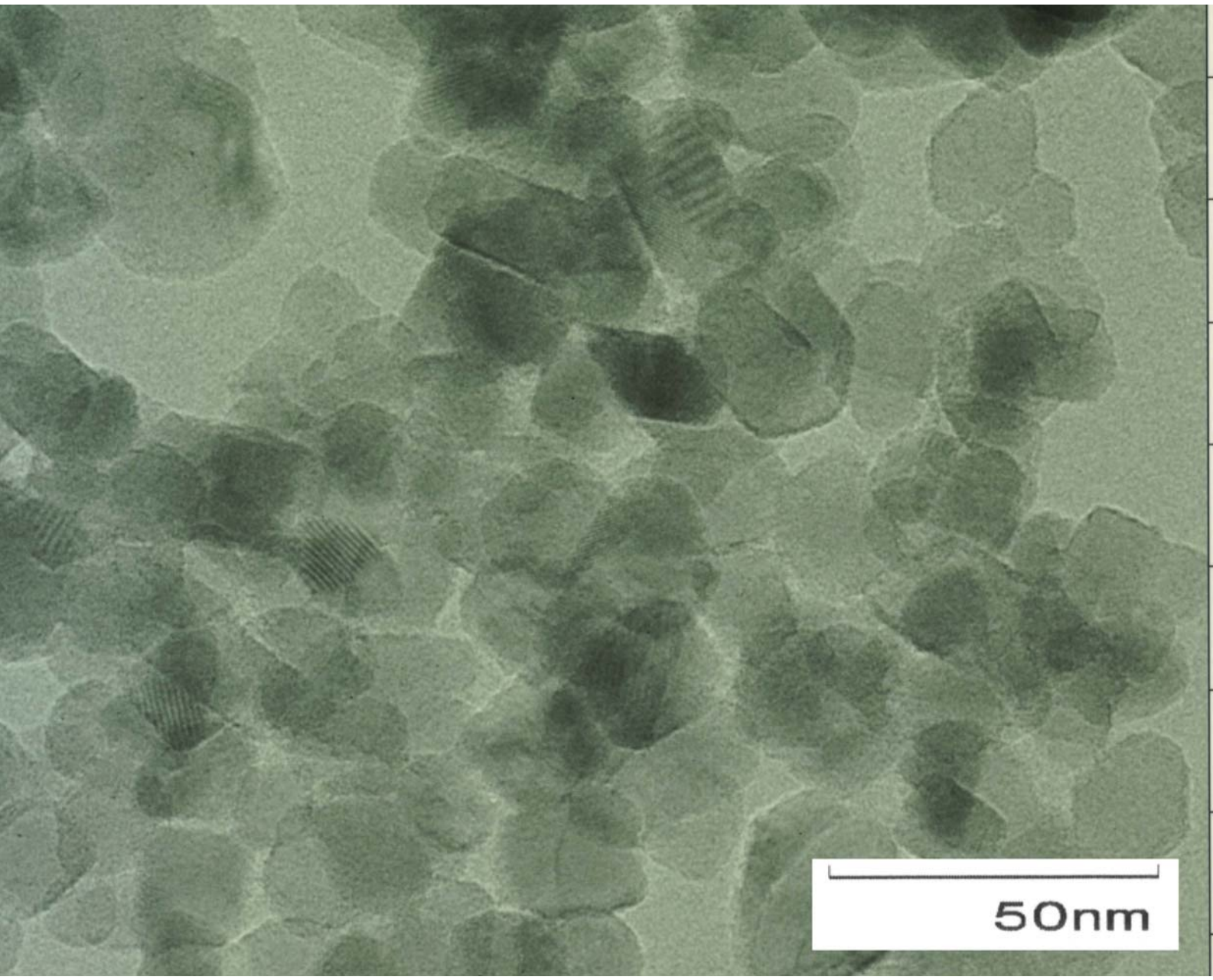
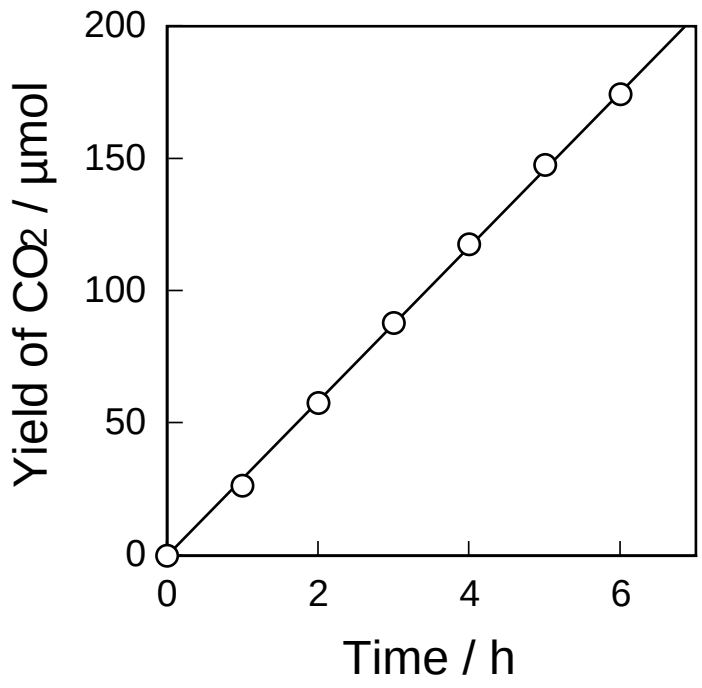
(d)
(c)
(b)
(a)
20
30
40
50
60
70
2θ / degree


50nm



Kominami et al., Fig. 3