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journal or publication title	Applied Catalysis A: General
volume	406
number	1-2
page range	119-123
year	2011-10-18
URL	http://hdl.handle.net/10228/00006569

doi: <https://doi.org/10.1016/j.apcata.2011.08.017>

Controlled structure of anatase TiO₂ nanoparticles by using organic additives in a microwave process

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Abstract

Synthesis of anatase nanoparticles was carried out in a microwave system. Crystal morphology was controlled by organic additives including PAAc (polyacrylic acid) and PVP (polyvinylpyrrolidone). Modified TiO₂ particles were compared to the bare TiO₂ anatase structure. The synthesis of materials via the microwave system has great advantages due to the short reaction period and low energy requirement and is therefore an environmentally friendly process. The decomposition of acetaldehyde was studied to determine the photocatalytic activity of the modified anatase TiO₂ material.

Keywords:

Photocatalysis; decahedral TiO₂ anatase; polyacrylic acid;

1. Introduction

Semiconductor materials provide solid surfaces that can influence both the chemical reactivity of a wide range of adsorbates and the ability to initiate, propagate, and terminate light-induced oxidation-reduction (redox) reactions. Simultaneous redox reactions occur upon photoexcitation of several semiconductors. The conversion proceeds by oxidation of an organic reactant in which the carbon bound in the reactant species is converted to carbon dioxide. The photocatalyst material should be stable under photolytic conditions for practical applications. Photocatalytic reactions can occur in gas and liquid phases. Reactions in which gas-phase species were adsorbed and then reacted on solid surfaces were investigated to evaluate the effect of modified TiO₂ particles by decomposing acetaldehyde, a process referred to

as heterogeneous (gas/solid) photocatalysis [1]. In a heterogeneous photocatalytic system, photo-induced molecular reactions occur at the surface of the catalyst. Therefore, photocatalytic activity strongly depends on the arrangement of surface atoms. For this reason, modification of the faces and structure of crystals is necessary to increase the photocatalytic conversion of toxic pollutants into CO₂. A strong correlation between degradation rates and concentration of the organic pollutant adsorbed to the surface also implies that the hydroxyl radicals or trapped holes are directly available at the surface [2]. Besides, various syntheses processes have been reported to modify the structure of the anatase TiO₂ configuration have been reported. Gao synthesized anatase TiO₂ particles with a cubic-like shape in the presence of organic additives [3]. Chemseddine et al. reported the synthesis of anatase TiO₂ crystals with hexagonal and short rod-like morphologies in an alkaline environment [4]. Penn et al. prepared anatase TiO₂ particles with a zigzag pattern in acidic conditions [5]. Anatase TiO₂ crystals with bullet, diamond and rod forms and with a branched rod-like form have been synthesized in the presence of lauric acid [6]. Morphologies and microstructures of bipyramids were further investigated by Deng et al., who obtained one of the largest anatase bipyramids structures synthesized [7].

In this study, different organic additives were investigated in order to control the morphology of anatase nanoparticles by using a microwave process. Since polyvinylpyrrolidone (PVP) is widely used for synthesis of shape-controlled nanoparticles due to its preferred adsorption on specific surfaces [8,9], it was tested as a controller additive of the TiO₂ anatase crystal surface. The relationship between morphology of the synthesized anatase TiO₂ and its photocatalytic activity was also investigated.

2. Experimental Section

2.1 Chemicals

All chemical reagents used in the present study were commercial products without further treatments. A titanium precursor (titanium-ethoxide) was purchased from Sigma-Aldrich. Other chemicals were purchased from Wako (all of reagent grade). The organic additives PVA (polyvinyl alcohol), PAAc

(polyacrylic acid), PVP (polyvinylpyrrolidone), PEG (polyethylene glycol) and PAANa (polyacrylic acid sodium) were employed to control the crystallinity and morphology of TiO₂ particles. Bare TiO₂ material was also prepared under the same reaction conditions in the absence of any additive.

Anatase TiO₂ fine particles (ST-01) were purchased from Ishihara Sangyo as reference TiO₂ particles. The relative surface area of ST-01 is 298 m²/g.

2.2 Synthesis procedure

The anatase TiO₂ synthesis reactions were performed in a microwave apparatus (Wave Magic Eyela MWO-1000S/500W). The amorphous TiO₂ suspension (prepared from the Ti-ethoxide) was deposited in a Teflon reactor and subsequently introduced into the microwave. Initially, experiments were carried out at different time periods varying from 6 to 20 minutes. Syntheses were realized at different pH values to observe changes in the crystallinity and photocatalytic improvement of anatase particles. Optimized working parameters were determined in alkaline media at pH 10 with a 400 rpm stirring speed and 400 watts for 10 minutes.

2.3 Characterization

Specific surface area was determined with a surface area analyzer (Quantachrome, Autosorb-1) by using the Brunauer-Emmett-Teller (BET) method. Crystal structures of the samples were confirmed by using an X-ray diffractometer (Rigaku, MiniFlex II) with Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$). The morphology of the samples was observed by transmission electron microscopy (TEM; Hitachi, H-9000NAR).

2.4 Photocatalytic decomposition of acetaldehyde

Photocatalytic experiments were carried out in gas phase by the decomposition of acetaldehyde measuring the activity through the produced CO₂. TiO₂ particles (100 mg) were spread on a glass dish, and the glass dish was placed in a Tedlar bag (AS ONE Co. Ltd.) with a volume of 125 cm³. Then 500 ppm of gaseous acetaldehyde was injected within the Tedlar bag in a mixture of synthetic air (20% O₂ and 80% N₂). Photoirradiation was carried out at room temperature after acetaldehyde adsorption had reached an

equilibrium. A 500-W xenon lamp (Ushio, SX-UI501XQ) was used as the light source. The photoirradiation wavelength was determined with a UV-light cut-off filter (350 nm) (Asahi Techno Glass 35 filter). The light intensity was adjusted to 12 mW cm⁻². Concentrations of acetaldehyde and carbon dioxide (CO₂) were estimated by gas chromatography (Shimadzu, GC-8A, FID detector) with a PEG-20 M 20% Celite 545 packed glass column and by gas chromatography (Shimadzu, GC-9A, FID detector) with a TCP 20% Uniport R packed column and methanizer (GL Sciences, MT-221), respectively. Before evaluation, all of the TiO₂ samples were pretreated with black UV-light irradiation in order to remove contaminants on the TiO₂ surface. All photocatalytic evaluation experiments were carried out under the same conditions.

3. Results and Discussion

3.1 Selection of an appropriate controlling additive

XRD patterns and TEM images of TiO₂ particles synthesized by a microwave process are shown in Figs. 1 and 2, respectively. All XRD patterns of synthesized TiO₂ were assigned to anatase crystal structure. Bipyramidal anatase nanoparticles were obtained by a microwave synthesis process at 180 °C for 10 minutes using bare titanium ethoxide as a precursor without any organic additive. The suspension in an alkaline medium (pH 10) was stirred at 400 rpm while anatase TiO₂ nanoparticles were generated in the microwave apparatus. The optimum pH reaction condition is pH10, which will be discussed later. The effects of various organic additives, including PVA, PEG, PAANa, PVP and PAAc, on anatase morphology were examined. It was found that the morphology of anatase TiO₂ can be controlled by PVP and PAAc additives. The functional coordination groups of additives are considered to be one of the important factors for controlling the TiO₂ morphology. The pKa values of PVP and PAAc are 5 and 4.25, respectively [10,11]. Under the condition of pH 10, the PAAc polymer has negative charges (COO⁻) by losing its protons of the side chains functional group that interact easily with Ti cations for controlling TiO₂ crystal phase at pH 10. Decahedral anatase TiO₂ particles were obtained in the presence of PAAc as an additive. Therefore, PAAc was effective for exposing (001) and (101)

crystal faces. The ketone group of PVP is also thought to coordinate Ti^{4+} ions in controlling TiO_2 crystal structure. Consequently, PVP or PAAc plays an important role for controlling TiO_2 crystal structure and morphology as shown in Fig. 1. However, extra addition of these additives did not have any effect on relative surface area as shown in Table 1.

Small crystallite sizes (approx. 50 nm) of the prepared TiO_2 particles were obtained by microwave heating (Fig. 2). Under microwave irradiation, the temperature of the reaction solution is raised so rapidly that a large amount of nuclei can be generated in a very short time, which inhibited crystal growth of the product. Without any additive, a TiO_2 bipyramidal anatase structure was obtained (Fig. 2a). A low crystal quality (001) surface was exposed by using PVP as an additive (Fig. 2b). As shown in Fig. 2c, a decahedral anatase structure of TiO_2 was obtained with polyacrylic acid (PAAc).

3.2 Dependence of synthesis on pH

pH of the reaction solution plays an important role in the synthesis of TiO_2 nanoparticles in our system. The content of crystal phases was drastically changed with pH in the presence of PAAc as shown in Fig. 3. The XRD patterns exhibited a pH dependence by using PAAc as polymer. In acidic (pH 4) or neutral media (pH 7), compositions of anatase and rutile were 67:33% and 97:3%, respectively. On the other hand, the XRD patterns showed only peaks corresponding to anatase morphology at pH 10. pH 10 is also the optimum condition for the synthesis of pure anatase phase in the case of PVP or with no additive. The obtained TiO_2 anatase nanoparticles were thermally treated in order to evaluate the stability of the morphology and crystal structure. No change in crystal structure or morphology was observed after calcination at 350 °C.

3.3 Photocatalytic activity

Figure 4 shows photocatalytic activities of the synthesized anatase TiO_2 and ST-01. Photocatalytic activities of synthesized photocatalysts obtained by the

microwave process are much higher than that of the commercially available ST-01 TiO₂ anatase fine particles tested through the mineralization of acetaldehyde in gas phase. Commonly, the photocatalytic activity in TiO₂ photocatalysis was directly proportional to the number of surface hydroxyl radicals and was related to the ability for surface adsorption of hydroxyl ions shown by zeta-potential data [12]. The number of surface hydroxyl radicals is closely related to the concentration and coordination number of Ti ions on the surface. The (101) surface exhibits a stepped structure with two types of 5-coordinated Ti-ions and one type of 4-coordinated Ti ions, while the (001) surface contains one type of 5-coordinated Ti ions. Therefore, particle morphology (surface property) is an important factor in TiO₂ photocatalysis. Ohno et al. reported that rutile TiO₂ exposed crystal faces show higher photocatalytic activity than that of a spherical TiO₂ shape because of separation of the reaction sites [13]. It is notable that all of the synthesized particles showed considerably higher photocatalytic activity than that of ST-01 even though the commercial photocatalyst ST-01 has the largest surface area among the samples. The highest photocatalytic activity was achieved when PAAc was used as an additive. This is due to effective charge separation by increasing the “oxidative side” generated on the (001) surface. Although the morphology of octahedral anatase TiO₂ is different from that of anatase TiO₂ modified by PVP, photocatalytic activities of the samples were similar because the overall exposed Ti ions might be remained in a same proportion.

The results suggested that decahedral TiO₂ anatase morphology has an advantage over to octahedral TiO₂ anatase morphology. Therefore, the (001) face may have high oxidative capacity for improvement of further photocatalytic applications.

3.4 Importance of decahedral anatase morphology

Photocatalytic activity is known to be highly dependent on morphology evolution, and the (101) surface should be more active than the (001) surface since 4-coordinated Ti ions in the stepped edge of the (101) surface play a decisive role in the adsorption of hydroxyl ions [12]. On the other hand, other

authors have observed the importance of the (001) face concerning the photocatalytic improvement for decomposing pollutants [14-15]. Bae and Ohno reported that the (110) face provides reductive sites and that the (001) face provides stronger oxidative sites in rutile TiO₂ nanorods after etching treatment [14]. The photocatalytic activity of decahedral anatase TiO₂ is higher than that of octahedral anatase TiO₂ prepared by the microwave process without an additive. All of the TiO₂ particles prepared by the microwave process showed higher activity than that of the commercially available ST-01. These results suggested that exposure of crystal faces of TiO₂ is a more important factor than the surface area for improvement of photocatalytic activity.

In addition, TiO₂ crystals having two kinds of high-quality faces resulted a more important factor to increase the photocatalytic activity.

In the anatase TiO₂ structure, the (101) face provides oxidative sites and the (001) face provides reductive sites. This suggests that the crystal faces facilitate separation of electrons and holes, resulting in improvement of the photocatalytic activity (Fig. 5). However, PVP is not a good additive for exposing high-quality faces compared to PAAc. The charge separation between photo-excited electrons and holes should be improved by optimization of the exposed crystal surfaces in order to increase the photocatalytic activity.

The catalytic activity depends greatly on the arrangement of surface atoms and the number of dangling bonds on different crystal facets. Choosing a suitable titanium precursor with an appropriate transformation process is very important because it can directly influence the crystal phases, sizes, shapes, and exposed facets of TiO₂. It is been reported that anatase TiO₂ morphological transformation occurred during the hydrothermal chemical reaction in neutral solution [16,17]. However, toxic compounds such as ammonium fluoride and hexadecyltrimethylammonium bromide (CTAB) were used as additives to obtain octahedral TiO₂ exposing high-energy (001) facets [16]. The hydrothermal treatment required a longer period of time (~24 h). However, the microwave assisted hydrothermal method shows a rapid heating rate, homogeneous and selective heating of reaction solutions in comparison with the conventional hydrothermal method [18]. Both the

structure and size of the nanoparticles used affect the photocatalytic efficiency of the material [19].

4. Conclusion

The reaction time and energy power of the microwave are important parameters for controlling the synthesis of anatase TiO₂. The reaction time of the microwave process is significantly reduced compared to that of the hydrothermal process saving time and energy, obtaining an efficient and competitive process with the optimized specifications.

PAAc was found to be an appropriate polymer for controlling the formation of a defined decahedral anatase structure.

A pH value of 10 is the optimum condition for obtaining highly efficient decahedral TiO₂ anatase nanoparticles.

Large specific surface area and small crystal sizes as well as high crystallinity of TiO₂ might play important roles in the enhancement of photocatalytic activities. However, separation of reaction sites on the photocatalyst particle by the exposed crystal surface of TiO₂ anatase seems to be a more important factor for improvement of photocatalytic activity.

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Table 1. Specific surface areas (BET) of TiO₂ anatase synthesized with different additives at pH 10 and the commercial ST-01 (Ishihara Sangyo) TiO₂ anatase photocatalyst.

Materials	Blank	PVP	PAAc	ST-01
Specific Surface area (m ² /g)	91.8	89.4	102.9	298

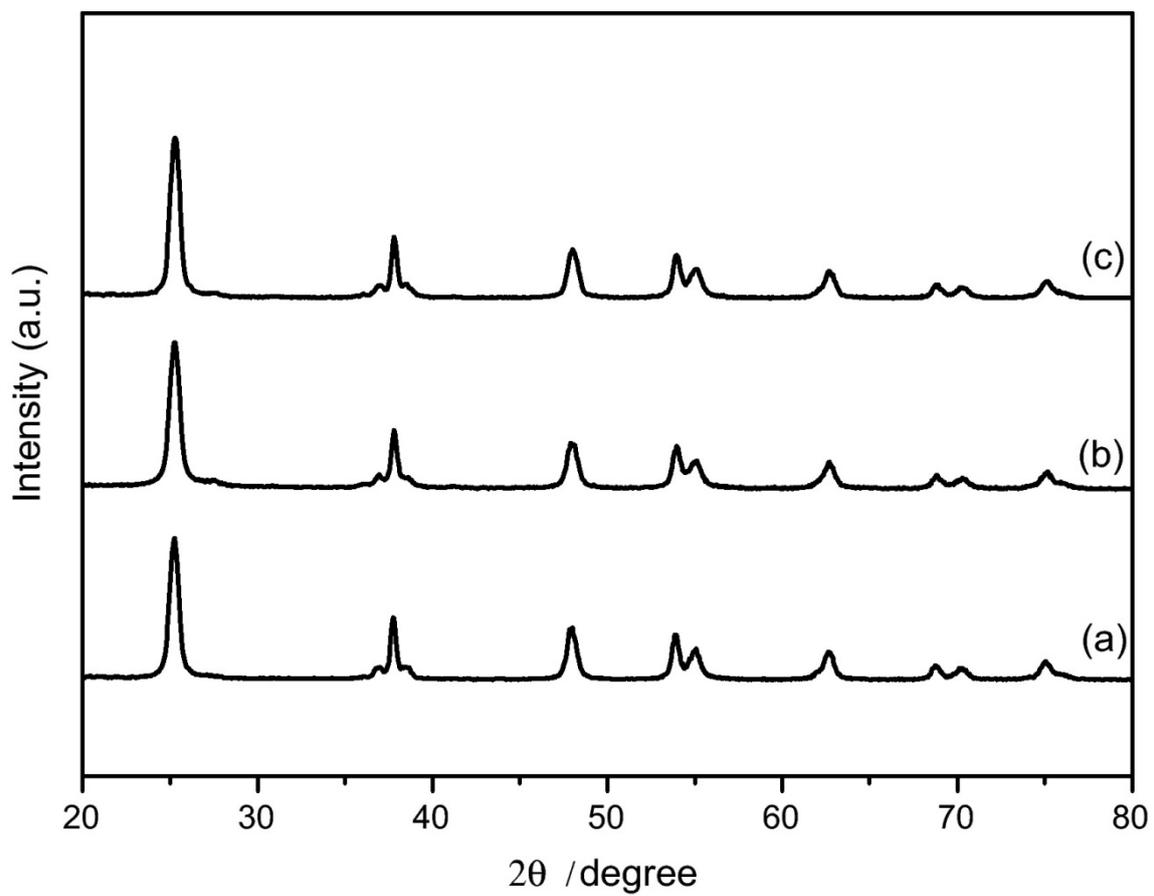


Fig. 1. XRD patterns of different synthesized anatase TiO_2 particles by applying diverse controlling polymers at pH 10: (a) blank without additive, (b) particles treated with PAAc and (c) particles treated with PVP.

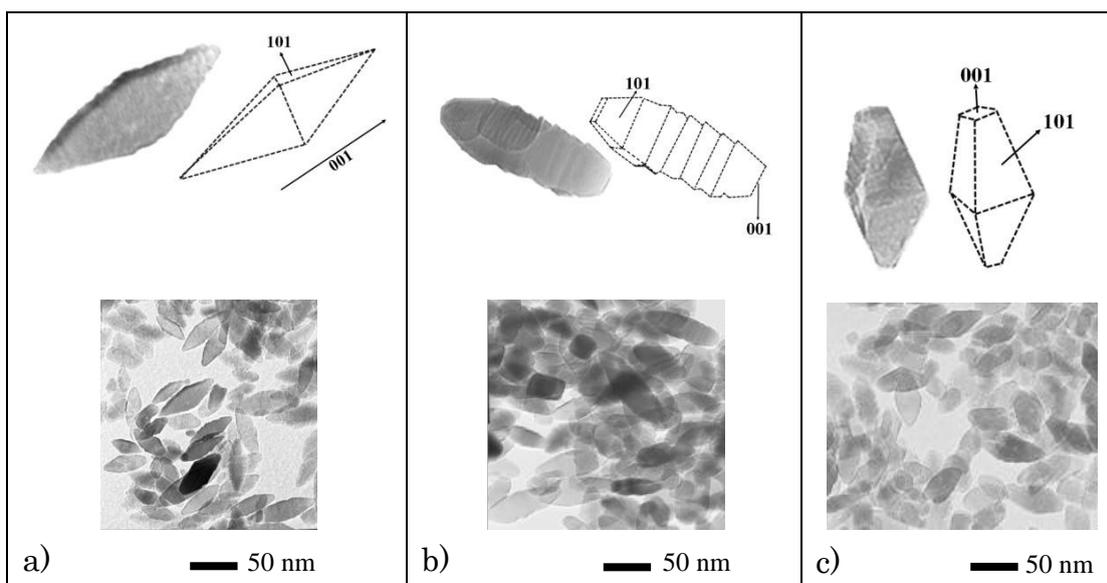


Fig. 2. TEM images of anatase nanoparticles synthesized by a microwave process: a) no additive used, b) PVP additive to obtain elongated particles and c) PAAc additive applied for controlling morphology of the decahedral TiO_2 structure at pH 10.

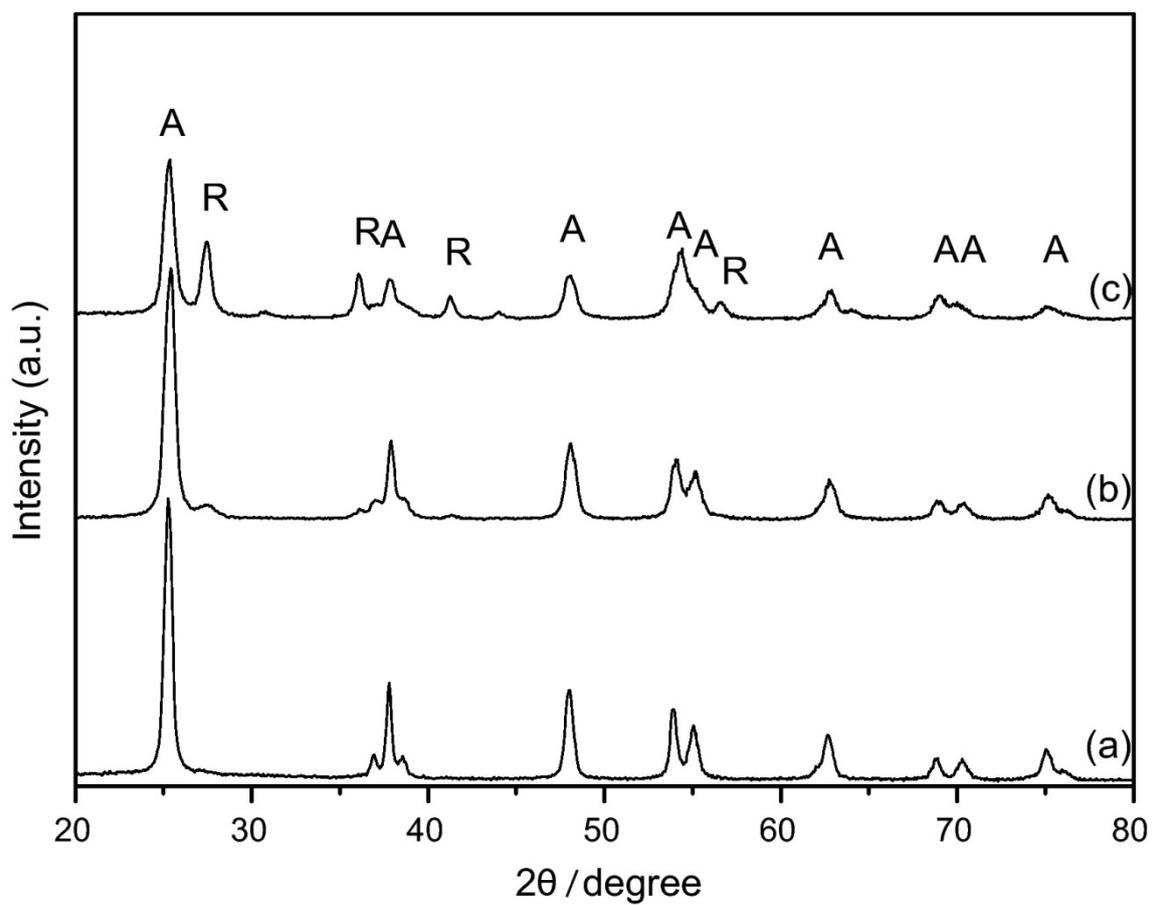


Fig. 3. XRD patterns of decahedral anatase prepared by the microwave process with PAAc additive at different pH conditions: (a) pH 10, (b) pH 7 and (c) pH 4. “A” corresponds to anatase peaks and corresponds “R” to the rutile peaks.

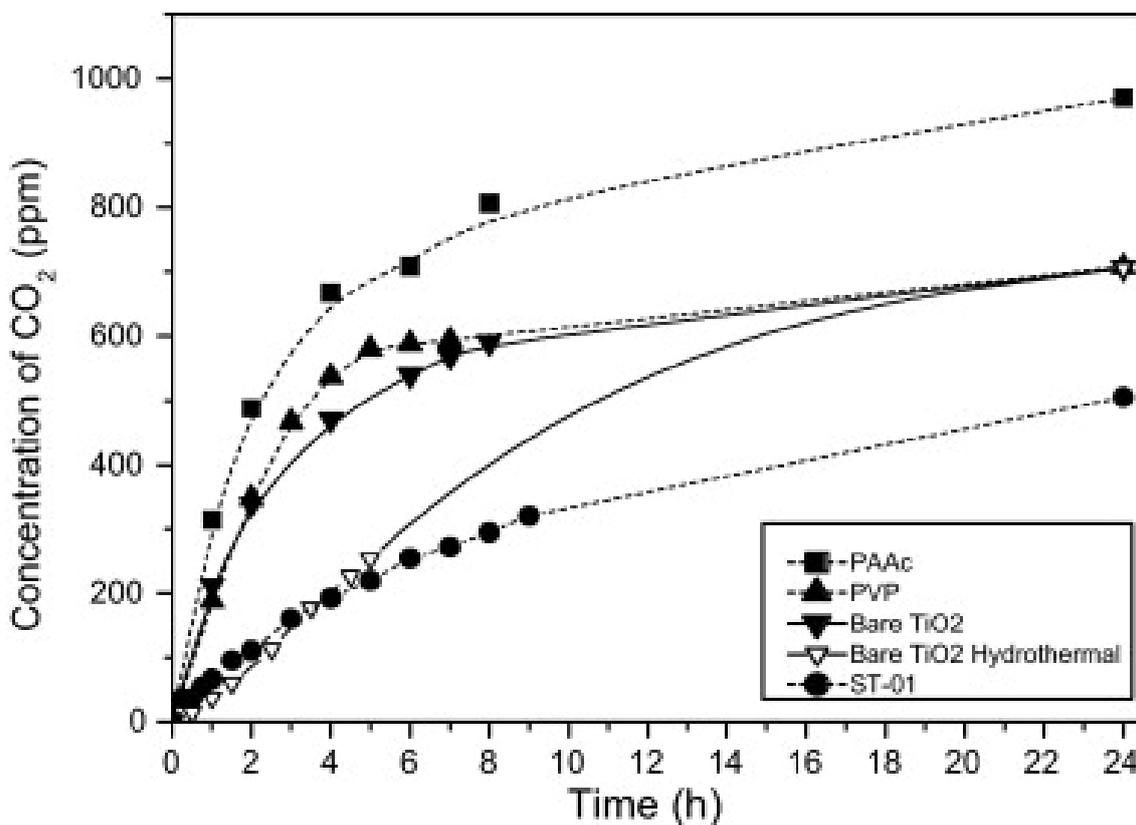


Fig. 4. Comparison of TiO₂ anatase particles synthesized by using various polymers and ST-01 photocatalyst. Acetaldehyde decomposition was followed by the measurement of CO₂ conversion under UV-light irradiation using a 350 nm cut-off filter and an intensity of 12 mW/cm².

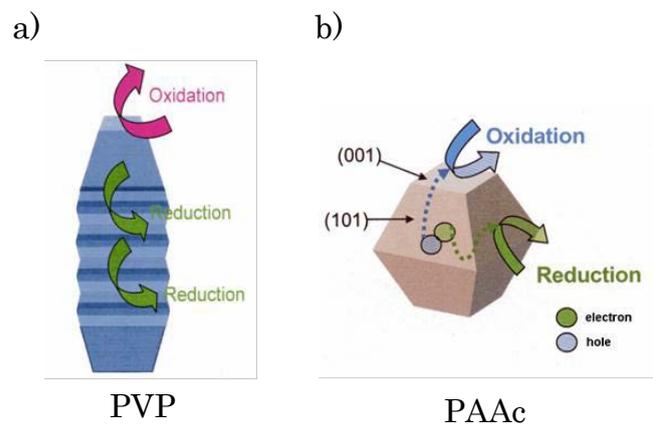


Fig. 5. Schematic differences between a) elongated TiO₂ anatase and b) decahedral TiO₂ anatase synthesized by the microwave process showing oxidative and reductive sites.