



Application of immobilized nanotubular TiO₂ electrode for photocatalytic hydrogen evolution: Reduction of hexavalent chromium (Cr(VI)) in water

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ABSTRACT

In this study, immobilized TiO₂ electrode is applied to reduce toxic Cr(VI) to non-toxic Cr(III) in aqueous solution under UV irradiation. To overcome the limitation of powder TiO₂, a novel technique of immobilization based on anodization was applied and investigated under various experimental conditions. The anodization was performed at 20 V–5 °C for 45 min with 0.5% hydrofluoric acid, and then the anodized samples were annealed under oxygen stream in the range 450–850 °C. Based on the results of the experiments, the photocatalytic Cr(VI) reduction was favorable in acidic conditions, with ~98% of the Cr(VI) being reduced within 2 h at pH 3. Among the samples tested under same anodizing condition, the nanotubular TiO₂ annealed at 450 and 550 °C showed highest reduction efficiencies of Cr(VI). In addition, the surface characterizations (zeta potential, XRD, and SEM) of these samples proved that the Cr(VI) reduction efficiency was higher under acidic conditions and at a lower annealing temperature. From this research, it was concluded that the anodized TiO₂ has the potential to be a useful technology for environmental remediation as well as photocatalytic hydrogen production from water.

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1. Introduction

Photocatalysis has been used as an attractive technology for hydrogen production by water splitting and environmental treatment. During the past several decades, many studies have been conducted in an attempt to obtain a higher efficiency of hydrogen production and environmental remediation with photocatalysts. However, the photocatalytic process has been simultaneously criticized as being uneconomical compared to other systems, due to its inherently low efficiency, and the limitations of immobilization, which may increase the overall costs [1].

Conventional photocatalysis was based on slurry type TiO₂ which presents a problem of catalyst recovery after the reaction. Therefore, in this study, we focus on the reduction of toxic chromium (Cr(VI)) to non-toxic chromium (Cr(III)) with an immobilized TiO₂ photocatalyst under various water conditions.

The band-gap energy of TiO₂ is 3.2 eV, which is equivalent to UV light with a wavelength of 380 nm, and TiO₂ is therefore photoexcited by near UV illumination. The holes that are generated on the TiO₂ are highly oxidizing, and there has been abundant literature about the utilization of TiO₂ in the oxidative degradation

of organic contaminants by OH radicals (OH[•]). In addition, inorganic species with a reduction potential more positive than that of the conduction band of a semiconductor can consume the electrons and complete the redox reaction cycle. Recently, increasing attention has been paid to the photocatalytic reduction of inorganic contaminants. The TiO₂ photocatalytic reduction process has been reported to be effective for the removal of various toxic metal ions, such as Hg(II) [2], As(V)/As(III) [3,4], and Cr(VI) [5–9]. Besides TiO₂, the use of ZnO [10] and CdS [11] in the photocatalytic reduction of Cr(VI) to Cr(III) has also been reported.

Chromium occurs in two common oxidation states in nature, Cr(III) and Cr(VI). Cr(VI) is toxic to most organisms, carcinogenic in animals, and causes irritation and corrosion of the skin in humans. It is highly soluble in water and forms the mono- and divalent oxyanions, chromate (HCrO₄⁻/CrO₄²⁻) and dichromate (Cr₂O₇²⁻), respectively, depending on its concentration and pH. Because it is only weakly sorbed onto inorganic surfaces, Cr(VI) is mobile in nature. On the other hand, Cr(III) is readily precipitated or sorbed on a variety of inorganic and organic substrates at neutral or alkaline pH. Cr(VI) has a toxicity one hundred times higher than that of Cr(III) [12,13].

Cr(VI) is a frequent contaminant in water, arising from industrial processes such as electroplating, leather tanning and paint-making, and it has been regulated in many countries due to its acute toxicity, carcinogenic action and high mobility in water. Therefore, the

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reduction of Cr(VI) to Cr(III) is highly desirable in order to reduce toxicity and contain mobility of chromium ions. After Cr(VI) reduction, Cr(III) can be separated by several procedures, which can be precipitated in neutral or alkaline solution in the form of $\text{Cr}(\text{OH})_3$ [14,15].

2. Materials and methods

2.1. Apparatus and analysis

Experiments were conducted in a photocatalytic reactor. The volume of the reactor was 200 ml and it contained an aqueous solution whose initial concentration of Cr(VI) and pH were adjusted. The outside of the reactor was water-jacketed to keep the reaction temperature. Prior to the reaction, the immobilized nanotubular TiO_2 was fixed in the middle of the aqueous solution with UV light.

The light source used was a 1000 W xenon lamp (Oriental, USA), which was filtered through a 10-cm IR filter. The light emission was above the wavelength of 300 nm, and the irradiated light intensity was measured to be ca. 68 mW cm^{-2} (300–400 nm) by using a portable radiometer (UM-360, MINOLTA, Japan). Furthermore, the light intensity absorbed by the TiO_2 seemed to be slightly lower than the irradiated intensity, due to loss by reflection and absorption at the window and water.

The crystal phase and size were determined by X-ray diffraction (XRD, Miniflex, Rigaku, Japan; $k = 0.89$, $\lambda = 0.15418$ for Cu $\text{K}\alpha$ X-ray, 30 kV, 15 mA) and the concentration of Cr(VI) was analyzed colorimetrically using UV–vis spectroscopy (SCINCO, S-3150, Korea). In this analysis, 1,5-diphenylcarbazide method was used [16,17]. The structure and morphological characterizations were conducted using scanning electron microscopy (SEM, Hitachi S-4700, Japan).

The surface charge of the TiO_2 was measured by using zeta potential measurements. The zeta potential measurement of the photocatalyst was performed by an electrophoretic method using a commercial instrument (ELS-8000, Otsuka Electronics, Japan) with a latex solution. In the electrophoresis cell, asymmetric electroosmotic flow occurs due to the accumulation of ions on the TiO_2 sample during the electrophoresis. The electrophoretic flow of a standard particle then takes place due to the induced electroosmotic flow and the zeta potential was correlated with the electrical mobility by laser light scattering. In this study, the zeta potential was measured at pH 3–9 with HCl or NaOH [18,19].

2.2. Preparation of anodized nanotubular TiO_2

All chemicals were used without further purification. Anodized nanotubular TiO_2 was used as a reference for the reduction of Cr(VI) which was used as the photocatalyst for measuring the reactivity. Titanium foils (0.25 mm thickness, 99.6% purity, Goodfellow, England) were cut into pieces (1 cm × 2 cm, 1 cm × 4 cm, or 2 cm × 4 cm) for anodization. A two-electrode configuration was used for anodization. A coil-shaped platinum electrode served as the cathode. The anodization was performed at 20 V–5 °C for 45 min with magnetic stirring, after which the samples were annealed under oxygen (400 ml min^{-1}) stream in the range 450–850 °C. The nanotubular TiO_2 arrays were formed by anodization of the Ti foil in 0.5% hydrofluoric acid (HF, DC Chemical) [20–22].

3. Results and discussion

3.1. Photocatalytic reduction of Cr(VI) under various conditions

A series of experiments were conducted with anodized TiO_2 at the same voltage (20 V) with 0.5% HF solution and different

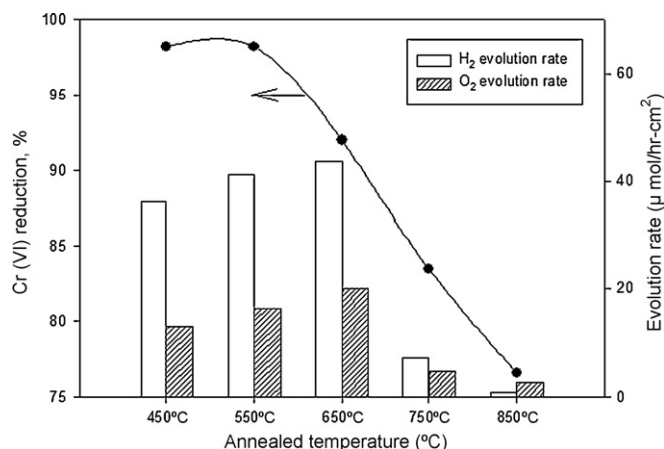


Fig. 1. Comparison of Cr(VI) reduction and H_2/O_2 evolution with anodized TiO_2 (annealed at 450–850 °C in ambient oxygen 400 mL min^{-1}).

annealing temperatures in the range of 450–850 °C in order to investigate the photocatalytic reduction under acidic conditions. Prior to the Cr(VI) reduction tests conducted in this study, the anodized TiO_2 was used as a photo-anode for hydrogen evolution tests in an enzymatic photo-electrochemical system (PEC). Fig. 1 shows the Cr(VI) reduction and the evolution rate of hydrogen and oxygen by photocatalytic water splitting with the same anodized TiO_2 samples [21]. On the basis of the hydrogen evolution experiment, TiO_2 annealed at 650 °C was found to show better hydrogen production than the other thermal treated TiO_2 samples. However, TiO_2 annealed at 450 °C showed a higher reduction efficiency in the photocatalytic Cr(VI) reduction. In these results, both the hydrogen evolution rate and Cr(VI) reduction efficiency significantly decreased as the annealing temperature was increased, because of disappearance of the anatase, decrease of surface area, and change of morphology at temperature over 750 °C. Under acidic conditions (pH 3), the reduction efficiencies of Cr(VI) at different annealing temperatures were as follows: 450 °C (~98%) > 550 °C (~98%) > 650 °C (~91%) > 750 °C (~83%) > 850 °C (~75%).

As regards the effect of pH shown in Fig. 2, the Cr(VI) reduction efficiencies were higher at pH 3 than those at pH 5, 7, and 9. Even though the reduction efficiencies differed depending on the annealing temperature, the Cr(VI) reduction efficiency was always

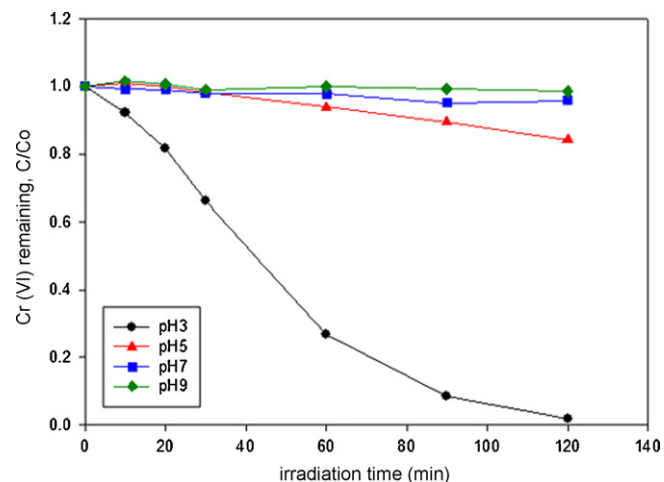


Fig. 2. Effect of pH on Cr(VI) reduction with anodized TiO_2 (annealed at 450 °C, $[\text{Cr}(\text{VI})]_0 = 2 \text{ mg L}^{-1}$).

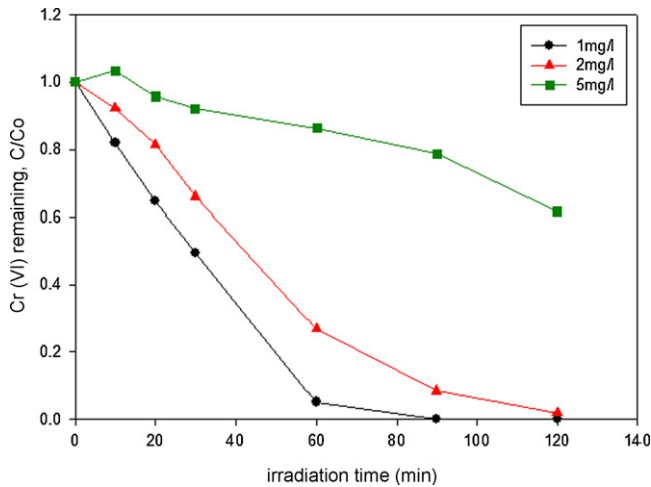
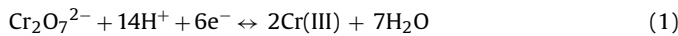


Fig. 3. Cr(VI) reduction at different initial concentrations (annealed at 450 °C, pH 3).

higher at pH 3 (Fig. 1). In addition, the efficiencies of Cr(VI) reduction at pH 9 were less than 5% for all of the TiO₂ samples. Based on the results shown in Fig. 1, the photocatalytic Cr(VI) reduction was performed at various pHs with TiO₂ anodized at 20 V and annealed at 450 °C, because this sample showed the best performance for Cr(VI) reduction among the various samples. At pH 3, Cr(VI) showed fast reduction with an efficiency of 98%, however, the efficiency decreased with increasing pH, being approximately 5–15% at pH 5–9. Generally, the Cr(VI) reduction efficiency was reported to higher under acidic conditions because Cr(VI) ions (Cr₂O₇²⁻) are the predominant species at medium to low pH values, the reduction of Cr(VI) by photogenerated electrons can be described as follows:



Based on the energy level of TiO₂ conduction band and redox potential of chromium ions as a function of pH, the reduction potential ($E_{\text{Cr(VI)/Cr(III)}}^0 = 1.33 \text{ V}$, E shifts 138 mV per pH unit) is more positive than that of the conduction band of TiO₂ [23,24]. As the number of studies reported [5,17,23,24], the reduction of Cr(VI) by the anodized nanotubular photocatalyst on Ti foil was in accordance with previous studies with powder TiO₂.

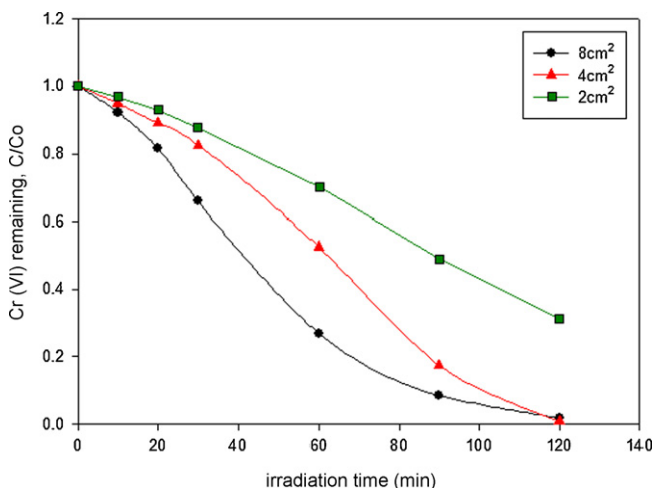


Fig. 4. Effect of reactive area on Cr(VI) reduction with various anodized TiO₂ (annealed at 450 °C, pH 3).

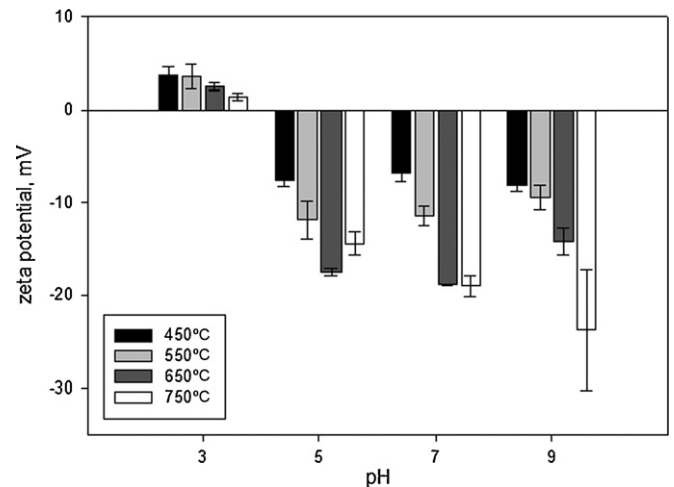


Fig. 5. Zeta potential measurement of anodized TiO₂.

The effect of the initial concentration of Cr(VI) on the reduction efficiency was investigated using anodized tubular TiO₂ at pH 3 with different initial concentrations of Cr(VI) ranging from 1 to 5 mg L⁻¹ of Cr(VI) (Fig. 3). The maximum reduction efficiency was obtained only for an initial concentration of Cr(VI) of 1 mg L⁻¹ within a reaction time of 90 min. Also, as expected, the reduction of Cr(VI) was shown less than 35% at an initial concentration of 5 mg L⁻¹ in these experiments, because a small amount of TiO₂ was grown on the Ti foil by anodization, which means that the dosage is insufficient to obtain a higher reduction efficiency of Cr(VI).

Fig. 4 shows the effect of the size of the anodized TiO₂ on the Cr(VI) reduction efficiency at 450 °C. As shown in Fig. 4, among the three different sizes, the largest size of anodized TiO₂, 8 cm² (2 cm × 4 cm), showed the highest reduction efficiency of ~98% after 120 min. In this study, the photocatalyst was immobilized TiO₂ anodized/annealed on Ti foil which was not a powder type catalyst such as commercial TiO₂. Therefore, the dosage of introduced into the photocatalytic reactor was not determined, but the effective size of the TiO₂ on the Ti foil was determined. Most of the tests were performed with a size of 8 cm² (2 cm × 4 cm), where the size can be directly related to the dosage if the density of the photocatalyst is known. Assuming the pho-

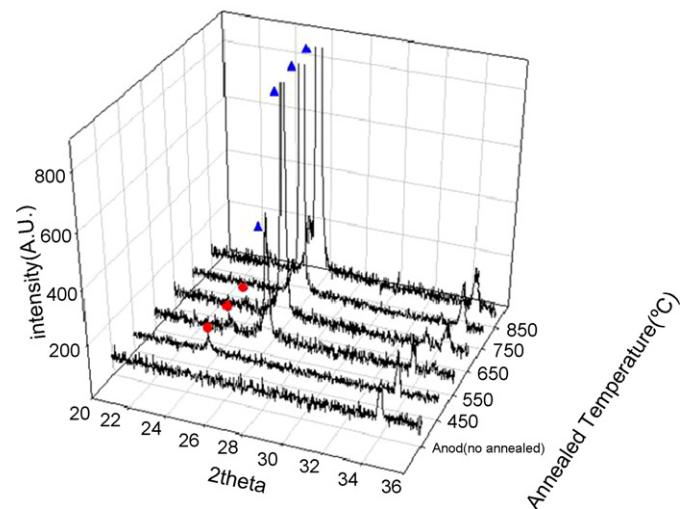


Fig. 6. XRD patterns of anodized TiO₂ at various annealing temperatures (● anatase phase, ▲ rutile phase).

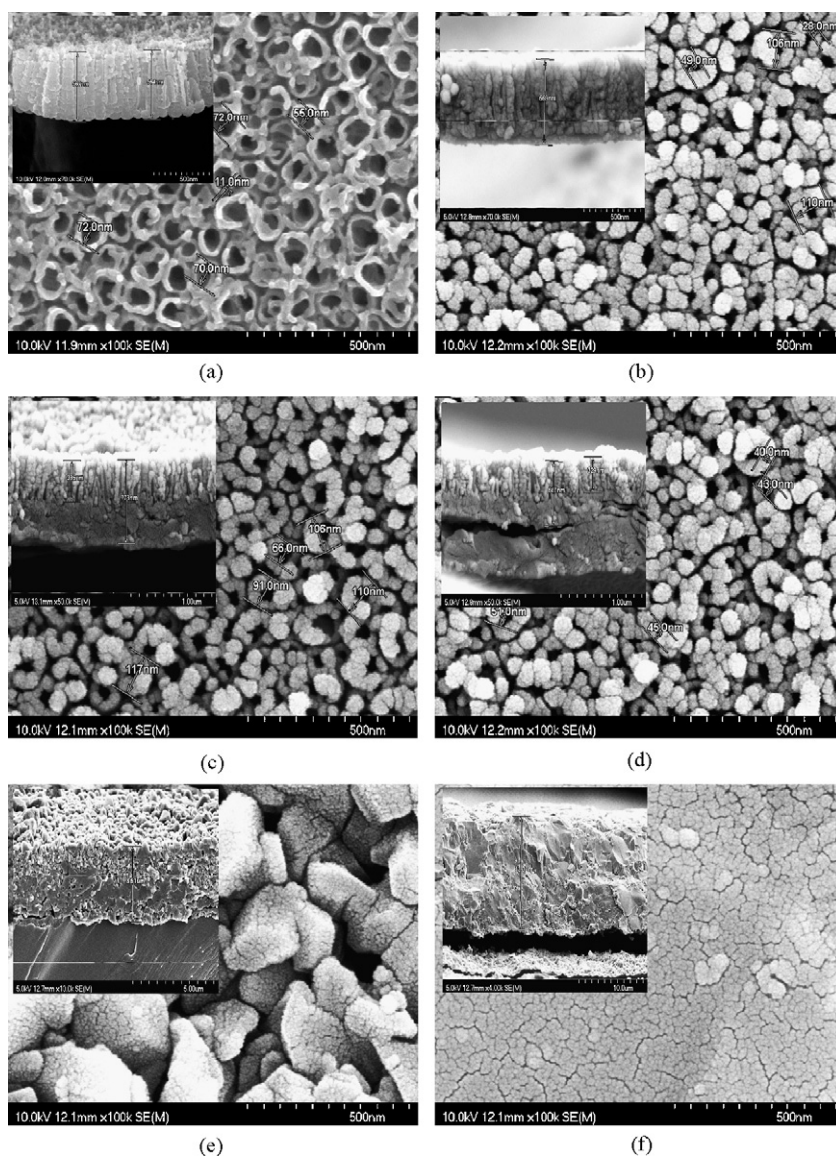


Fig. 7. SEM images of anodized TiO₂ at 20 V for 45 min and annealed at: (a) without annealing, (b) 450 °C, (c) 550 °C, (d) 650 °C, (e) 750 °C, and (f) 850 °C.

photocatalyst density is 3.9 g cm^{-3} based on a previous study [25] and the thickness of the anodized TiO₂ on the Ti foil is $\sim 1 \mu\text{m}$ based on SEM observation (Fig. 7), the quantity of anodized TiO₂ on the various sizes of Ti foil could be approximated; ~ 0.78 , ~ 1.56 , and $\sim 3.12 \text{ mg}$ for the sizes of 2, 4, and 8 cm^2 , respectively.

3.2. Characterization of anodized nanotubular TiO₂

TiO₂ surface has been reported in the literature to behave as a diprotic acid after the hydration of the surface functional groups [26]. The surface charge of TiO₂ is a function of the crystal types of TiO₂ and solution characteristics such as the pH and ionic strength. The surface charges of the anodized tubular TiO₂ annealed at temperatures ranging from 450 to 750 °C are presented in Fig. 5. The surface charges of all of the samples were positive at pH 3 and more negative with increasing pH. In this result, the zero point charge (pH_{ZPC}) was between 3 and 5, which is different from the reported pH_{ZPC} of P25 (≈ 6.8) [9,27,28]. The Cr(VI) species distribution in aqueous solution as a function of pH is based on the following

reactions:



The neutral chromic acid molecule, H₂CrO₄, was the dominant species at pH values less than 2, while the negatively charged HCrO₄⁻, CrO₄²⁻, and Cr₂O₇²⁻ species were dominant at pH values higher than 2. Since the pH_{ZPC} of anodized TiO₂ was determined to be between 3 and 5 in this measurement, the anodized TiO₂ surface is more positively charged at pH 3. A neutral species would exhibit little electrostatic affinity for a positive/negative charged surface. At pH values higher than pH_{ZPC}, the negatively charged species, HCrO₄⁻ and CrO₄²⁻, would be repelled from the negatively charged TiO₂, and thus significantly decrease the Cr(VI) reduction efficiency at higher pHs.

The measured XRD spectra of the anodized TiO₂ used for the photocatalytic Cr(VI) reduction are shown in Fig. 6. The XRD spectra show that the only anodized TiO₂ (not annealed) was amorphous

and the anodized TiO₂ annealed at 450–650 °C consisted of both the anatase phase (dark circle) and the rutile phase (dark triangle). However, the anodized TiO₂ annealed at 750 and 850 °C had broader rutile peaks. The XRD patterns supported the conclusion that the anodized TiO₂ composed of the anatase and rutile phases was more active and effective in the reduction of Cr(VI) than that composed of the only rutile (Fig. 1). Several properties are known to affect the photocatalytic activity, such as the particle size, crystal structure, crystallinity and so on. Among these properties, it is well known that for the degradation of most pollutants, the anatase phase is the most active phase of TiO₂ [29].

Fig. 7 shows the SEM images of the anodized TiO₂ used in this study. As shown in Fig. 7(a)–(d), the tubes grow perpendicular to the substrate forming an array. These tubes have a length of 350–600 nm, an inner diameter of 40–60 nm, and a wall thickness of 40–50 nm. In the case where the same electrolyte composition and anodization temperature are used, the annealing temperature determines the morphological shape, with tube arrays being observed on Ti foil at annealing temperatures in the range of 450–650 °C shown in Fig. 7(a)–(d) [30,31]. However, the same samples annealed at 750 and 850 °C shown in Fig. 7(e) and (f), respectively, have different morphology, i.e. a dense and thick film (with thickness of ~3.5 and ~13 μm, respectively). As the consequence of this morphological investigation, it was found that the one sample (not annealed) and the three samples showed a tubular shape at 450–650 °C and a dense film at 750–850 °C. In addition, as the annealing temperature was increased over 650 °C, the Cr(VI) reduction efficiencies were significantly decreased. These results are associated with the crystallinity (Fig. 6) and morphology (Fig. 7).

4. Conclusions

The aim of this work was to assess the feasibility of using immobilized TiO₂ prepared for environmental remediation as well as hydrogen production. To evaluate the immobilized TiO₂, pure Ti foil was anodized at 20 V in an electrolyte (0.5% HF) and annealed at various temperatures (450–850 °C). The major conclusions of this study are as follows: The photocatalytic Cr(VI) reduction efficiency increased with decreasing pH values. Under acidic conditions, the Cr(VI) reduction efficiencies at the different annealing temperatures were as follows; 450 °C (~98%) ≈ 550 °C (~98%) > 650 °C (~91%) > 750 °C (~83%) > 850 °C (~75%). On the other hand, the Cr(VI) reduction efficiencies of TiO₂ thermally treated under same conditions were less than 5% under the basic conditions (pH 9). In the experiments conducted with different initial concentrations and the sizes of anodized/annealed TiO₂, the Cr(VI) reduction efficiency was observed to increase with decreasing the initial concentration and increasing size of anodized/annealed TiO₂.

The results of the zeta potential measurements, XRD, and SEM explained the surface characteristics and the reactivity with Cr(VI); the zeta potential of all of the samples (except the sample annealed at 850 °C) became more positive with decreasing pH and stronger electrostatic affinity with the negatively charged Cr(VI). By the comparison of the XRD patterns, the samples having both the anatase phase and the rutile phase annealed at lower temperatures (450–650 °C) were shown to have higher reduction efficiencies than those annealed at higher temperatures (750–850 °C) having only the rutile phase. Finally, the SEM images supported the conclusion that the TiO₂ grown tubes was much more effective for Cr(VI) reduction.

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