Comparison of ZrO$_2$, TiO$_2$, and $\alpha$-Fe$_2$O$_3$ nanotube arrays on Cr(VI) photoreduction fabricated by anodization of Zr, Ti, and Fe foils

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Abstract

This paper presents the fabrication of self-organized ZrO$_2$, TiO$_2$, and $\alpha$-Fe$_2$O$_3$ nanotube arrays by anodization of Zr, Ti, and Fe foils, respectively in fluoride-containing EG electrolyte at 40 V for 20 min. The as-anodized nanotubes were annealed in a tube furnace at 400 °C for 3 h to induce the crystallization of the oxide film. Morphology, crystal structure, surface properties, and optical properties of the anodic ZrO$_2$ nanotubes (ZNTs), TiO$_2$ nanotubes (TNTs), and $\alpha$-Fe$_2$O$_3$ nanotubes (FNTs) were characterized by Field-Emission Scanning Electron Microscopy (FESEM), Transmission Electron Microscopy (TEM), x-ray Diffraction (XRD), Fourier-Transform Infrared (FTIR) spectroscopy, Photoluminescence (PL) spectroscopy, and UV–visible Near-Infrared Diffuse Reflectance Spectra (UV–vis NIR DRS) spectroscopy, respectively. Based on the FESEM and TEM micrographs, ZNTs possessed the longest nanotubes (i.e. 9.6 $\mu$m) compared with TNTs and FNTs under the same anodization condition. The aspect ratio of the nanotubes can be arranged in the order of ZNTs > FNTs > TNTs. The surface of the annealed ZNTs, FNTs, and TNTs was enriched with –OH groups to facilitate the Cr(VI) adsorption. According to the UV–vis NIR DRS spectra, strong visible light absorption was observed on the FNTs due to their low band gap. Whereas, the TNTs predominantly absorbs the UV light at $\lambda_{\text{max}}$ = 360 nm. Rapid Cr(VI) removal was observed on FNTs, i.e. 100% after 2 h activated by sunlight with negligible Cr(VI) removal for ZNTs and TNTs. When exposed to UVC ($\lambda$ = 254 nm), only 39% versus 37% Cr(VI) removal efficiencies were obtained on TNTs and ZNTs after 3 h suggesting sluggish electron transfer due to rapid charge carriers recombination as evident in the PL spectra.

1. Introduction

Hexavalent chromium, Cr(VI) is a toxic and carcinogenic heavy metal ion that released to the environment by steelmaking, lather tanning, chromate plating, and textile industries. As it is non-biodegradable, Cr(VI) can accumulate in the human body and induce adverse health effects like stomach irritation, dermatitis, liver damage, kidney circulation, nerve tissue damage, and death [1]. Cr(VI) must be eliminated from industrial wastewater. There are several ways to remove Cr(VI) from contaminated wastewater including adsorption, membrane filtration, ion exchange, and reduction. Among them, the reduction has been seen as a promising process whereby Cr(VI) can be reduced to trivalent chromium, Cr(III) before discharge. Cr(III) is far less toxic than Cr(VI) [2] and hence the release of Cr(III) to the environment does not induce any harmful effect.

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The reduction can be done by organic compounds [3], bacteria [4], and enzymes or nonenzymatic agents derived from plants [5]. Photoreduction process is an alternative route for the reduction of Cr(VI). It needs to be done in the presence of a heterogeneous photocatalyst. When a semiconductor photocatalyst is illuminated with photon energy (hν) greater than its band gap, electron-hole (e⁻ - h⁺) pairs are generated. Photoelectrons reside at the conduction band (CB) can be transferred to adsorbed Cr(VI) ions [6]. Cr(VI) is then reduced to Cr(III) via one-electron reducing step or a single three-electrons reduction step [7]. The photoreduction process usually conducted in acidic condition as H⁺ is required for the reduction of Cr(VI). However, recent studies reported the photoreduction also possible in neutral conditions [8, 9] but the performance is still lower than in acidic condition.

The photocatalytic activity of semiconductor oxides is influenced by the actual features of the oxide particles, concerning phases present within the oxide and morphological characteristics. To increase the photocatalytic activity, oxide morphologies can be tailored to have a high surface area as possible. For instance, in the form of aligned, one-dimensional nanotube arrays, the oxide is anticipated to have a much larger surface area as both the surface and interior of the oxide can be exposed to the solution to be treated. Moreover, a nanotubular structure allows for faster electron transfer, and enhanced charge carriers separation surface and interior of the oxide can be exposed to the solution to be treated. Furthermore, a nanotubular structure aligned, one-dimensional nanotube arrays, the oxide is anticipated to have a much larger surface area as both the activity, oxide morphologies can be tailored to have a high surface area as possible. For instance, in the form of anodized foils were annealed in a tubes furnace at 400 °C for 3 h under air atmosphere to induce the

2. Materials and methods

2.1. Anodization of Zr, Ti, and Fe foils
Zr (99.8% purity, 0.25 mm thickness, Strem Chemicals, USA), Ti (99.7% purity, 0.25 mm thickness, Strem Chemicals, USA), and Fe (99.9% purity, 0.25 mm thickness, Nilco, Japan) foils were cut into 1 cm × 1.5 cm dimension. All foils were ultrasonically cleaned by acetone, isopropanol, and ethanol before rinsed with deionized water (DI) and air-dried. Electrochemical anodization was performed by immersing a metal foil (anode) and a platinum electrode (cathode) in electrolyte bath consisted of EG/0.3 wt% NH₄F/3 vol% H₂O₂ at 40 V for 20 min. Then, the anodized foils were rinsed with acetone and DI water before air-dried. Finally, the anodized foils were annealed in a tubes furnace at 400 °C for 3 h under air atmosphere to induce the crystallization of anodic film.

2.2. Characterization
Morphology and crystal structure of nanotubes were characterized by FESEM (Variable Pressure, Zeiss Supra 35, Germany), TEM (Philips 420 T), and XRD (Bruker D8 Advance, Bruker GmBH, Germany), respectively. Surface properties of annealed nanotubes were characterized by FTIR (Perkin Elmer, England). Optical properties of nanotubes layer were evaluated by UV–Vis NIR DRS spectroscopy (JASCO V-670, Japan) and PL spectroscopy at excitation wavelength 325 nm (Perkin Elmer LS55; England).

2.3. Photocatalytic test
The photoreduction test was carried out by immersing a piece of the annealed foil (anodized area: 1 cm²) in 20 ml of 10 ppm or 70 ppm Cr(VI) aqueous solution for 1 h under dark condition at pH 2 to obtain an adsorption-desorption equilibrium at oxide|solution interface. ZNTs, TNTs, and FNTs were exposed under sunlight for 3 h. All the experiments were performed during the Sunny days (in Malaysia) from 10 am to 1 pm. Whereas, in another set of experiments, ZNTs and TNTs were irradiated with UVC (120 W germicidal light; λ = 254 nm) for 3 h. 3 ml aliquot was withdrawn for every 1 h interval. The concentration of Cr(VI) remaining
was determined by diphenylcarbazide (DPC) colorimetric method at $\lambda_{\text{max}} = 540$ nm by using the UV-Visible spectrophotometry (Varian Cary 50 Conc, USA). Percentage of Cr(VI) removal efficiency was calculated based on equation (1) where $C_0$ is the initial Cr(VI) concentration while $C_t$ is the concentration at certain irradiation time.

\[
\text{Removal efficiency (%) } = \frac{C_0 - C_t}{C_0} \times 100
\] (1)

3. Results and discussion

Figure 1 shows the FESEM and TEM micrographs of anodized Zr, Ti, and Fe foils in EG/0.3 wt% NH$_4$F/3 vol% H$_2$O at 40 V for 20 min. As seen, under similar anodization parameters, anodic films grown on the three metal foils are comprised of nanotube arrays but with different lengths and diameters. Based on cross-sectional micrographs, nanotubes grown on Zr (ZNTs) have the highest length of 9.6 $\mu$m. The nanotubes are also very well separated with an inner and outer diameters of 31.7 nm and 54.3 nm, respectively. The surface opening of the nanotubes is also clear for infiltration of Cr(VI) solution as seen from figure 1(a). On the other hand, nanotubes on Ti (TNTs) are shortest (2.9 $\mu$m) as shown in figure 1(e). The surface is not well etched (figure 1(b)) but the diameter from the TEM image shows that the nanotubes are larger with the inner diameter of 75.5 nm and the outer diameter of 137.4 nm. Anodic oxide on iron is also comprised of nanotubes (FNTs). The length is estimated to be 4.0 $\mu$m whereas the inner and outer diameters are 48.4 nm and 74.9 nm, respectively. By dividing length with internal diameter, the aspect ratios for ZNTs, FNTs, and TNTs are 302.8, 82.6, and 38.4, respectively. Figure 2 is the current density-time plot during anodization of Zr, Ti and Fe.

Figure 3 shows the XRD patterns for ZNTs, TNTs, and FNTs annealed at 400 °C for 3 h in air. All as-anodized nanotubes are amorphous. Annealing of the ZNTs resulted in the crystallization of monoclinic (ICSD #: 98-002-8057; space group $P1_21/c1$) and tetragonal (ICSD #: 98-002-7999; space group $P4_2/mmc$) ZrO$_2$ phases. Whereas, the annealed TNTs and FNTs were comprised of anatase TiO$_2$ (ICSD #: 98-006-6624; space group $I41/amd$) and $\alpha$-Fe$_3$O$_4$ (ICSD #: 98-004-6402; space group $R-3c$) and Fe$_3$O$_4$ (ICSD #: 98-011-1248; space group $Fd-3m$) mixture, respectively which $\alpha$-Fe$_3$O$_4$ is the predominant phase in the FNTs.

Surface hydroxyl (~OH) groups on the annealed ZNTs, TNTs, and FNTs were identified by FTIR. As shown in figure 4, broad absorption band at 3400 cm$^{-1}$ is attributed to ~OH. While weak peaks at 2856 cm$^{-1}$ and

![Figure 1](image-url).
Figure 2. Current density-time profiles during anodization of Zr, Ti, and Fe in EG/0.3 wt% NH₄F/3 vol% H₂O for 100 s.

Figure 3. XRD patterns for annealed (a) ZNTs, (b) TNTs, and (c) FNTs at 400 °C in air.

Figure 4. FTIR spectra of annealed (a) ZNTs, (b) TNTs, and (c) FNTs.
2927 cm\(^{-1}\) are assigned to the C–H bond. 1384 cm\(^{-1}\) and 1623 cm\(^{-1}\) peaks correspond to O–H vibration of absorbed water [13, 15]. The –OH groups are required for adsorption of Cr(VI) ions [15] before the reduction of Cr(VI) by the photogenerated electrons in the CB of the oxide nanotubes.

The photon absorbance of the annealed ZNTs, TNTs, and FNTs is shown in figure 5. As anticipated, FNTs demonstrate the strongest visible light absorption at maximum wavelength, \(\lambda_{\text{max}} = 570\) nm due to their small band gap. Whereas, the maximum photon absorption for TNTs and ZNTs is 360 nm and 420 nm, respectively. This suggests the FNTs and ZNTs can be activated under a visible spectrum while TNTs are more photoactive under UV. The visible light-harvesting capability of the ZNTs can be ascribed to the formation of defect states like oxygen vacancies that narrowing the band gap [13].

The presence of oxygen vacancies in ZNTs and TNTs can be evident in PL spectra shown in figures 6(a) and (b), respectively. Blue and yellow emissions are observed at 485 nm and 574 nm, respectively, that can be ascribed to shallow defects near to CB [17] and deep-level defects like oxygen vacancies [17], respectively. These shallow and deep-level defects are energetically distributed in the band gap to trap and capture electrons. Thus, the trapped electrons can be excited at various energy levels [17] upon irradiation. High intensity of PL emission in the ZNTs is ascribed to rapid charge carriers recombination due to annihilation of oxygen vacancies and impurities at high temperatures that used for charge carriers trapping [13, 18]. Conversely, low PL intensity of TNTs and FNTs indicate better charge carriers separation in the oxide.

Figure 5. UV/Vis-NIR DRS spectra for annealed ZNTs, TNTs, and FNTs at 400 °C in air.

Figure 6. (a) PL emissions of annealed ZNTs, TNTs, and FNTs at 400 °C in air and (b) enlarged PL spectra for the annealed TNTs and ZNTs.
that ascribed to poor visible light absorption of TNTs and rapid charge carriers recombination in the ZNTs and treated Cr
comparison. As seen, 100% of Cr
(mass
which was rather small compared to others. The mass of the FNTs was determined from the equation;
fi
be transferred to the oxide surface for reduction of Cr
annealed ZNTs can be activated under sunlight due to their high catalyst loading
low band gap, high Cr
capacity of FNTs denoted by 33% of Cr
adsorption on FNTs is indicated by 5% Cr
reduction is further accelerated.

Conversely, negligible Cr(VI) removal is observed on TNTs and ZNTs that ascribed to poor visible light absorption of TNTs and rapid charge carriers recombination in the ZNTs and as indicated in figures 5 and 6, respectively. Therefore, less e\(^{-}\) - h\(^{+}\) pairs can be photogenerated in the TNTs for redox reaction. Meanwhile, the rapid e\(^{-}\) - h\(^{+}\) recombination in the ZNTs reduces the chances of the electrons to be transferred to the oxide surface for reduction of Cr(VI). In contrast with our previous report [13], the annealed ZNTs can be activated under sunlight due to their high catalyst loading (1 g l\(^{-1}\)) and free from underneath metal substrate (in the form of freestanding nanotubes). So that, more active sites can be exposed to the Cr(VI) ions. In addition, the intensity of PL emission for freestanding ZNTs annealed at 400 °C is far much lower than the PL intensity indicated above implying better charge carriers separation for ZNTs grown in carbonated fluoride electrolyte [13]. However, the high photocatalytic activity of FNTs can be attributed to their low band gap, high Cr(VI) adsorption, and enhanced charge carriers separation as shown in figure 7. Good Cr(VI) adsorption on FNTs is indicated by 5% Cr(VI) removal after 1 h in dark condition. When irradiated with sunlight, the rate of Cr(VI) reduction is further accelerated.

The reduction of 70 ppm of Cr(VI) solution on FNTs is also shown in figure 7 and can be seen to be lower (71% after 2 h) than when more diluted Cr(VI) solution was used. Nevertheless, we observed high adsorption capacity of FNTs denoted by 33% of Cr(VI) removal after 1 h in dark implies strong affinity of α-Fe\(_2\)O\(_3\) on Cr(VI) ions [19].

Table 1 shows the comparison of 10 ppm Cr(VI) reduction from several publications with FNTs formed in this work. As seen, the FNTs are rather efficient in Cr(VI) removal even without the need for other materials such as graphene or carbon nanotubes. Moreover, the catalysts loading used in this work was estimated as 0.1 g l\(^{-1}\) which was rather small compared to others. The mass of the FNTs was determined from the equation;

\[
\text{mass} (m) = \text{density} (\rho) \times \text{volume} (V).
\]

The volume of FNTs grown on Fe foil was estimated 4 \times 10^{-4} cm\(^3\) (V = 1 cm length \times 1 cm width \times 0.0004 cm thickness). The thickness of FNTs is shown in figure 1(f).

The reusability of anodic FNTs on photoreduction of Cr(VI) activated by sunlight is shown in figure 8 obtained by three cyclic runs. After each cycle, the immersed FNTs were taken and rinsed by deionized water.
several times before dried in an oven at 80 °C for 1 h. As can be seen from figure 8, the high removal efficiency is maintained suggesting that this photocatalyst possesses good reusability for Cr(VI) photoreduction.

Since the low photocatalytic activity of ZNTs and TNTs were observed under sunlight, they were exposed under UVC irradiation (λ = 254 nm) for 3 h as shown in figure 9. The removal efficiency was improved in the presence of UV due to high charge carriers formation in the TNTs with their removal efficiency is 39% that slightly higher than ZNTs i.e. 37%.

Mechanism of Cr(VI) photoreduction on ZNTs, TNTs, and FNTs can be attributed to synergistic reactions between adsorption and reduction. Before reduction can happen, the Cr(VI) ions must be adsorbed on the oxide surface. At low pH, Cr(VI) exists as HCrO4−. These ions were adsorbed preferentially at –OH groups on the surface of the oxide via electrostatic attraction [13, 15]. Then, the adsorbed Cr(VI) ions were reduced by the photogenerated electrons in the CB of oxide semiconductors according to equation (2). The reduction of Cr(VI) by CB electrons are possible on ZNTs, TNTs, and FNTs as the CB edge levels for ZrO2, TiO2, and α-Fe2O3 are more cathodic than the reduction potential of Cr(VI) to Cr(III) i.e. E0° = +1.35 V versus NHE at pH = 0 [23, 24] as shown in figure 10. The reduction of Cr(VI) by CB electrons over oxide semiconductor is supported by Electron Spin Resonance (ESR)- 5,5-Dimethyl-1-pyrroline N-oxide (DMPO)’s result obtained by Pu et al [25]. Whereas, water will be oxidized by holes in the VB of semiconductors producing O2 [7] as stated in equation (3). This is consistent with Zhong et al [26] findings that observed O2 production during Cr(VI) photoreduction that also analyzed using the ESR-DMPO method. Despite O2 is known to be an electron scavenger that could hinder the reduction of Cr(VI), the reaction with electrons also can produce O2−, HO2−,
and H₂O₂ species that result in the reduction of Cr(VI) to Cr(III) [13, 25].

\[
\begin{align*}
HCrO_4^- + 7H^+ + 3e^- &\rightarrow Cr^{3+} + 4H_2O \\
2H_2O + 4h^+ &\rightarrow O_2 + 4H^+
\end{align*}
\]

4. Conclusion

From this work, it is evident that nanotubes formed on Zr are longer compared to on Ti or Fe under the same anodization condition. Nevertheless, the aspect ratio of nanotubes was not the predominant factor in affecting the Cr(VI) photoreduction. FNTs are the most photoactive photocatalyst on the reduction of Cr(VI) under sunlight attributed to their low band gap, high Cr(VI) adsorption, and enhanced charge carriers separation. Improved Cr(VI) photoreduction on ZNTs and TNTs were observed under UV due to higher charge carriers formation.

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