Hierarchical Porous $\alpha$-Fe$_2$O$_3$ Formation by Thermal Oxidation of Iron as Catalyst for Cr(Vi) Reduction

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Abstract. $\alpha$-Fe$_2$O$_3$ is a semiconductor photocatalyst that can adsorb and reduce heavy metal ions from contaminated water. Here, hierarchical porous structured $\alpha$-Fe$_2$O$_3$ was synthesised by thermal oxidation of iron wire at 400 °C – 700 °C in the presence of water vapour for 1 hour. The mechanism of formation of the iron oxide nanowires is proposed to follow stress-driven mechanism and when the nanowires merged, nanoblades resulted hierarchical porous structure. Field emission electron microscope (FESEM) images of the oxidized iron had shown the formation of surface oxide comprising of a hierarchical porous structures. High resolution transmission electron microscope (HRTEM) and Raman spectroscopy results confirmed that the iron oxide is consisted of $\alpha$-Fe$_2$O$_3$ in the surface whereas Fe$_3$O$_4$ and FeO are in the inner layer. The oxides were immersed in Cr(VI) solution and illuminated under sunlight to produce reducing electrons. The highest reduction percentage of Cr(VI) at pH 2 on the hierarchical porous structure is 80.78% for synthesized sample at 500 °C. It may be due to the higher surface area of the porous hierarchical structure which provide more catalytic reaction sites hence improving the photocatalytic activity.

1. Introduction

Chromium is one example of toxic heavy metal pollutant in industrial effluents. When discharged to water bodies, unlike most organic contaminants, being inorganic, chromium ions do not undergo degradation. This impose severe treats to aquatic life and through bioaccumulation and food chain, chromium ions can find their way to human. The extent of toxicity depends on the specific metal oxidation state with Cr(VI) to be known as highly toxic than Cr(III). At low pH, the most soluble,mobile and toxic forms of Cr(VI) is dichromate (Cr$_2$O$_7^{2-}$) while at higher pH, Cr(VI) exists as chromate (CrO$_4^{2-}$) [1]. Both are harmful to human and the environment.
Various methods have been employed to remove Cr(VI) from wastewater such as ion exchange, electrochemical treatment, chemical precipitation, membrane filtration, adsorption, and photocatalytic technology [1 - 2]. Among all these, photocatalytic technology is one of the most efficient remediation strategies. The process utilize oxidation–reduction reactions on a solid photocatalyst surface, converting Cr(VI) to Cr(III). Electron donors are produced from the photocatalysts when illuminated. In this work, we produced photocatalyst in nanoscale as nanoscale material has higher surface area for more sites for sorption and reaction. We choose iron oxide as the catalysts since it is low cost, non-toxic and abundant. More importantly, it can be activated under sun light.

When iron oxide is illuminated under light irradiation with energy higher than its band gap, electron-hole pairs are generated. The photoelectrons must then diffuse to the surface of the oxide and can then be transferred out to adsorbed Cr(VI) ions on the oxide surface. Reduction will take place to produce Cr(III). The use of material in nanoscale can help in improving the charge transfer process as electrons will only need to travel a shorter distance to the surface for reduction to take place. This can reduce recombination, ensuring more reduction process to take part on the surface of the oxide [1, 3]. In this work, iron oxide was fabricated by a simple thermal oxidation process. Iron oxides normally exists in three common forms: hematite ($\alpha$-Fe$_2$O$_3$), maghemite ($\gamma$-Fe$_2$O$_3$), and magnetite (Fe$_3$O$_4$) [4-5]. Hematite ($\alpha$-Fe$_2$O$_3$) is an n-type semiconductor with small energy gap of 2.2 eV and is photoactive. It is extremely stable compared to other phase of iron oxides and hence can be expected to be the main product of thermal oxidation of iron [5]. There have been a number of researches on the application of iron oxides on Cr(VI) removal such as flower-like $\alpha$-Fe$_2$O$_3$ [6], Fe@Fe$_2$O$_3$ core-shell nanowires [7], and iron (III)-based metal-organic frameworks [8].

Different approaches have been studied to synthesis nanostructure iron oxides such as metal-organic chemical vapour deposition [9], sol-gel deposition [10], hydrothermal [11-12], and thermal oxidation [13-15]. Nevertheless, the assembly of the low dimensional building blocks (particles, wires, tubes, and flakes) into a complex 3-D nanostructures (hierarchical structures) is still considered rather challenging. Hierarchically structured iron oxides can be formed by employing templated methods [6], [16]. But in this work the thermal oxidation process was observed to be successful in producing 3-D hierarchical $\alpha$-Fe$_2$O$_3$ nanostructures. The oxide was then used as a photocatalysts to reduce Cr(VI) under sunlight. To the best of our knowledge no other work has reported on the use of 3-D hierarchical $\alpha$-Fe$_2$O$_3$ nanostructures derived from thermal oxidation of commercially available iron as Cr(VI) reduction catalyst.

2. Methods and materials

1 cm long high purity iron wire (Nilaco Corporation, 99.5%), was used as the starting material. The wire was polished with SiC sand paper #1200 grit to remove impurities and native oxide from the surface. The polished wire was then cleaned in ultrasonic bath with aceton, and ethanol for 3 minutes respectively. After that, it was rinsed by deionised water throughly and dried by air gun.

The wire was then subjected to thermal oxidation process with rapid quenching process. Horizontal tube furnace (Lenton 1200) was heated up to a desired temperature (400 °C – 700 °C) then the wire was pushed into it. After an hour the wire was removed from the furnace and cooled down naturally until room temperature. Another set of experiment was done by varying oxidation times: 15, 30, and 60 minutes. In order to supply water to the furnace, aerosol of water was produced by ultrasonicating the water with nebuliser (Omron NE-U17). The water aerosol was changed to water vapour once it entered the furnace.

For photocatalytic reduction of Cr(VI) experiment, 10 ppm of Cr(VI) 30 mL solution (pH 2) was first prepared. Oxidised iron was then placed in the solution and was then left in the dark for 1 hour to reach equilibrium. Then, it was placed under sunlight in the morning (~ 10 am). 3 mL solution was taken out for 10 minutes interval for an hour and colouration method was used to investigate the success of the reduction process. UV-Vis spectroscopy was used to detect the absorbance at 540 nm using the diphenylcarbazide (DPC) method.
Several characterization techniques were performed to investigate the oxidised samples. Field emission scanning electron microscopy (FESEM – Zeiss Supra 35 VP) and transmission electron microscopy (TEM - Tecnai G2 20 S-Twin) were used to observe the morphology of the samples. For phase identification, and crystal analysis, X-ray diffractometer (XRD - Bruker Advanced X-Ray Solution D8 with Cu-Kα radiation (λ = 0.154 nm)) and Raman spectrometer (RENISHAW inVia 9P1567) were carried out. UV-visible spectrometer (Varian Cary 50) was used to measure the reduction of Cr(VI).

3. Results and discussion

Figure 1 shows the FESEM images of the oxidised iron wires at 400 °C – 700 °C in dry air. Micrographs of iron oxidised at similar temperature range but in water vapour are shown in Figure 2. As can be seen, oxidation in dry air at 400 °C (Figure 1 (a)) resulted in nanowires formation. However, when water vapour was injected in the furnace, the surface oxide is seen to have hierarchical porous structures (Figure 2 (a)). The structure seems to consist of sheets of oxide, interconnected from one to another. Oxidation at 500 °C resulted in nanoblades (nanosheets) formation (Figure 1 (b)). Upon the addition of water vapour, hierarchical porous structures is also observed but with thicker sheet thickness compared to sample oxidised at 400 °C (Figure 2 (b)). Increase of temperature to 600 °C yield surface oxide with hierarchical porous structure even in dry air condition (Figure 1 (c)). At 700 °C in both conditions, the walls of the porous structure thicken (Figure 1 (d) for air and Figure 2 (d) for water vapour). This observation shows that the surface morphology of oxidised iron is dependent on the oxidising atmosphere and temperature.

It is known that during oxidation process, iron oxide will form when iron lost its electrons and react with oxygen ions from the surrounding [14]. It is obvious that oxidation requires oxidant for oxide formation and in here; oxidant was supplied by the surrounding air or water vapour [16]. It is well documented that oxidation of iron will result in multilayered oxide with the surface oxide comprised of α-Fe₂O₃. Depending on the oxidation temperature, inner oxide scale can consist of either Fe₃O₄, or a mixture of Fe₃O₄ and FeO phases [14], [17]. In order to investigate the phase of the oxide formed, HRTEM imaging was done on the sheet as seen in Figure 3, interplanar distance determined from the sheet is 0.25 nm which is corresponding to the (1 0 0) plane of α-Fe₂O₃.

![Figure 1](image1.png)

**Figure 1.** FESEM images of iron wires oxidised at (a) 400 °C, (b) 500 °C, (c) 600 °C, (d) 700 °C in dry air for 1 hour.

![Figure 2](image2.png)

**Figure 2.** FESEM images of iron wires oxidised at (a) 400 °C, (b) 500 °C, (c) 600 °C, (d) 700 °C in water vapour for 1 hour.
Figure 3. HRTEM image of nanostructured formed on iron oxidised at 600 °C (1 h) in water vapour

Figure 4 is the corresponding Raman shift of iron wires oxidised at different temperature in the presence of water vapour. Only sample oxidised at 500 °C shows rather intense Raman peaks. For this sample, bands at 225, 247, 292, 412, 500, and 612 cm⁻¹ are seen which correspond to α-Fe₂O₃. However, for sample oxidised at 400 °C and 600 °C, α-Fe₂O₃ peak at 247 cm⁻¹ is rather strong as well. Weak bands at 380 and 717 cm⁻¹ can be attributed to γ-Fe₂O₃. A small peak of Fe₃O₄ at 667 cm⁻¹ is also detected for sample oxidised at 500 °C. It can be concluded that α-Fe₂O₃ is the main phase formed on the iron wire, followed by traces of γ-Fe₂O₃ and Fe₃O₄.

Figure 4. Raman shift of oxidised iron wires at (a) 400 °C, (b) 500 °C, (c) 600 °C, and (d) 700 °C.

The growth mechanism of hierarchical porous structure iron oxide by thermal oxidation with rapid quenching process consists of three main parts: (1) initial oxidation, (2) oxide scale formation, and (3) assembly of nanostructure. In the initial oxidation of iron wire in dry air, chemisorption of oxygen ions (O²⁻) on iron substrate occurred. It can stimulate iron ion (Fe²⁺) to diffuse from iron substrate to the adsorbed oxygen ions plane [18]. The growth of iron oxide layers can be described by the outward diffusion of Fe²⁺ through the oxide layer and inward diffusion of O²⁻ across the oxide layer [18][19]. While in water vapour atmosphere, the vapour will be adsorbed at first and dissociated as express in equation 1 and 2 [20]. Water vapour acts as a source of hydrogen which dissolves as hydrogen ion, H⁺ (or proton) in oxide of iron. The formation of proton resulting from dissociation of water will change the defect properties of oxide and affect to the increasing of diffusion between hydroxyl ions and iron ions.

\[
\begin{align*}
\text{H}_2\text{O}_{(\text{ads})} + V_{o''} & \leftrightarrow \text{OH}_{o'} + \text{H}^+ \quad (1) \\
2 \text{H}^+ + 2e^- & \leftrightarrow \text{H}_2 \quad (2)
\end{align*}
\]

During oxidation process, several iron oxide phases were formed on the substrate. The difference of volume between the oxide phases at high temperature will induce either compressive stress or tensile stress within these layers. The growth of nanostructures on the surface is believed to be the result of the release of this stress through boundary from the interface layer Fe₂O₃ | Fe₃O₄ to the outermost surface of Fe₂O₃ which is stress free. This process is called stress-driven mechanism [13].
The formation of hierarchical porous structures started from the formation of nanowires and nanosheets during oxidation process. It can be seen in figure 5 which only nanowires and few nanosheets occur for 15 minutes of oxidation, and more nanosheets, less nanowires for 30 minutes of oxidation. It proves that nanostructure grows wider as oxidation time goes longer. It can be concluded that when nanowires are close enough to each other, the surface diffusion will lead to lateral growth which cause the nanowires merge together at the bottom part and continue to grow to a sheet-like form. In the other hand, when oxidation time reach 60 minutes, nanosheets evolve to hierarchical porous structures. It is believed that lateral diffusion is predominant resulting the nanosheets merge with the neighbouring nanosheets to form hierarchical porous structures.

![Figure 5. Oxidised iron wire at 500 °C in water vapour for (a) 15 min, (b) 30 min, (c) 60 min](image)

Also, as the oxidation is conducted in water vapour atmosphere, the inward transport of hydroxyl ions (OH\(^-\)) originated from water vapour and outward transport of iron ions (Fe\(^{2+}\)) will form iron oxides and H\(^+\) ions which create defects in the oxides leading to the faster oxidation process and the formation of hierarchical porous structures. Figure 2 proves that it can be formed at samples oxidised in water vapour atmosphere. For samples oxidised in dry air, the same structure is not observed for samples oxidised at 400°C, and 500°C (figure 1 (a and b)). However, as diffusion is temperature activated process, this can explain why at higher temperature in dry air atmosphere (600°C), the hierarchical porous structure is observed due to the temperature was increased which favoured the growth and merging of nanostructures.

In photocatalytic reduction experiment, oxidised iron wire in the presence of water vapour at 400°C - 700°C were used to assess the performance of hierarchical porous structures iron oxide on Cr(VI) reduction. As seen in figure 6, sample oxidised at 500°C gives the best performance among all samples (80.78%). This result is better than previous works [22][23][24] which the photoreduction performances are below 60%.

The better performance of hierarchical porous structures iron oxide can be attributed to the highly porous structure and high surface area of the iron oxides. This provides more site for Cr(VI) ions to be adsorbed and increase the number of catalytic reaction sites which benefits the improvement of the photocatalytic activity of the iron oxide photocatalyst.

![Figure 6. Reduction of Cr(VI) in solution without catalyst and in the presence of synthesised iron oxide at 400°C - 700°C in water vapour atmosphere](image)
4. Conclusion

Hierarchical porous structures iron oxide was successfully fabricated through rapid quenching process by thermal oxidation. It was found that hierarchical structure formed in the presence of water vapour during oxidation at 400°C-500°C. The mechanism of formation of nanostructured iron oxide is suggested to follow the stress-driven mechanism and the fast growing blades would consume the smaller nanowires and resulted in hierarchical porous structure.

The performance of hierarchical porous structures iron oxide was investigated by photocatalytic reduction experiment for Cr(VI). The reduction percentage of Cr(VI) by sample oxidised at 500°C is the highest (80.78%) followed by sample oxidised at 600°C, 400°C, and 700°C, respectively.

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