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Tailoring Parameters to Produce Nanowires on Metal Surface via Surface Oxidation Process

Subagja Toto Rahmat¹, Chan Yi Hong¹, Faisal Budiman¹, Wai Kian Tan², Go Kawamura³, Atsunori Matsuda³, and Zainovia Lockman¹*

¹ Green Electronic nanoMaterials Group, Nanomaterials Niche Area (School of Materials and Mineral Resources Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia)
² Center for International Education (Toyohashi University of Technology, Toyohashi, Aichi, 441-8580, Japan)
³ Department of Electrical and Electronic Information Engineering (Toyohashi University of Technology, Toyohashi, Aichi, 441-8580, Japan)

Email: zainovia@usm.my

Abstract. Thermal oxidation of iron, tungsten, titanium and copper was done in dry air to produce Fe₂O₃, WO₃, TiO₂ and CuO nanowires, respectively, at 500 – 600 °C. Whilst nanowires were observed on iron and copper, no nanowires were seen on titanium and tungsten. Keeping the temperature constant, oxidation of titanium and tungsten was continued but in the presence of water vapour. Through this method nanowires were successfully formed on titanium but not on tungsten. Potassium halide vapour was then introduced to the oxidation furnace for tungsten and after an hour of oxidation, nanowires were produced on the tungsten surface. Nevertheless, the growth mechanism of the nanowires on tungsten is thought to be very much different than iron, copper and titanium whereby on tungsten catalytic induced reaction is likely. Oxide nanowires on iron and titanium were further studied as oxide films on copper and tungsten were not well adhered to the substrate. Under sunlight radiation, ~ 90% of Cr(VI) was successfully removed on Fe₂O₃ nanowires compared to on TiO₂ nanowires (~ 40 % removal) after an hour process. This is due to the smaller energy band gap of Fe₂O₃ compares to TiO₂.

1. Introduction

Metal oxidation can be considered as a degradation process of metal occurring when the metal is subjected to oxygen and/or other oxidising environment. Transition metals like copper, iron, tungsten and titanium in ambient conditions are thermodynamically unstable and hence they will oxidize [1]. A thin layer of native oxide (transition metal oxide (TMO)) will be formed on their surfaces. When exposed to high temperature the growth of the TMO increases rapidly, forming a thick scale of oxide. Growth mechanisms of TMO scale follow several well-documented laws with Wagner’s model for high-temperature oxidation of metals as one of the most accepted. Apart from growth mechanisms the phases of oxides that formed i.e. the oxidation products and perhaps their position within the TMO
scale have also been studied [1]. In this work, the surface oxide is off importance since the surface oxide was exploited for its absorbance and photocatalytic properties. For these properties, the morphologies of the surface oxide are also important. Here the surface oxide is tailored to comprise of nanowires. During growth of TMO at high temperature, the rate limiting step is the lattice diffusion of cations through point defects in the scale. Therefore, at high temperature the scale would be expected to exhibit a flat oxide layer at the scale-gas interface. The oxide is also anticipated to compose of columnar grains. At lower oxidation temperature, grain boundary diffusion dominates. The resulting oxide grains are often observed to be shallow-dish shaped, with slight ridges at their boundaries. At this temperature regime, prolonging oxidation times may induce the growth of oxide resulting in elongated, whiskers structure. On the other hand at an intermediate temperature, growth of whiskers (nanowires) is more obvious [2]. Temperature is therefore an important parameter to determine the morphology of surface oxide. Classification of temperature regime is dependent on the melting points of the oxidized metal. In here, oxidation was conducted at 500 or 600 °C on metal of different melting point: copper (1085 °C), iron (1538 °C), titanium (1,668 °C) and tungsten (3,422 °C). Apart from temperature, oxidation condition for instance the presence of water can also influence nanowires formation especially on metal with rather high melting point [3–6]. An extremely high melting point metal like tungsten on the other hand appears to be much more difficult to be oxidized to form nanowires with or without the presence of water vapour. Catalysts are required for the growth of tungsten oxide nanowires on tungsten.

As already mentioned, thermal oxidation of iron, tungsten, titanium and copper was done to produce Fe₂O₃, WO₃, TiO₂ and CuO, respectively. These oxides are typical binary oxide semiconductors with applications ranging from photocatalysts to energy devices. In this work, the four metal oxides were made in a form of nanowires and the photoactivity of the oxide was studied by assessing their ability to reduce Cr(VI) to Cr(III) [7]. To the best of our knowledge, no other works have reported on the use of these oxides in a form of nanowires derived from oxidation of their parent metal as photocatalysts for Cr(VI) ions reduction. Cr(VI) is a typical example of heavy metal ion and has long known to be toxic to humans and animals. The toxicity of chromium depends on the oxidation state with Cr(VI) being more toxic than Cr(III). Moreover, Cr(VI) is more readily absorbed when inhaled or consumed leading to various harmful effect to human. Some of the Cr(VI) compounds are also corrosive and due to this, high dosage may results in systemic toxicity. Therefore method to remove them is necessary. In here, as mentioned, TMO nanowires formed were used to remove Cr(VI) by adsorbing and reducing the ions to Cr(III).

2. Methods and materials

Iron, copper, tungsten and titanium foils or wires were degreased, cleaned and rinsed in deionised water. They were then placed in an alumina crucible and positioned at the hot zone in an horizontal tube furnace (Lenton 1200). They were subjected to oxidation process at either 500 °C or 600 °C for < 2 hours. The oxidised samples were quenched after dwelling time was reached and cooled down naturally until room temperature. A set of oxidation was also done with water mist injected to the furnace. A nebulizer was used to produce the water mist (Omrón NE-U17). After reaching the desired dwelling time, the sample was quenched from the furnace. Imaging was then done on the surface of the oxidised samples using field emission scanning electron microscopy (FESEM – Zeiss Supra 35 VP). The morphology desired would be in a form of nanowires. For phase identification, and crystal analysis, X-ray diffractometer (XRD - Bruker Advanced X-Ray Solution D8 with Cu-Kα radiation (λ = 0.154 nm)) was carried out on the samples. As no nanowires were formed on tungsten, a catalytic route was selected whereby potassium halide solution like (potassium fluoride, chloride or halide) was nebulized to the furnace during oxidation. To assess the photoactivity of the oxidised metals, 10 ppm of Cr(VI) solution was produced by dissolving 0.8481 mg of K₂Cr₂O₇ in 30 mL deionized water. HCl was added in to reduce the pH of the solution to 2. Of all four metals oxidised, only oxidised Ti and Fe samples were tested as the surface oxide was adhered to the substrate. The sample was then placed in the
solution and was left in the dark for 1 hour to reach equilibrium. Only, oxidised titanium, copper and iron were subjected to this process as surface oxide on tungsten peeled off at some parts of the foil. Cr(VI) solution was then placed under sunlight in the morning (10 am) and left for reduction. 3 mL Cr(VI) solution was taken out from the tube at 10 minutes interval until 1 hour. The reduction of the solution can be seen from colour changes from yellowish to clear liquid. UV-VIS spectrometer was used to assess on the reduction of the Cr(VI).

3. Results and discussions

Fig. 1 shows oxide surfaces on (a) tungsten, (b) iron, (c) titanium and (d) copper after oxidation at either 500 or 600 °C in dry air. Morphologies of oxidised titanium and tungsten are consisted of rather flat oxides whereas on copper and iron whiskers are obvious. The whiskers grew perpendicular to the substrate with tips in nanoscale whereas based in submicron scale. This is more obvious for the case of iron as compared to copper. The whiskers termed nanowires in this work are seen to be covering the surface of iron rather evenly but not so on copper. It is known that the driving force for oxide scale formation is the free energy change associated with the formation of the oxide [1]. On titanium, copper, iron and tungsten, the surface oxides are TiO$_2$, CuO, Fe$_2$O$_3$ and WO$_3$. Surface oxide is often the stable oxide phase which will not dissociate in ambient oxygen pressure. The standard free energy of oxide formations is a function of temperature and during the process of oxidation the stable oxide will grow and crystallize. The corresponding dissociation pressures of oxides can be referred to Ellingham/Richardson diagram and based on the diagram, stable oxide formed on the four metals can be predicted. On Fe and Cu, the nanowires are likely to be and $\alpha$-Fe$_2$O$_3$ [4, 5, 6] and CuO [3].

![Figure 1](image)

Figure 1. FESEM morphologies of oxidised (a) tungsten (600 °C), (b) iron (500 °C), (c) titanium (600 °C) and (d) copper (600 °C). Oxidation was done in dry air.

As mentioned, melting points of copper, iron, titanium and tungsten are 1085 °C, 1538 °C, 1,668 °C and 3,422 °C respectively. If intermediate oxidation temperature can be defined as $0.5T_m \leq T \leq 0.75T_m$ whereas low temperature is $< 0.5T_m$, then 500-600 °C can be regarded as intermediate oxidation temperature regime for copper and low temperature regime for iron, titanium and tungsten. At low or intermediate temperature regime the rate of metal oxidation is likely to be controlled by transport along defects in the oxide especially dislocations. Dislocations can provide transport paths for elongated
surface structure formation and hence explaining the nanowires development. The primary mechanism is via surface diffusion along a tunnel (dislocation core) centered on one dislocation or a bundle of parallel dislocations. Dislocations could either be inherited from the metal substrate, lattice mismatch or volume expansion, or generated by oxidation growth stresses. Growth stresses can occur due to the layered nature of the growing scale. Oxidation of copper results in scale with Cu$_2$O as the first layer (inner oxide) on Cu follows by CuO as the outer oxide [3]. Iron on the other hand is consisted of magnetite, Fe$_3$O$_4$ as the inner oxide and hematite, $\alpha$-Fe$_2$O$_3$ as the outer oxide [4-7]. Due to the different molar volumes between the oxide phases, stress is generated at the interface region between the oxide phases forming dislocation which promote the nanowires growth. Growth occurs from the base to the tip with flux of cations to the surface provided by surface diffusion along the dislocation pipe. To compare the physical appearance of oxidized Cu to Fe, it was observed that the oxide on Cu was easily peeled off and hence limiting its applicability as a photocatalysts.

It appears that 600 °C was not adequate for nanowires growth on titanium despite the melting point of iron and titanium is not very much different. Morphologic feature is therefore not dependent solely on reaction temperature but also upon the gaseous environment; choice of gas, pressure and flow rate. Oxidation condition was then altered by injecting water vapour to the furnace whilst keeping the oxidation temperature at 600 °C. Similarly we performed oxidation of tungsten at 600 °C in water vapour as well. Fig. 2 shows the surface of (a) titanium and (b) tungsten after oxidation in the presence of water vapour. As can be seen, on titanium, nanowires are observed with diameter of ~ 15 nm. It is evident here that water vapour has helped in the formation of TiO$_2$ nanowires by direct heating in water vapour at 600 °C.

However, no nanowires can be observed on tungsten. Formation of TiO$_2$ nanowires at low temperature oxidation in water vapour can then be explained by the more rapid dissociation of adsorbed H$_2$O compared to O$_2$ molecules [2]. If the oxidant dissociation step is accelerated, then the arriving cations from the titanium are incorporated into lattice growth locally at the tip, resulting in the increase of nanowires length. Therefore, even at rather lower temperature regime, oxidation of titanium can be resulted in nanowires formation provided water vapour is used.

Figure 2. Surface oxide on (a) titanium and (b) tungsten in water vapour (WV) at 600 °C, (c) tungsten in potassium halide vapour (PHV) at 600 °C and (d) tungsten in potassium halide vapour (PHV) at 500 °C.
Oxidation of tungsten was then done in the presence of potassium halide solution vapour at 600 °C. Fig. 2 (c) is the surface morphology of the oxide. Formation of elongated structure is obvious; indicating the success in the use of potassium halide vapour to aid in nanowires formation but the diameter is rather big. Oxidation temperature was then reduced to 500 °C and as evidence in Fig. 2 (d) the surface oxide is consisted of much smaller whiskers with diameters ranging from 20 – 60 nm. This indicates the success in the formation of nanowires on tungsten at low temperature provided vapour of potassium halide was injected during oxidation process. Note that all oxidation processes were done in one step (i.e. direct heating process) at < 2 h and hence the rate of formation of these nanowires can be considered rather high with less complex process compares to reported works in literature [8]. The formation mechanism of nanowires on tungsten is different than that of nanowires on copper, iron or titanium. It is speculated here that the vapour-solid-liquid process is responsible on the formation of the nanowires with potassium halide acting like crystal droplets at 500 – 600 °C [8]. Nonetheless, the use of potassium halide complicates the formation process. Moreover, the adherence of the oxide to the foil was found to be rather poor making it not suitable to be used as photocatalysts.

XRD patterns for oxidised Ti and Fe are shown in Fig. 3 (a) and (b) respectively. The XRD patterns reveal the presence of mostly rutile TiO$_2$ on Ti agreeing with previous works on oxidation of titanium [9] whereas on iron peaks from hematite (H), $\alpha$-Fe$_2$O$_3$ are detected along with magnetite (M), Fe$_3$O$_4$ peaks. Similar findings have been reported by [4-6].

![XRD Analysis](image_url)

**Figure 3.** XRD analysis of (a) $\alpha$-Fe$_2$O$_3$ (hematite (H)) and Fe$_3$O$_4$ (maghemite (M)) nanowires and rutile (R) TiO$_2$ nanowires formed by thermal oxidation. Unmarked peaks are from the parent substrate.

Cr(VI) removal experiments were then done on these two samples: rutile TiO$_2$ and hematite $\alpha$-Fe$_2$O$_3$ nanowires under morning sunlight as mentioned. Photocatalytic reduction is proposed to be one of the main mechanisms in Cr(VI) removal whereby excited electrons can be transferred to the adsorbed Cr(VI) ions on the nanowires. It is apparent from the plot in Fig. 4 that removal on (b) hematite is much more (~ 90 % removal) compared to on (a) rutile nanowires (~ 40 % removal) after an hour of exposure to sunlight. This is obvious since hematite has narrower band gap (2.5 eV) than rutile and hence photoelectrons generation are thought to be much more compared to rutile. TiO$_2$ is a wide gap semiconductor with energy gap of ~ 3.1 eV and can only be excited under the UV part of the solar spectrum.
Figure 4. Cr(VI) reduction (%) on (a) TiO$_2$ nanowires and (b) α-Fe$_2$O$_3$ nanowires under sunlight

4. Conclusion

Growth of nanowires was observed on the surfaces of iron and copper in dry air but not on titanium and tungsten at 500 or 600 °C. Nanowires can however be formed on titanium when the furnace was injected with water vapour and on tungsten, potassium halide vapour was needed for nanowires formation. Nevertheless, the growth mechanism of the nanowires on tungsten is thought to be very much different than iron, copper and titanium whereby on tungsten catalytic induced reaction is likely. On iron, copper and titanium, stressed induced mechanism and surface diffusion via dislocation core are the main mechanism of formation. Majority of oxide nanowires on iron are α-Fe$_2$O$_3$ whereas on titanium, rutile TiO$_2$ was the dominant phase. As both of the oxides are semiconductors, electron-hole pairs are expected to be formed when the oxides were irradiated under sunlight. Photoelectrons were used to reduce Cr(VI) with 90 % Cr(VI) reduction after an hour of exposure on α-Fe$_2$O$_3$ compared to on 40 % removal on TiO$_2$ nanowires.

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