Fabrication and Characterization of Chromium Nanotube Using (AAO) Template

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Abstract

In the current research, the fabricating of Cr nanotubes was done by electrochemical deposition in anodic aluminum oxide (AAO) as template. Characterization of fabricated Cr nanotubes were a achieved by XRD, SEM/EDS and TEM. These techniques indicated that the deposited chromium nanotubes have high purity within experimental conditions, the peaks in XRD was good agreement with JCPDS cards, SEM images showed the growth of ordered nanotubes in one plane perpendicular to the template (AAO). The purity of fabricating nanotubes was confirmed by EDS analysis, while the produced single walled nanotubes was shown from TEM images with open ends of tubes. 60 nm as diameter was obtained for fabricating Cr nanotubes.

The fabrication of Cr nanotubes suggests producing quintuple bonds (Cr ≡ Cr) to form tubes without any chance to deposit chromium as particles.

Keywords: Chromium; Nanotube; AAO; Electrodeposition.

الخلاصة

في البحث الحالي تم تصنيع Cr Nanotube بعملية الترسيب الكهروكيميائي وذلك بترسيبها على أساس من الألمنيوم المؤنود AAO كذلك تم تشخيص الأنابيب الكروم النانوية بواسطة XRD, SEM/EDS and TEM . وقد تبين من خلال هذه التقنيات إن الأنابيب الكروم النانوية كانت تمتلك نقاوة عالية جدا ، ومن خلال تقنية SEM لوحظ نمو منتظم للأنابيب النانوية على مستوى عمودي للـــ AAO. وكذلك يتضح ذلك من خلال تقنية TEM والتي يظهر فيها الأنابيب ذات جدار منفرد single wall بقطر مقارب إلى 60nm.

كلمات مفتاحية : كروم ، نانوتيوب ، AAO ، ترسيب كهروكيميائي .

Introduction

Nanotubes are the one – dimensional nanostructured materials like nanowires and nanorodes. Materials in the nanometer scale may exhibit physical properties distinctively different from that of bulk . For example, crystals in the nanometer scale have a remarkable low melting point. Crystal structures stable at elevated temperatures are stable at much lower temperatures in nanometer sizes, so ferroelectrics and ferromagnetics may lose their ferroelectricity and ferromagnetism when the materials are shrunk to the nanometer scale. Bulk semiconductors become insulators transferred to nano scales (Fabio , 2013).

Some of properties may be included *Chemical properties* that take advantage of large surface to volume ratio for catalysis, this ratio is important in many applications; *Mechanical properties* involve improved strength hardness in light-weight nanocomposites and nonmaterials, compression properties, nanomechanics of molecular structures. Also *Optical properties* that involve absorption and fluorescence of nanocrystals, single photon phenomena, photonic bandgap engineering and *Fluidic properties* give rise to enhance flow using nanooparations, nanoscale adsorbed films. *Thermal properties* give increased thermoelectronic performance of nanoscale materials and interfacial thermal resistance that also important (Kirk-Othmer, 2012).

One dimension structures with nanometer diameters have great potential for testing and understanding fundamental concepts about the roles of dimensionality and size on physical properties (Basal, 1997 ; Guozhong Cao, 2004) .

The researches mostly were focused on carbon and TiO_2 nanotube in addition to little studies about other nanotubes. These researches highlighted on characterization and study some properties of fabricated nanotubes, in addition to studies about incorporation between Titania and Carbon nanotubes for various applications.

In the present work, chromium nanotubes were fabricated for first time by deposition in fabricating AAO at certain conditions.

A large number of chromium (III) compounds are known and chromium minerals as pigments came to the attention in the 18^{th} century. Chromium compound determined experimentally to contain a Cr-Cr quintuple bond. Trivalent chromium (Cr^{3+}) was identified as an essential nutrient in the late 1950s and later accepted as a trace element for its roles in the action of insulin, a hormone critical to the metabolism and storage of carbohydrate, fat and protein. The precise mechanism of its actions in the body, however, has not been fully defined, leaving in question whether chromium is essential for healthy people. Also (Cr^{3+}) occurs in trace amounts in foods, wine and water, in contrast, hexavalent chromium (Cr^{6+}) is highly toxic and mutagenic when inhaled.

Ingestion of chromium (VI) in water has been linked to stomach tumors, and it may also cause allergic contact dermatitis (ACD). Chromium deficiency, involving a lack of Cr (III) in the body, or perhaps some complex of it, such as glucose tolerance factor is controversial. Some studies suggest that the biologically active form of chromium (III) in an oligopeptide called low-molecular-weight chromium-binding substance, which might play a role in the insulin signaling pathway.

Chromium content of common foods is generally low (1-13 micrograms per serving). Chromium content of food varies widely due to differences in soil mineral content, growing season, plant cultivar, and contamination during processing.

In addition, large amounts of chromium (and nickel) leach into food cooked in stainless steel. Because chromium compounds were used in dyes, paints, and tanning compounds, these compounds are often found in soil and groundwater at abandoned industrial sites.

Now needing environmental cleanup and remediation. Primer paint containing hexavalent chromium is still widely used for aerospace and automobile refinishing applications.

Materials and Chemicals

Preparation of AAO Template

Aluminum sheet with thickness (0.5mm) was cut to circle shapes with (20mm) diameter to prepare anodic aluminum oxide template for depositing the nanotubes. Cleaning with acetone has been done for Al specimens and to get more active Al surface, the Al specimens were treated with 3M NaOH and then electrochemically polished also done.

Oxalic acid with concentration 0.3 M was prepared in distilled water to use it as electrolyte for anodization . The anodization was achieved in two steps, in the first; the Al specimen was connected to the positive terminal of power supply to act as anode and stainless steel 316L as rod was used as cathode in electrochemical cell with applying 30V. The period time of first anodization was 8 hrs. at room temperature and then the specimen was treated with (H_3PO_4+$H_2Cr_2O_4$) mixture to open the pores for 1 hr at 60^{o}C.

The second anodization was achieved in the same electrolyte for 6hrs and then the specimens were wished with deionized water and ethanol. The immersion in acetone at 60^{o}C for 1 h was performed to remove the remained alumina (Spicia, 1987 ; Spicia, 1986) .

Deposition of Cr Nanotube

Chromium sulfate [$Cr_2(SO_4)_3$] 0.5 M in boric acid 30 g/L was used as electrolyte to deposit the Cr nanotube. The AAO template was act as cathode in electrochemical cell with Cr rode acts as anode. The voltage of deposition was 10 V for 15 min.

Characterization of Nanowires

XRD technique was used to characterize the Al sheet, prepared AAO and fabricated nanotube with Cu as target at scan rate 40.0 (kV) and current= 30.0 (mA).

Scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS) and Transition electron microscopy (TEM) also used for characterization of fabricated nanotubes. These inspections were achieved for partial and complete removal of template after deposition of nanotubes. The partial dissolving of AAO was performed by 10% HCl and ethanol, while complete dissolving was by 6 M KOH solution.

Atomic force microscopy (Veeco dinnova model) was used to observe the sample's surface in tapping mode, using cantilever with linear tips. The scanning area in the images was 5 μm × 5 μm and the scan rate was 0.6 HZ /second.

Results and Discussion

XRD analysis of pure Al and anodized Al was shown in Fig. (1). This figure shows the XRD pattern of Al as substrate to prepare anodic aluminum oxide (AAO) as template which further used to deposit Cr nanotubes. XRD pattern of Al is a good agreement with JCPDS card No. (04-0787) at 2θ=38.473º (111), 44.739º (200) and 65.135º (220), while the XRD pattern of prepared AAO is a good agreement with JCPDS card No. (46-1215) at 2θ=45.716º (400) and 67.197º (046) and the intensive peaks confirm the formation of γ-Al_2O_3.

XRD of fabricated Cr nanotubes is shown in Fig. (2), which indicates the most intensive peaks at 2θ=44.4189º (110) and 2θ=64.5960º (200) which agreement with JCPDS card No. (06-0694). Fig. (3) shows the SEM of Cr nanotubes. In Fig. (3-a), can be seen the top view of fabricated Cr nanotubes within AAO template, this image also shows the tubular and uniform morphology of nanotubes with narrow size and regular distribution. Also, highly oriented tubes are obtained under optimized conditions as represented in this figure with no defects in fabricating nanotubes. This is orientation can candidate Cr nanotubes for applications like electric field emission devices. In Fig. (3-b), the nanotubes after completely dissolving of AAO template can be seen in addition to confirming the presence of nanotubes not nanowires or nanorodes. The inner and outer diameter is very clear in this image.

EDS analysis confirm the purity of fabricated Cr nanotubes by getting 100 wt% as illustrated in Fig. (4). For deeper information on obtaining nanotubes, TEM analysis of the nanotubes have been done as shown in Fig. (5). This analysis indicates that these tubes were hollow with an open end having needle shape structures with diameter equal to 60nm. These images also, show that Cr nanotubes are uniform, single walled and are up to several hundred nm in length. No chromium nanoparticles exist around the nanotubes, proving high conversion of nanoparticles into nanotubes under applied experimental conditions.

The chromium sulfate dissociates in solution as follow:

$$Cr_2(SO_4)_3 \rightarrow Cr^{3+} + SO_4^{=}$$

At anode, chromium rode also dissolves as follow:

$$Cr \rightarrow Cr^{3+} + 3e$$

While at cathode (AAO), chromium ions reduce to form chromium nanotubes within the experimental conditions. Chromium (III) is the most stable and most important oxidation state of the element. The chemistry of Cr^{3+} in aqueous solutions is coordination chemistry. It is demonstrated by the formation of kinetically inert outer orbital octahedral complexes. Cr^{3+} is characterized by a marked tendency to form polynuclear complexes. Literally thousands of Cr^{3+} complexes have been isolated and characterized and, with a few exceptions, are all hexacoordinate (Spicia, 1986). This is assisted to fabricate nanotubes as in carbon nanotubes.

The hexaaqua ion $[Cr(H_2O)_6]^{3+}$ is a regular octahedral, and the hydroxo ion condenses to give dimeric hydroxo bridged species. On further addition of base, a precipitate is formed that consists of H-bonded layers of $Cr(OH)_3(H_2O)_3$, which readily redissolves in acid. Within 1 min, this precipitate begins ‘‘aging’’ to an oligomeric or polymeric structure that is much less soluble (Mohammad, 2003 ; Waqar, 2009). This property candidates replacing carbon nanotubes by Cr nanotubes for some applications because of difficulty of functionality of carbon nanotubes. On the other hand, chromium has an ability to form quintuple bond. Quadruple bonds are rarer but are currently known only among the transition metals, especially for Cr, Mo, W, and Re as illustrated in Fig. (6). This is may help chromium to produce nanotubes.

Conclusion

Chromium nanotubes were fabricated by simple deposition in (chromium sulphate + boric acid) electrolyte on electrochemical cell acting chromium as anode and anodic aluminum oxide as cathode. The characterization showed that Cr nanotubes were deposited in a perfect and regular orientation with high purity to get single wall nanotubes with diameters of 60 nm.

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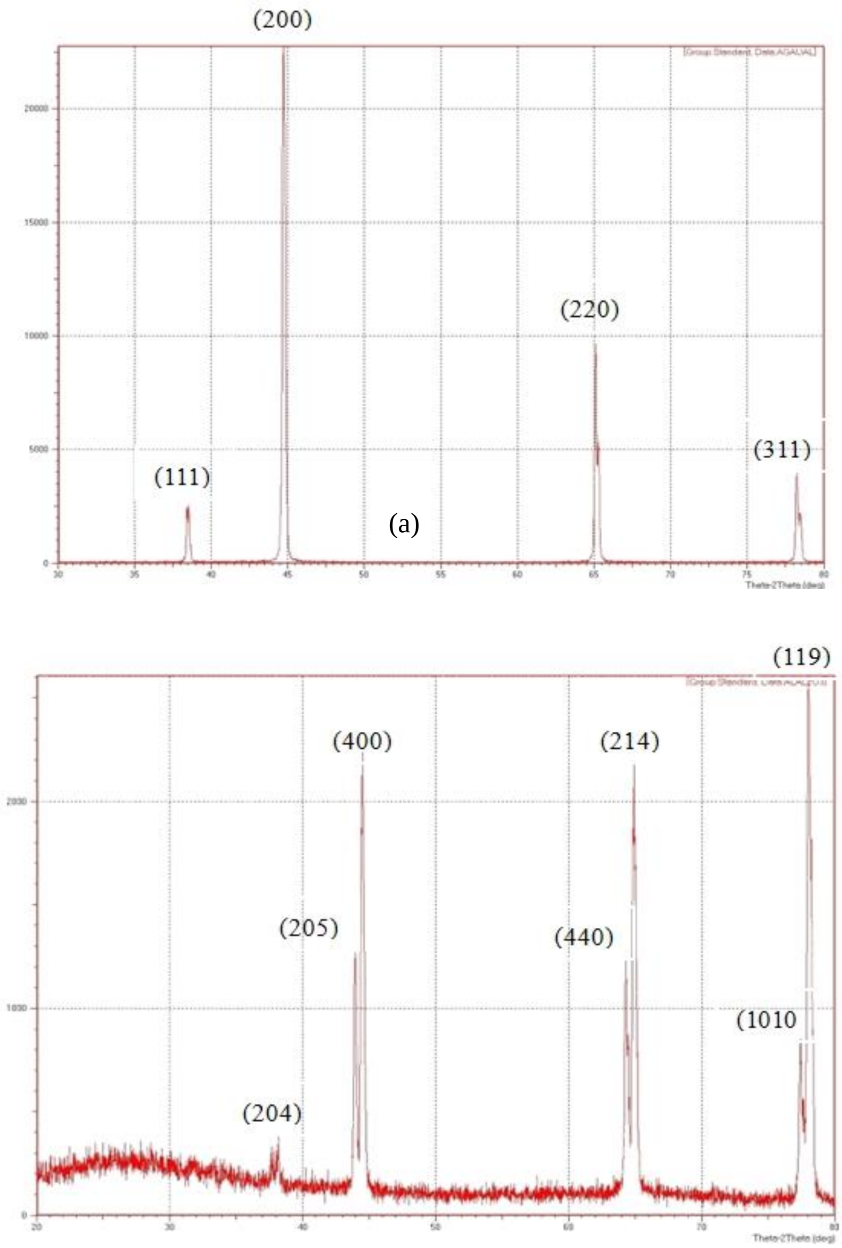
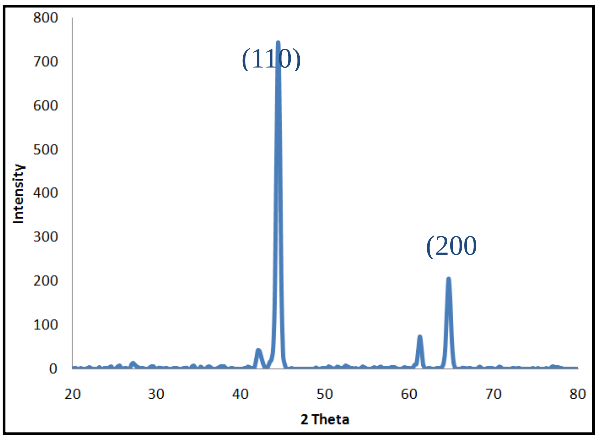


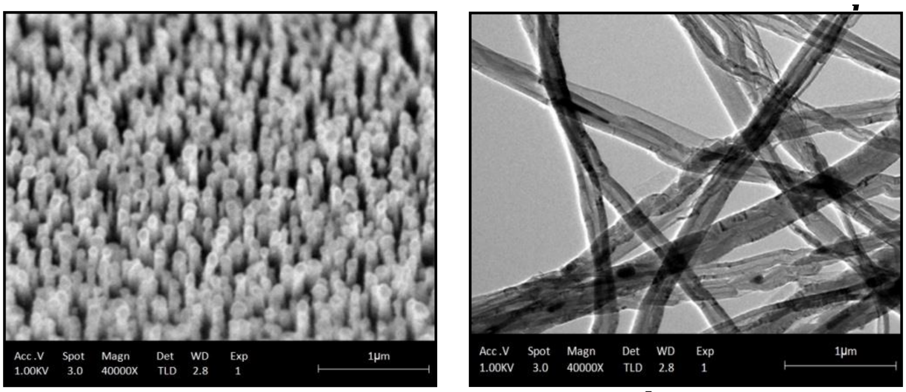
(b)

Fig. (1) XRD pattern of used Aluminum (a) and prepared AAO (b).



	2 Theta		*Intensity*	
	Standard	***Measured***	***Standard***	***Measured***
1	44.392	44.4189	100	100
2	64.581	64.5960	16	28

Fig. (2) XRD of fabricated Cr nanotubes.



a **b**

Fig. (3) SEM images for Cr nanotubes; (a) Top view within AAO and (b) Nanotube after dissolving AAO.

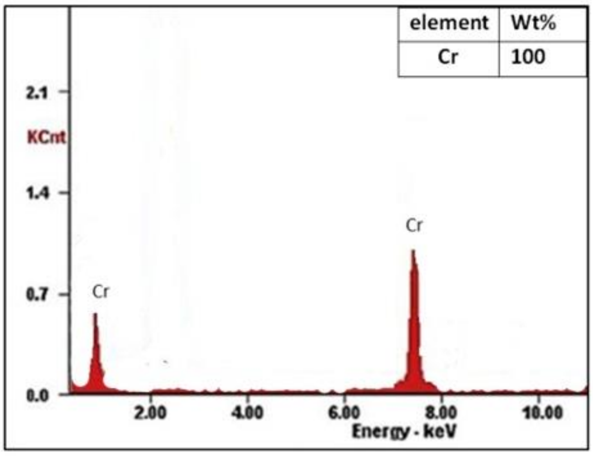
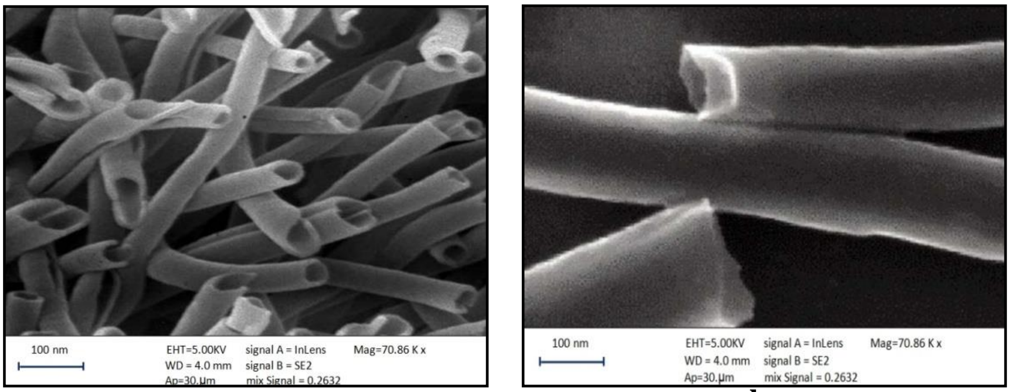


Fig. (4) EDS analysis of Cr nanotubes.



a b

Fig. (5) TEM images of fabricated Cr nanotubes.

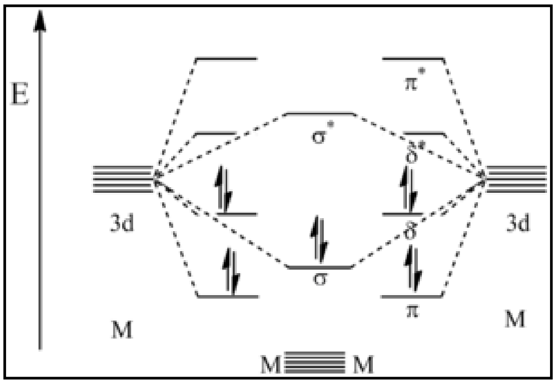


Fig. (6) Energy levels to produce metal–metal quadruple bonds.