

# Optical properties of calcium chromate 1D-nanorods synthesized at low temperature from secondary resources



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## ABSTRACT

Calcium chromate 1D-nanorods have been synthesized from tannery waste solution. The solution was filtered to get rid of insoluble matters followed by addition of ammonia to precipitate calcium and chromium as hydroxide gel. The gel was heated within the temperature range 300–600 °C. At 300 °C amorphous phase of calcium chromate was formed. At 400 °C compounds of CaCrO<sub>4</sub>, Cr<sub>2</sub>O<sub>3</sub>, CaCO<sub>3</sub> and minor amount of Mg<sub>2</sub>CO<sub>3</sub>(OH)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub> (Artinite) were detected. At 500 °C, CaCrO<sub>4</sub> compound was the major product together with traces of Cr<sub>2</sub>O<sub>3</sub>, CaCO<sub>3</sub> and MgO. At 600 °C, a crystalline compound of CaCrO<sub>4</sub> was formed. Nanorods of calcium chromate structured during heating associated with the crystal growth. Properties of heated products are evaluated with the help of XRD, TEM and FT-IR measurements. Optical properties of the obtained calcium chromate were estimated. A thermodynamic model of the involved reactions is suggested to explore the findings.

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## 1. Introduction

Calcium chromate (CaCrO<sub>4</sub>) of zircon structure is one of the ABO<sub>4</sub>-type ternary metal oxides (where A and B are two different metallic elements with oxidation states of +2 and +6, respectively). Among these oxides ternary metal chromate oxides have vast utility and are technically important materials for various applications such as photoluminescence [1], scintillation [2], photosensitization [3], Raman scattering behavior [4], catalysis [5], photoconductive dielectric materials, humidity sensing resistors, yellow pigments, effective solid lubricants and in industrial wastewater treatment [6–10]. Calcium chromate CaCrO<sub>4</sub> has long been used as a cathode material in thermally activated electrochemical cells [11]. It has also been used as an intermediate compound involved in many industrial processes [12,13].

Calcium and chromium elements are available in some secondary resources such as a wastewater of the tanning industry. This industry generates about 600,000 t of solid waste each year worldwide. Such large amounts of solid waste may require land filling [14]. Alternatively separation of chromium from the waste resources can help to be recycled back to the tanning process [15,16]. Such process recovered a voluminous chromium containing-sludge that can be filtered to “chrome cake”.

Chromates compounds have been synthesized using different routes like reverse micellar [17], hydrothermal [18,19] and micro-

emulsion [20]. Additionally, polycrystalline CaCrO<sub>4</sub> were synthesized by the conventional solid-state method [21–23], from CaO and Cr<sub>2</sub>O<sub>3</sub> in 2:1 mol ratio. The mixture was homogenized and heated in MgO crucible at 850 °C under air for 30 days to prepare CaCrO<sub>4</sub> [24]. Calcium chromate, CaCrO<sub>4</sub> is also, prepared by precipitation from an aqueous solution of CaCl<sub>2</sub> and chromic acid in a slightly alkaline medium (pH 8.0) [24].

To date, there have been a few reports on the preparation of calcium chromate [20–24], but no efforts were put to synthesize CaCrO<sub>4</sub> nanorods, and to investigate their related optical properties. The aim of this work is to prepare calcium chromate nanorods from wastewater left after tanning industry and to study its optical properties. The parameters affecting the nanorods preparation such as pH, temperature and time have been considered. A thermodynamic model of the involved reactions was suggested to explain the findings. Characterization of the prepared calcium chromate was carried out using XRD, SEM, FT-IR and transmission electron microscope TEM investigation. The optical properties of CaCrO<sub>4</sub> nanorods were also studied using photoluminescence (PL).

## 2. Experimental

### 2.1. Materials and procedure

About 2 m<sup>3</sup> of an industrial waste tannery solution was obtained from local industrial tannery plant. It was filtered and stored in PVC containers. Chemicals were analytical grade. Ammonium chloride

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(99.7%, RPS Chemical Co. Ltd., UK), ammonium hydroxide (25%, ADWIC, Egypt), was used for pH adjustment. Bi-distilled water was used for chemical analysis and washing process.

Filtration of the waste solution was carried out using a cloth silk screen Nr. 1000, Switzerland. The solids left over the filter were discarded. A sample of the filtered waste solution was dried in a laboratory oven maintained at 85 °C. Dried solids were ground (~15 g) and examined with XRF in order to investigate the chemistry of the samples. Co-precipitation of chromium, calcium and magnesium as hydroxide gel from the filtrate was carried out by the addition of ammonia solution in the presence of ammonium chloride as a buffering salt. Addition of ammonia was carried out dropwise to attain a pH value of 8.5 compared to 3.3 of the as received waste solution. The dried precipitate was washed with hot water several times to get rid of sodium chloride and then dried again at 105 °C. The dried precipitate was heated at different temperatures in the range 300–600 °C, using clean porcelain crucible in ambient conditions. Heating was performed using a muffle furnace type Netbertherm, Netherland, equipped with an automatic temperature controller. The temperature increased at a rate of 0.5 °C/min starting from room temperature.

The filtered water after the separation of the calcium and chromium gel contains sodium chloride having a concentration of 75 g/l, can be recycled in the tanning industry. Pure water can be obtained from the saline applying any of the desalination methods.

Fig. 1 shows a schematic diagram of the synthesis method followed in this research to prepare calcium chromate from tannery waste solution.

## 2.2. Characterization of the intermediate and end products

Phase identification, purity and crystallite size of the synthesized compounds and byproducts were carried out at room temperature using X-ray diffraction (XRD) examination, Bruker axs D8, Germany with Cu K $\alpha$  ( $\lambda = 1.5406 \text{ \AA}$ ) radiation and secondary mono-chromator  $2\theta$  in the range of 20–80°. Relative crystallite size was estimated utilizing the strongest peak with highest displayed in the XRD pattern. Transmission electron microscopy (TEM, JEOL-JEM-1230, Japan) was used to observe the microstructure of the produced chromium oxide samples. Infrared absorption spectroscopy (IR) was carried out by JASCO 3600 spectrophotometer. Axios, Sequential WD-XRF, Panalytical 2005 (Netherlands) was used to analyze the chemistry of the prepared powders and obtained quantitative information about the metallic impurities. Photoluminescence (PL) spectra investigation using a Shimadzu RF-5301PC fluorescence spectrophotometer (Shimadzu, Kyoto, Japan) with 50 W xenon lamp was conducted at room temperature. The weight changes of the sample(s) during heating were examined by thermogravimetric (TGA) and differential thermo-gravimetric (DTA) analysis.

## 3. Results and discussion

### 3.1. XRF and gel formation

Chemical analysis of the solid samples in the tannery waste solution using XRF is shown in Table 1. The results revealed the presence of sodium chloride, magnesium sulfate, chromium sulfate and basic calcium hydroxide. The weight percentage of these compounds decrease in the same order; (74.95%, 9.82%, 9.0% and 3.697% respectively). Other metals are impurities. Measurement of pH value shows that the waste solution is slightly acidic (3.3). Fig. 2 shows the effect of pH value on the precipitation of such heavy metals as a hydroxide gel. During the precipitation process, increasing the pH from the starting value 3.3–8.5 exhibited no sig-

nificant precipitation up to pH value of 5.5. With higher pH value at 6–8.5, precipitation of chromium hydroxide and calcium magnesium hydroxide gel takes place as an amorphous phase. Chromium hydroxide precipitates more readily as compared to calcium magnesium hydroxide.

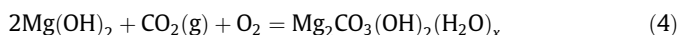
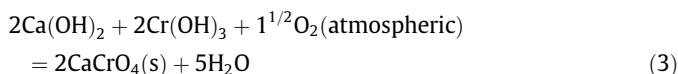
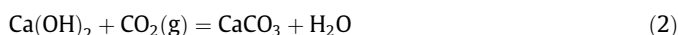
### 3.2. Effect of heating the hydroxide gel up to 600 °C

The dried gel was heated at temperatures up to 600 °C. During heating, chemical reactions took place, according to the following model. Trivalent chromium ( $\text{Cr}^{+3}$ ) hydroxide trihydrate  $\text{Cr}(\text{OH})_3$  decomposed at 154 °C to divalent chromium hydroxide  $\text{Cr}(\text{OH})_2$  associating water loss:



At 300 °C  $\text{Cr}^{2+}$  and  $\text{Ca}^{2+}$  ions in the hydroxide react to form a primary oxide system ( $\text{Cr}_2\text{O}_{3+x} + \text{CaO}$ ). The latter oxide system reacted at 400 °C to form  $\text{CaCrO}_4$  with  $\text{Cr}^{+6}$  atom. At the main time, collagen contaminant in the waste chars to carbon and carbon dioxide gas. Magnesium and calcium hydroxides react with carbon dioxide forming calcium carbonate and magnesium bicarbonate (Artinite), respectively as shown in the following equations.

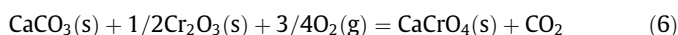
At 400 °C



At 500 °C, the following processes take pl

- Formation and growth of  $\text{CaCrO}_4$  nanorods
- The primary oxide system ( $\text{Cr}_2\text{O}_{3+x} + \text{CaO}$ ) reacts to form chromium hexavalent ( $\text{CaCrO}_4$ ).
- Magnesium carbonate decomposes to magnesium oxide.

At 600 °C, the products of the reaction (2) ( $\text{CaCO}_3$ ) and reaction (5) ( $\text{Cr}_2\text{O}_3$ ) react to yield  $\text{CaCrO}_4$ . This is confirmed from completely disappearance of  $\text{CaCO}_3$  and  $\text{Cr}_2\text{O}_3$  in the XRD chart. Kinetically, formation of  $\text{CaCrO}_4$  compound is a first order temperature-dependent reaction.



### 3.3. XRD of calcium chromate

Fig. 3 shows the XRD patterns of calcium chromate 1D-nanorods synthesized by heating the primary ( $\text{Cr}_2\text{O}_{3+x} + \text{CaO}$ ) at a temperature range (400–600 °C) for 3 h. Results are exhibited as multiple plots. It is seen that the precipitated hydroxide gel at pH 8.5 and heated at 300 °C has an amorphous phase. The pattern of the powder sample heated at 400 °C shows different significant sharp XRD peaks. It consists of two different phases of chromium oxide. One is  $\text{CaCrO}_4$  with a tetragonal zircon-type structure ( $I41/amd$ ) (JCPDS card No. 87-1647) and the other phase is  $\text{Cr}_2\text{O}_3$  (JCPDS card No. 76-0147). In addition, calcium carbonate (calcite) (JCPDS card No. 05-0586) and  $\text{Mg}_2\text{CO}_3(\text{OH})_2(\text{H}_2\text{O})_3$  (Artinite) (JCPDS card No. 73-2088) are also formed [25]. With further increase of heating temperature up to 500 °C, the stable crystalline  $\text{CaCrO}_4$  is formed. In addition, chromium oxide and calcium carbonate are slightly present. MgO (JCPDS card No. 77-2364) [25]

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