



# Synthesis, structural and optical properties of Eskolaite nanoparticles derived from Cr doped polyanthranilic acid (CrPANA)



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## ABSTRACT

Cr doped polyanthranilic acid (Cr PANA) has been used as a molecular precursor of Cr<sub>2</sub>O<sub>3</sub> nanoparticles. Potassium dichromate acted as an oxidant and a dopant in Cr PANA synthesis. The spectral, optical and thermal properties of the precursor have been described. Thermogravimetric Analysis (TGA) and differential scanning calorimetric (DSC) were used to clarify the thermal stability of Cr PANA. The optical band gap ( $E_g$ ) measurements indicated that Cr PANA has wider optical band than the pure PANA. Calcination of Cr PANA at 600 °C produced Eskolaite (Cr<sub>2</sub>O<sub>3</sub>) nanoparticles. The obtained nanoparticles have been characterized by XRD and TEM. The average size of the nanoparticles was found to be 70 nm. The measured optical band gap of Eskolaite nanoparticles is 0.35 eV wider than the bulk.

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## 1. Introduction

The use of coordination compounds as molecular precursors in metal oxide nanoparticles synthesis is an important synthetic route [1–3]. Among the categories of coordination compounds are the doped polymers. There are several advantages in use of doped polymers as precursors in the synthesis of metal oxide nanoparticles as, the high purity, homogeneity of the morphology, the relatively low temperature used in processing, the environmental friendliness of the method and the applicability on commercial scale [4–7]. The common trend in nano-composite synthesis is the addition of inorganic compounds to the polymer [4]. Recently, synthesis of metal oxides [8–14], selenides [15] and sulfides [16,17] nanoparticles from the doped polymers as molecular precursors has attracted much more attention. Many of these previous reports indicated the relation between both the particle size and the shape of the synthesized nanoparticles with that of the molecular precursor used [18].

Chromium oxide (Cr<sub>2</sub>O<sub>3</sub>) is a hard oxide, with high corrosion resistance, low friction and good optical properties. These characteristic properties enable Cr<sub>2</sub>O<sub>3</sub> to be a good protective coating in microelectronic and tribological applications. It has also, important applications in space fields [19–22].

In the present work, CrPANA has been used as a precursor of Cr<sub>2</sub>O<sub>3</sub> nanoparticles. The precursor and the synthesized Cr<sub>2</sub>O<sub>3</sub> nanoparticles have been characterized by different techniques. The optical band gap of Cr<sub>2</sub>O<sub>3</sub> nanoparticles was measured to clarify its optical properties.

The present work has several advantages as it provides the synthesis of Cr<sub>2</sub>O<sub>3</sub> nanoparticles by simple green chemistry method from cheap available chemicals. The synthesized Cr<sub>2</sub>O<sub>3</sub> nanoparticles have wider optical band gap than the bulk. This wide band gap makes Cr<sub>2</sub>O<sub>3</sub> nanoparticles applicable in optoelectronic devices.

## 2. Experimental

The chemicals used were of analytical grade and were used without further purification. Anthranilic acid (≥98%) and potassium dichromate (≥99%) were purchased from (Sigma-Aldrich). IR spectra were carried out on a Mattson 5000 FTIR Spectrometer equipped with fast recovery deuterated triglycine sulfate (DTGS) detector, the resolution is 4 cm<sup>-1</sup> and the scan no is 32 scan. The

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samples were carried out in the form of KBr discs. Thermal analyses (TGA) and differential scanning calorimetric (DSC) were carried out on a Shimadzu model 50 instrument, with nitrogen flow rate  $20 \text{ cm}^3/\text{min}$  and heating rate  $10 \text{ }^\circ\text{C}/\text{min}$ . The sample weight is 20 mg sample. The electronic spectra were measured on a UV2 Unicam UV/Vis. Spectrometer with 1 cm silica cell by using DMF as solvent. Philips XPERT-PRO device with nickel filtered Cu  $K\alpha$  ( $\lambda = 1.5405 \text{ \AA}$ ) radiation was used to record XRD pattern. Electron microscopes of the type CM 20 PHILIPS was used to take TEM images.

### 2.1. Preparation of PANA by ammonium persulphate oxidation

Anthranilic acid (0.014 mol) was dissolved in 5 mL concentrated HCl (diluted by 30 mL distilled water) by stirring the solution. 3.99 g (0.017 mol) of ammonium persulphate dissolved in 20 mL distilled water was added dropwise to the anthranilic acid solution. The mixture was kept overnight at room temperature, and then 12 mL (33%)  $\text{NH}_4\text{OH}$  diluted with 12 mL distilled water was added till pH 10. The resulting polymer was filtered off, washed with distilled water, and then dried at  $40 \text{ }^\circ\text{C}$  [23].

FTIR (KBr;  $\text{cm}^{-1}$ ): 3438 (O–H), 1682 (COO), 1566 (C=C), 1500 (C=N), 1239 (C–N), 1084 ( $\delta(\text{OH})$ ).

### 2.2. Synthesis of the precursor Cr PANA

Cr PANA was synthesized by mixing 0.014 mol (2.0 g) of anthranilic acid in 5 mL concentrated HCl (diluted with 30 mL distilled water) with 4.29 g (0.014 mol) of potassium dichromate in 60 mL distilled water. The reaction mixture was allowed to stand for 24 h at room temperature. Ammonia solution (33%) was added until precipitation is formed. The formed polymer was isolated by filtration, washed with distilled water and dried at  $40 \text{ }^\circ\text{C}$ .

Anal. Calc. for  $[\text{Cr}(\text{C}_4\text{H}_4\text{NO}_2)\text{Cl}_3 \cdot 4\text{H}_2\text{O}]$  according to monomeric unite: C, 23.0; H, 3.3; Cr, 14.2. Found: C, 22.5; H, 3.7; Cr, 14.50%. FTIR (KBr;  $\text{cm}^{-1}$ ): 3424 (O–H), 1614 (COO), 1566 (C=C), 1512 (C=N), 1246 (C–N), 1070 ( $\delta(\text{OH})$ ).

### 2.3. Synthesis of $\text{Cr}_2\text{O}_3$ nanoparticles

1 g of Cr doped (PANA) precursor was calcined in a muffle furnace at  $600 \text{ }^\circ\text{C}$  for 2 h in air.  $\text{Cr}_2\text{O}_3$  nanoparticles were resulted.

## 3. Results and discussion

Potassium dichromate oxidizes the monomer of anthranilic acid forming polyanthranilic acid (PANA) and Cr(III) ion. When polyanthranilic acid is kept in contact with Cr(III) ion, it coordinates to it forming Cr PANA. The doped polymer was calcined at  $600 \text{ }^\circ\text{C}$  to produce  $\text{Cr}_2\text{O}_3$  nanoparticles.

### 3.1. IR spectra

Table 1 contains some important IR bands of PANA and Cr PANA and the spectra are represented in Fig. 1. From the spectrum of PANA, a band is observed at  $1682 \text{ cm}^{-1}$  due to  $\nu_{\text{as}} \text{COO}^-$ . The bands at 1566 and  $1500 \text{ cm}^{-1}$  are characteristic to  $\nu \text{C}=\text{C}$  and  $\nu \text{C}=\text{N}$

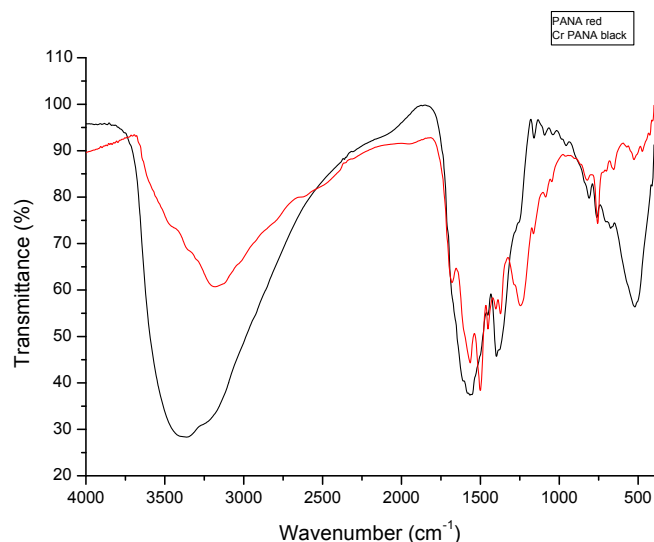


Fig. 1. IR spectra of PANA and Cr doped PANA.

vibrations of benzoid and quinoid rings, respectively. Two bands at 1239 and  $1170 \text{ cm}^{-1}$  belong to  $\nu \text{C}-\text{N}$  of the quinoid and benzoid rings, respectively [24–28]. The bands at 3431, 3208 and  $3170 \text{ cm}^{-1}$  were attributed to  $\nu \text{OH}$ ,  $\nu \text{NH}$  and  $\nu \text{CH}$ , respectively. The spectrum exhibits a band at  $759 \text{ cm}^{-1}$  due to  $\nu \text{C}-\text{C}$  and  $\nu \text{C}-\text{H}$  stretching of the benzoid moiety. The bands  $\gamma \text{COOH}$  and  $\rho \text{COOH}$  vibrations were observed at 650 and  $515 \text{ cm}^{-1}$ , respectively. The above mentioned bands confirm that the compound formed is PANA (Fig. 2). Doping of chromium ion into the (PANA) matrix led to deformation in the electron density of some active sites of the pure PANA. This deformation appears in the form of shifts in the coordinated group bands. The comparison of Cr PANA spectrum with that of pure PANA shows that the band at  $1500 \text{ cm}^{-1}$  due to  $\nu \text{C}=\text{N}$  in the spectrum of pure PANA was reduced in intensity and turned to a shoulder, shifted to  $1512 \text{ cm}^{-1}$  in the spectrum of Cr PANA. The shift resulted from the coordination of the polymer orbits with that of the chromium ion. This shift supports that the azomethine group takes part in coordination to Cr ion. The bands at 3438 and  $1084 \text{ cm}^{-1}$  due to  $\nu \text{OH}$  and  $\delta \text{OH}$ , respectively in the spectrum of PANA was shifted in the spectrum of Cr PANA to 3424 and  $1070 \text{ cm}^{-1}$ , respectively. This shift suggests the participation of COOH group in bonding without the displacement of hydrogen ion. The bands of the  $\text{COO}^-$  group was shifted to lower wavenumber ( $1614 \text{ cm}^{-1}$ ) in case of Cr PANA. This shift confirms that the carboxyl group takes

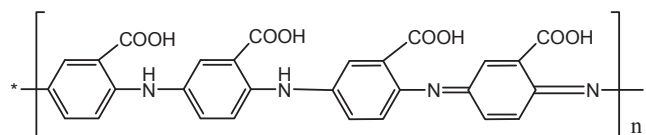


Fig. 2. Suggested structure of PANA.

Table 1  
Some important IR bands of PANA and its doped Cr PANA polymers.

Compound	$\nu \text{OH}$	$\nu \text{NH}$	$\nu_{\text{as}} \text{COOH}$	$\nu \text{C}=\text{C}$	$\nu \text{C}=\text{N}$	$\nu_{\text{s}} \text{COOH}$	$\nu \text{C}-\text{N}$	$\nu \text{M}-\text{N}$
PANA	3438	3208	1682	1566	1500	1402	1239	–
CrPANA	3424	3249	1614	1566	1512	1368	1246	506

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