Single-phase $\alpha$-Cr$_2$O$_3$ nanoparticles’ green synthesis using Callistemon viminalis’ red flower extract

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**ABSTRACT**
This contribution reports for the first time on the synthesis and the main physical properties of single-phase pure $\alpha$-Cr$_2$O$_3$ nanoparticles synthesized by a facile, rapid and eco-friendly process using Callistemon viminalis flower’s extract as an effective oxidizing/reducing agent. These crystalline nanoparticles exhibit a cubic-like platelet shape with sharp edges with an average particle diagonal size of $\sim$92.2 nm. The room temperature physical properties of these pure highly crystalline Eskolaite $\alpha$-Cr$_2$O$_3$ nanoparticles were carried out using complementary techniques such as high-resolution transmission electron microscopy (HRTEM), energy-dispersive X-ray spectroscopy (EDS), XRD, FTIR-ATR, Raman and XPS.

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1. Introduction
The trivalent oxide, Cr$_2$O$_3$, is recognized as a stable oxide in the Cr–O binary system. Other well-known oxides in this system are CrO$_3$ and CrO$_2$ (1). Although many other formulae have been reported as higher oxides in the past few decades, the accepted ones are Cr$_5$O$_8$, Cr$_5$O$_{12}$, Cr$_2$O$_5$ and Cr$_6$O$_{13}$ (2, 3). Except for the purely hexavalent chromium in CrO$_3$ and tetravalent Cr in CrO$_2$, the valencies of chromium in these higher oxides are combinations of Cr$^{3+}$ and Cr$^{6+}$. Of these higher oxides, $\alpha$-Cr$_2$O$_3$ is the most stable and is the oxide of choice. Known to have a wide band gap ($E_g \sim 3.4$ eV), it crystallizes in a corundum-type structure and is antiferromagnetic with a Neel temperature of $T_N$-307 K. Depending on its growth conditions, $\alpha$-Cr$_2$O$_3$ can exhibit n-type or p-type semiconductor behaviour. With one of the highest hardness values for metal oxides in the bulk form, 29 GPa as compared to 12 GPa for zirconia,
it is useful for applications that require high wear resistance. Its optical band gap makes it the green colourant of choice in the pigment industry for ceramics, coatings, paints and printing. Because of its high chemical stability, $\alpha$-Cr$_2$O$_3$-based catalysts are also of importance for the chemical industry in the preparation of several important commodity chemicals and have also been investigated for their potential as Li cathodes (4–10). As a result of its high refractive index, it is also finds use in cerments designed for low and medium temperature-selective solar absorbers (11–16).

Several physical and chemical process methods have therefore been used to prepare $\alpha$-Cr$_2$O$_3$ particularly in its nano-scaled form among which are laser-induced deposition, hydrothermal synthesis, thermal decomposition, microwave-plasma assisted growth, sonochemical synthesis, sol–gel synthesis, hydrothermal synthesis and combustion synthesis (17–20). In the case of nano-scaled $\alpha$-Cr$_2$O$_3$ for functional and colour pigment applications, two mass-scale methods of synthesis have been used which consists of solid state and hydrothermal processes. With a host of these methods, the use of environmentally harmful chemicals is generally needed. To mitigate the problem of adding to the environment toxic and hazardous wastes generated by these processes, greener methods of synthesis are being researched. One such promising method for green synthesis of metal oxide nanoparticles is that of the bio-reduction/oxidation of metal precursor salts using plant-based extracts. This biosynthesis method makes possible rapid synthesis of stabilized metal/metal oxide nanoparticles in a manner that is easy and cost-effective (21–23). While significant work has been reported on the use of plant-based extracts to prepare various metal/metal oxide nanoparticles, not much is reported on the use of these extracts for the green synthesis of Cr$_2$O$_3$ nanoparticles.

Through this contribution, we report for the first time, the use of the dye extract from the red Callistemon as an effective agent for facile and rapid biosynthesis of pure Eskolaite $\alpha$-Cr$_2$O$_3$ cubic-like nanoparticles. The fact that no inorganic/organic solvents or surfactants are used in this method of synthesis makes the process eco-friendly.

2. Experimental and results

2.1. Biosynthesis process via C. viminalis aqueous extract

*C. viminalis* is a plant originally found in Australia. Various phytochemical studies have been carried out on extracts made from different part of these tree species which are the leaves, stem barks, fruits, seeds as well as the flowers. In general, these studies show that the red dye extracts obtained from the red Callistemon flowers are very rich in flavonoids, saponins, steroids, alkaloids and triterpenoids (24). A summary of the isolated active compounds obtained from this red dye extracts can be viewed in Table 1.

For the synthesis, fresh red flowers of *C. viminalis* were collected from around the Western Cape site of iThemba
LABS, South Africa. In a typical set-up, 6.65 g of the bottle-brush-shaped red flowers were heated in 250 ml of de-ionized water at a temperature between 75°C and 85°C for 2–3 h yielding a red-coloured extract of pH = 3.75. To the filtered red aqueous extract obtained after cooling to room temperature, was added to 10.12 g of Cr(NO₃)₃·9H₂O salt. At room temperature, while swirling, the Cr(III) salt was observed to dissolve completely in the aqueous extract under 3 min, bringing about a change in colour of the solution from red to black. The resultant solution was allowed to settle over a period of 1–2 h after which a black-coloured precipitate was observed. The precipitate was then separated from the aqueous extract, first by decanting then by centrifuging at 3500 rpm two to three times over successive additions of de-ionized water – this is to wash the precipitate of any residual aqueous extract. The resultant precipitate obtained after decanting the precipitate/H₂O separation was then dried at 250°C then heated in air at 500°C for 2 h.

2.2. Surface morphology and elemental analysis

Figure 1 reports the high-resolution transmission electron microscopy (HRTEM) micrographs and the corresponding small area electron diffraction (SAED) pattern obtained on the green Cr₉O₅ powder following annealing at 500°C of the initially brownish green precipitate. The HRTEM was carried out using a FEI Tecnai G2 Field Emission Gun HRTEM operating at 200 kV. From this it can be established that generally, yet agglomerated (Figure 1(a)), the nanoparticles are cubic-like platelets with sharp edges with a non-negligible degree of polydispersity (Figure 1(c)). Particle size distribution analysis carried out using Image J software showed an average particle diagonal size to of ∼92.2 nm. Likewise, and in view of the HRTEM (Figure 1(c) and 1(d)) and the SAED patterns (Figure 1(b)), the bulk of the nanoparticles exhibit a significant atomic ordering. An enlargement of Figure 1(c), that is, Figure 1(d) shows the highly ordered atomic reticular planes. The atomic double periodicity within the scale shown in green in Figure 1 is of the order of 9.91 Å corresponding to a lattice periodicity of 4.95 Å, similar to the value of the crystal lattice parameters of α-Cr₂O₃ (〈a_bulk〉 = 〈b_bulk〉 = 4.953 Å). As indicated in the enlarged section (Figure 1(d)) one can distinguish a variety of defects such as atomic plane dislocations and atomic twisting. The HRTEM of the α-Cr₂O₃ nanoparticles with nearly nine observable aligned atomic layers seems to suggest that the α-Cr₂O₃ nanoparticles grow by a layer-by-layer process, that is, a Frank Van der Merwe type growth. The preliminary HRTEM investigation was followed by elemental analysis obtained through energy-dispersive X-ray spectroscopy (EDS) carried out using an Oxford instruments X-Max solid state silicon drift detector (20 KeV) coupled to the Tecnai G2 HRTEM. The obtained spectrum (Figure 2) confirmed the presence of Cr and oxygen in the annealed powders. The observed peaks of Cu are attributed to the Cu grids that make up the support on which the samples were placed. The peaks due to carbon are assigned to the carbon coating layer onto the Cu grid.

**Table 2.** Indexation and reticular planes characteristics of α-Cr₂O₃ nanoparticles.

| Miller Indices | d₀₀₁ (Å) | 2θ (Deg) | FWHM (Deg) | Lattice parameters |
|----------------|----------|----------|------------|--------------------|
| (0,1,2)        | 3.627    | 24.487   | 0.202      | 〈a_exp〉 = 4.951 Å |
| (1,0,4)        | 2.665    | 33.672   | 0.243      | 〈b_exp〉 = 4.951 Å |
| (1,1,0)        | 2.473    | 36.382   | 0.223      | 〈c_exp〉 = 13.516 Å |
| (0,0,6)        | 2.256    | 39.8     | 0.211      |                     |
| (1,1,3)        | 2.168    | 41.592   | 0.235      |                     |
| (0,2,4)        | 1.815    | 50.234   | 0.296      |                     |
| (1,1,6)        | 1.671    | 54.917   | 0.289      |                     |
| (2,1,4)        | 1.463    | 63.56    | 0.352      |                     |
| (3,0,0)        | 1.431    | 65.186   | 0.33       |                     |

Note: FWHM, full width at half maximum.

**Figure 2.** EDS spectrum of the α-Cr₂O₃ nanoparticles annealed at 500°C for 2 h.

**Figure 3.** Room temperature X-ray diffraction pattern of α-Cr₂O₃ in the Eskolaite phase.
2.3. Crystallographic structure and phase identification

To identify the crystallographic phase of the suspected \( \alpha-\text{Cr}_2\text{O}_3 \) nanoparticles, room temperature XRD analysis (Figure 3) was carried out using a Bruker Advanced D8 diffractometer with monochromated Cu Ka radiation of wavelength 1.5406 Å operating at a current of 40 mA and a voltage of 40 kV in the Bragg-Brentano geometry. Figure 3 reports a typical XRD profile obtained on the green \( \text{Cr}_x\text{O}_y \) powder following the annealing at 500°C of the initially black-coloured precipitate. The profile shows a series of intense peaks at the various angular positions of \( \sim 24.48°, 33.67°, 36.38°, 39.80°, 41.59°, 50.23°, 54.92°, 63.56° \) and \( 65.19° \) which indexed to JCPDS card 74-0326 could be ascribed to reflections from the (012), (104), (110), (006), (113), (024), (116), (112), (214) and (300) reticular planes, respectively. This is in line with the pure Eskolaite phase of green \( \alpha-\text{Cr}_2\text{O}_3 \). This corundum structure consists of a hexagonally closed-packed array of oxide anions with two-thirds of the octahedral holes occupied by chromium. It belongs to the rhombohedral Bravais lattice with space group R-3c (167) and unit cell lattice parameters \( a_{\text{bulk}} = b_{\text{bulk}} = 4.953 \) Å and \( c_{\text{bulk}} = 13.578 \) Å. Comparison of the experimental (nanoscale) and bulk crystallographic data (Table 2) indicates a slight increase in \( \langle a_{\text{exp}} \rangle \) and \( \langle b_{\text{exp}} \rangle \) and a slight decrease in \( \langle c_{\text{exp}} \rangle \) in the nano-scaled \( \alpha-\text{Cr}_2\text{O}_3 \). This variation can be related to a form of compression of the unit cell along the [001] direction. The observed value of \( \langle c_{\text{exp}} \rangle / \langle a_{\text{exp}} \rangle = 2.73 \) is slightly less than the standard value of 2.742 of the rhombohedral bulk structure which again lends credence to the existence of compressive strain in the powders. The semibroad nature of these peaks at their base suggests the nano-scaled nature of the Eskolaite \( \alpha-\text{Cr}_2\text{O}_3 \) particles.

The crystallite size of the \( \alpha-\text{Cr}_2\text{O}_3 \) nanoparticles cannot be estimated using the classical Debye Scherrer approximation as they exhibit a net shape anisotropy.

2.4. Chemical bonding and vibration spectroscopy

To re-confirm that the prepared powder is Eskolaite \( \alpha-\text{Cr}_2\text{O}_3 \) and to detect any additional surface/interface bonded compounds, attenuated total reflection-FT-IR spectroscopy was carried out on the heat-treated nanopowder at room temperature. The ATR-FT-IR typical spectrum as shown in Figure 4 could be split into two regions, the first lying between the 400 and 800 cm\(^{-1}\) and the second between 2100 and 2700 cm\(^{-1}\). The vibrational modes observed at 418, 558 and 643 cm\(^{-1}\) are typical of metal oxide single bonds in the bending mode. The relatively weak absorption band at 418 cm\(^{-1}\) and the strong absorption band at 558 cm\(^{-1}\) can be attributed to Cr–O bonds in the bending mode, while the strong absorption band at 643 cm\(^{-1}\) is reported by Henderson et al. (25) as a clear evidence for the presence of crystalline \( \alpha-\text{Cr}_2\text{O}_3 \). The broad band of low intensity at 1060 cm\(^{-1}\) can be attributed to surface Cr–O stretching vibrations. More accurately, and based on group theory, the bands centred at 558 and 643 cm\(^{-1}\) are
attributed to E_u modes while that centred at 418 cm\(^{-1}\) can be attributed to the IR active A_2u vibration mode. The relatively strong broad band observed at 3440 cm\(^{-1}\) can be attributed to O-H stretching modes of what could be waters of hydration. The weak broad band at 1600 cm\(^{-1}\) may well be attributed to the presence of waters of adsorbed moisture at the surface of the \(\alpha\)-Cr\(_2\)O\(_3\) powders.

As a complimentary study to the ATR-FTIR investigation above, Raman spectroscopy was carried out. The Raman spectrum observed for the \(\alpha\)-Cr\(_2\)O\(_3\) nanopowder (Figure 5) was obtained at room temperature using a 514.5 nm excitation line of an Ar\(^+\) laser source in the spectral range of 300–700 nm. Bulk \(\alpha\)-Cr\(_2\)O\(_3\) is known to have a corundum structure that belongs to the D\(^{3d}\) group. The site symmetry for the Cr atoms is C\(_3\), while the O atoms are on sites having C\(_2\) symmetry. The corresponding optical modes in the crystal are 2A\(_1\)g, 2A\(_1\)u, 3A\(_2\)g, 2A\(_2\)U, 5E\(_g\) and 4E\(_u\) vibrations with only two A\(_1\)g and five E\(_g\) vibrations which are Raman active. From the Raman spectrum, one can distinguish one intense peak centred at about 575.4 cm\(^{-1}\) with a shoulder at ~543.3 cm\(^{-1}\) that can be ascribed to A\(_1\)g modes. Relatively less-intense broad peaks at 356.9 and 640.0 cm\(^{-1}\) correspond to the vibrations in E\(_g\) modes. Similar vibrations have been reported by Mougin et al. (26) on \(\alpha\)-Cr\(_2\)O\(_3\) nanoparticles.

2.5. Chemical valence states by X-ray photoelectron spectroscopy

To further confirm the Eskolaite nature of the green nanopowders, X-ray photoelectron spectroscopy was carried out. The initial calibration of the instrument was conducted with a binding energy (BE) of 284.5 eV for a C 1s electron. As shown in Figure 6, high-resolution energy scans on the sample give two main peaks at BE 576.9 and 586.8 eV correspond, respectively, to Cr 2p\(_{3/2}\) and Cr 2p\(_{1/2}\) valence states of \(\alpha\)-Cr\(_2\)O\(_3\) (27). The splitting between these two states is about 10 eV. The O1s peak at a B.E of 530.6 eV can be ascribed to O atoms in the \(\alpha\)-Cr\(_2\)O\(_3\) nanoparticles and is in agreement with data reported by Jin et al. (27). The O1s peaks can be deconvoluted into three peaks centred at 529.5, 531.1 and 532.8 eV as reported by Maetaki and Kishi (28). These deconvoluted peaks can respectively be assigned to lattice oxygen (O\(^{2-}\)) surface adsorbed oxygen (O\(^{-}\)) and an O hydroxyl from O1s, and respectively, account for ~29.1%, 41.8% and 29.1% of the total oxygen content. The observed XPS profile strongly suggests the absence of impurities within the synthesized nanoparticles of Eskolaite \(\alpha\)-Cr\(_2\)O\(_3\).

In view of the potential applications of the synthesized pure Eskolaite \(\alpha\)-Cr\(_2\)O\(_3\), it was shown that they do exhibit superior supercapacitance response in a
composite form with graphene (12). Likewise, they display a tunable photo-induced magnetism as demonstrated recently (14, 16) and hence the possibility to engineer novel photo-tunable magnetic devices. From the biomedical aspect, the ongoing antimicrobial studies of such nano-scaled α-Cr₂O₃ indicate a significant efficiency against several bacteria such as E. coli (K12), S. aureas (25923), P. vulgarias (ATCC). More precisely, using disc diffusion methods α-Cr₂O₃ nanoparticles showed a large inhibition in all bacterial species and this were compared with the standard positive control (antibiotic). In addition, emulsions of the α-Cr₂O₃ nanoparticles are in process for green ink and paints applications.

3. Conclusion

Green synthesis of pure Eskolaite α-Cr₂O₃ nanoparticles via the bio-modification, at room temperature, of a precursor Cr(NO₃)₃·9H₂O salt was carried out using aqueous extracts from red flowers of C. viminalis. The resultant brownish green precipitate when annealed in air, for 2 h, at 500°C, gave rise to Cr₂O₃ stabilized in the base-centred monoclinic phase. Besides HRTEM investigations, XRD, ATR/FT-IR, X-Ray photoelectron spectroscopy as well as Raman spectroscopy were used to confirm the formation of Eskolaite α-Cr₂O₃ nanoparticles. Future work is required to identify the specific bioactive components in the aqueous extract of the red flowers of C. viminalis that are responsible for the bio-transformation of the Cr(NO₃)₃·9H₂O salt.

Disclosure statement

No potential conflict of interest was reported by the authors.

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