Article

Bioengineered Crystalline Single-Phase Potassium Chromate Nanocrystals

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Abstract

This article reports for the first time on the possibility of the biosynthesis of single-phase potassium chromate (K_2CrO_4). This was achieved by using the natural extract of dried citrus peel as both an effective chelating agent and an original green source of potassium (K). For the bioengineering of K_2CrO_4 at room temperature and atmospheric pressure, H_2O as the unique universal solvent and $Cr(NO_3)_3 \cdot 9H_2O$ as Cr source were used. The validation of such a bioengineered K_2CrO_4 was carried out specifically via Raman spectroscopy. In this investigation, the various intrinsic Raman modes of single-phase K_2CrO_4 were observed in full agreement with B_{2g} (352 cm^{-1}), $A_g + B_{2g}$ (396 cm^{-1}), $A_g + B_{2g}$ (853 cm^{-1}), B_{3g} (875 cm^{-1}) and Ag (905 cm^{-1}) inherent in K_2CrO_4 (chromate) vibrational modes, which are different from those in $K_2Cr_2O_7$ (dichromate).

Keywords: green nanosynthesis; chromates; bioengineering; natural extract

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Nano-Horizons
Volume 4 | 2025 | 12 pages
https://doi.org/10.25159/3005-2602/16278
ISSN 3005-2602 (Online)

1 Introduction

Along with a number of stable KxCryOz compounds and their variations [1], it was established that there are two major potassium chromates: potassium chromate (K_2CrO_4) standard and potassium dichromate ($K_2Cr_2O_7$). Owing to the high Cr electronic valency, they are mostly used as paint pigments and anticorrosion agents. In the CrO_{2-4} complex, Cr is in the +6 oxidation state and has a d^0 structure. Instead of a d-d transition, the corresponding colour (yellow or orange) is the result of a charge transfer.

The two potassium chromates, K_2CrO_4 and $K_2Cr_2O_7$, are particularly interesting from a fundamental perspective, notably with regard to phase transition phenomena, despite their relative toxicity and being a health hazard. After heating and cooling to approximately 544 K and 502 K, respectively, crystals of phase II $K_2Cr_2O_7$ (space group P1) experience a first-order transition to a so-called phase I (space group supposedly P21/n) [2]. Krivovichev *et al*. [3] improved on this series of phase-transition investigations. More specifically, research has indicated that the 60° relative rotation of terminal O atoms in each tetrahedron during the gain or loss of the n-glide plane is the source of the first-order transition between phases I and II [4].

Likewise, potassium chromates K_2CrO_4 have been demonstrated to display anisotropy in their electrical characteristics, particularly in the c-axis direction, which is associated with a crystallographic phase transition [5]. An alternative conduction mechanism may be possible given that the cation migration energy, as determined from the conductivity variation vs 1/T plots, is marginally higher than the value typically found in potassium halides. Approximately 2.20 eV is the defect production energy, which is similar to values found in ionic solids.

In addition to the aforementioned essential characteristics, chromates serve as the primary starting point for the synthesis of various compounds containing chromium oxides, particularly the α-Cr_2O_3 eskolaite phase [6]. Several applications, including green pigments [7], a basis component for nano-composite batteries [8]–[9], gas sensors [10], magnetic materials [11] and solar energy materials [12], validated the technological applications of these chromates.

2 Method

Although a number of nanoscaled chromium oxides have been bioengineered by using a wide range of natural extracts [13]–[15], this is the first instance of using the K found in a natural extract as a source of potassium to create the single phase K_2CrO_4. The latter is this study's primary source of originality. Raman spectroscopy at room temperature was used to validate the bioengineering of nanoscaled K_2CrO_4.

The present chromate K_2CrO_4 was synthesised using the conventional green route as summarised in Figure 1, with citrus peel extract serving simultaneously as an effective chelating agent and an effective successful source of K. Reporting on the double role of the natural extract as both a source of K and reducing agent at the same time is the unique contribution of this study.

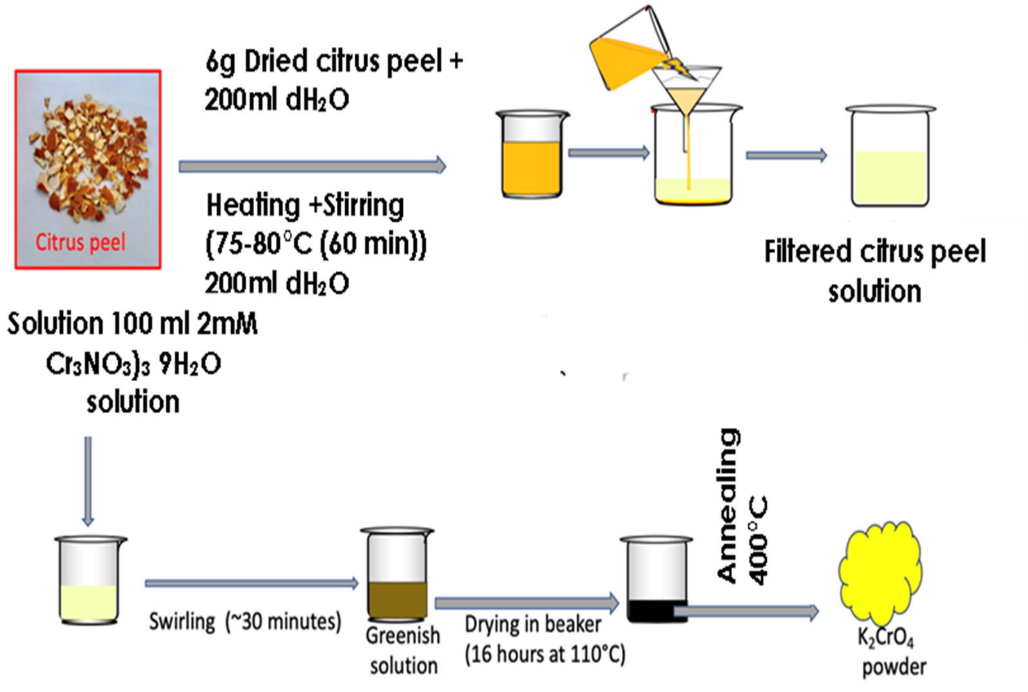

Figure 1: Schematic diagram illustrating the bioengineering process by using natural citrus peel extract

The standard synthesis of the desired K_2CrO_4 involved mixing 200 ml of deionised water with 6 g of dried citrus peel, then stirring the mixture for an hour at temperatures between 75 °C and 80 °C. Subsequently, 100 ml of 2 mM chromium (III) nitrate nonahydrate was combined with 50 ml of the filtered citrus peel solution in a beaker. The mixture was then agitated for approximately half an hour. The resulting greenish solution was then dried in the beaker at ~110 °C for approximately 16 hours using a standard oven. The powder was finally dried and then annealed. Figure 2 displays a typical transmission electron microscopy of the bioengineered chromate. The particles seem to be flakes that exhibit various shapes within the nanoscale in size while being polydispersed (Figure 2(a)). A relatively high magnification indicates the crystalline atomically ordered nanoparticles (Figure 2(b)).

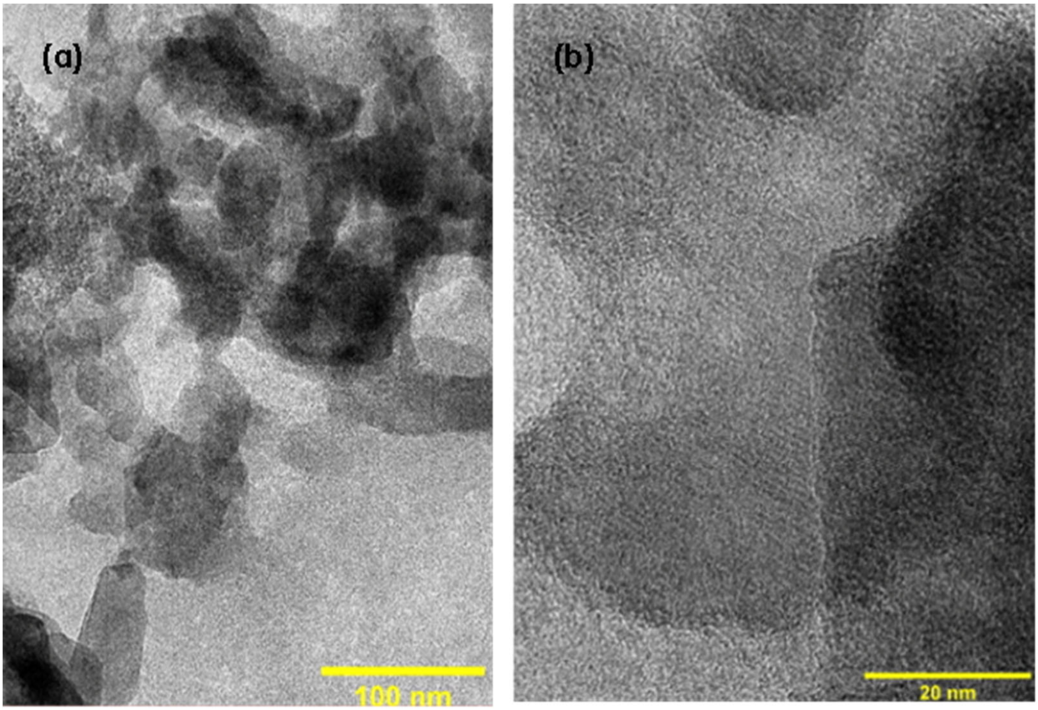

Figure 2: Low (a) and high (b) magnification of the transmission electron microscopy of the bioengineered K_2CrO_4

As a major approach to determine the characteristics, Raman spectroscopy was used. Figure 3(a) displays the orthorhombic space group Pmna within which the potassium chromate K_2CrO_4 crystallises [16]. The structure displays a total of 24 lattice modes: six vibrational modes ($1A_g + 2\ B_{1g} + 1\ B_{2g} + 2\ B_{3g}$), eight translational modes ($6A_g + 3\ B_{1g} + 6\ B_{2g} + 3\ B_{3g}$) and 18 internal modes ($6A_g + 3B_{1g} + 6\ B_{2g} + 3\ B_{3g}$). They are allowed by the structure's related factor-group analysis [16]. The spectral areas of 50–180 cm^{-1} and 300–950 cm^{-1} are where the exterior and internal modes are located at room temperature and atmospheric pressure [16], [17].

Figures 3(b), 3(c), 3(d) and 3(e) display the Raman active modes which are concentrated in the spectral area between 50 and 1 000 cm^{-1}. More particular, throughout the spectral positions of 355, 396, 855, 876 and 907 cm^{-1}, relatively strong Raman active modes are detected. They correspond almost exactly to the B_{2g} (352 cm^{-1}), $A_g + B_{2g}$ (396 cm^{-1}), $A_g + B_{2g}$ (853 cm^{-1}), B_{3g} (875 cm^{-1}), and Ag (905 cm^{-1}) [16], [17] of the single-phase crystalline K_2CrO_4.

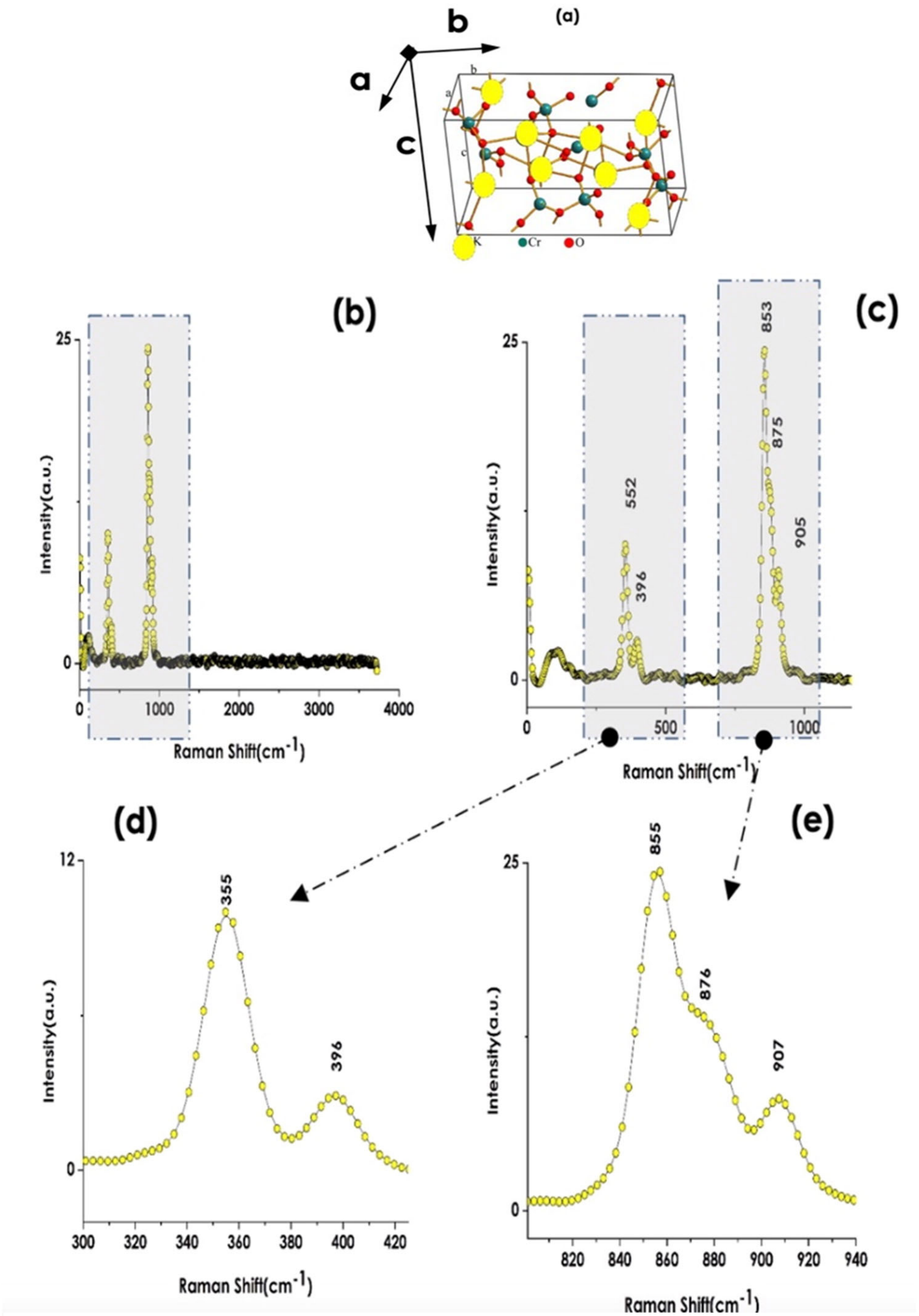

Figure 3: (a) The orthorhombic space group Pmna, (b) room temperature Raman spectrum of the bioengineered nanocrystals within the spectral range of (c) 0–1 100 cm^{-1}, and the corresponding zooms within the spectral ranges of (d) 300–425 cm^{-1}, and (e) 800–940 cm^{-1}

3 Findings and Recommendations

The finding indicates that the single-phase potassium chromate K_2CrO_4 was effectively bioengineered by using citrus peel extract, which served as a potential supply of potassium and also as an efficient chelating agent. A follow-up investigation will aim to validate this innovative green approach for the bioengineering of other possible potassium compounds such as $K_2Al_2O_4$, K_2AsO_4, K_2MoO_4 and K_2WO_4.

4 Conclusion

This study validated the possibility of bioengineering single-phase K_2CrO_4 by using natural extract of citrus peel as both an effective chelating agent and a significant source of potassium. This green approach could open new opportunities for the synthesis of chromium compounds. These compounds continue to attract interest as they represent the most widely used group of oxidising agents in organic chemistry, and are capable of oxidising almost every organic functional group.

5 Acknowledgements

This work received support from the World Academy of Sciences and Cheikh Anta Diop University, for which we are grateful.

6 References

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