

Research Article

Synthesis of CuAl_2O_4 Nanoparticle and Its Conversion to CuO Nanorods

V. Andal ¹, G. Buvaneswari ², and R. Lakshmipathy ¹

¹Department of Chemistry, KCG College of Technology, Chennai, 600097 Tamil Nadu, India

²Materials Division, School of Advanced Sciences, VIT University, Vellore, 632014 Tamil Nadu, India

Correspondence should be addressed to R. Lakshmipathy; lakshmipathy.che@kcgcollege.com

Received 27 May 2021; Revised 20 July 2021; Accepted 22 August 2021; Published 7 September 2021

Academic Editor: P. Davide Cozzoli

Copyright © 2021 V. Andal et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The molten salt approach was used to convert CuAl_2O_4 nanoparticles to CuO nanorods in this study. Molten hydroxide (NaOH) synthesis was chosen over molten salts (NaCl/KCl) for removing aluminium oxide from copper aluminate at low temperatures. The molten salt process is environmentally beneficial. Polymeric precursors were used to make nanosized copper aluminates. Alginic acid polymer is used to gel aqueous solutions of copper acetate and aluminium nitrate, yielding precursor after further heating. The precursor provides 14 nm nanosized copper aluminates after being heated at 900°C for 5 hours. XRD, FTIR, SEM, and TEM were used to characterize the nanosized copper aluminate powder. Solid state mixing and solution technique were used to investigate molten hydroxide treatment of spinel CuAl_2O_4 . The products of the reaction were identified using XRD. FTIR and SEM are also used to analyze the sample. Using UV-DRS absorbance spectrum analysis, the optical characteristics of CuAl_2O_4 and CuO nanorods were examined. Using the Tauc plot method, the band gaps of CuAl_2O_4 and CuO were calculated to be 4.3 and 3.93 eV.

1. Introduction

Spinel oxides are interesting due to their various physical and chemical properties [1, 2]. They are applied widely in different fields such as multiferroics, spintronics, superconductors, optoelectronics, and cathodes for rechargeable lithium batteries [3–7]. Among them, transition metal aluminates having spinel structure are of current importance due to their technological applications in various fields such as catalysis, refractories, heat-resistant pigment, and degradation of organic compounds [8–13]. Reduction in the size of their metal aluminates yields improved properties such as lower temperature sinterability, greater thermal stability, increased hardness, better diffusion, and ductility [14]. Generally, nanostructured transition metal aluminates are prepared by different routes such as sol-gel, microemulsion, templating process, hydrothermal, coprecipitation, and solution combustion [10, 14–18]. However, these methods have some drawbacks, such as the utilisation of expensive metal alkoxide precursors, effective templating agents, homogeneity, stoichiometric control, and high temperatures.

Copper aluminate is an inverse spinel with a low band gap which makes it a potential candidate as photocatalyst [19]. Various methods such as coprecipitation, sol-gel, hydrothermal, and combustion have been reported for the synthesis of nanosized CuAl_2O_4 [20–22]. Weizhong et al. synthesized nanosized copper aluminate spinel by precursor approach with the help of ultrasound irradiation in the presence of argon atmosphere [11]. In the present study, we synthesized nanosized copper aluminate by alginate precursor approach without using argon atmosphere and ultrasonic irradiation.

CuO nanostructures have excellent applications such as electrode materials for lithium batteries, catalyst, and adsorbent [22]. In particular, CuO nanostructures are prepared by hydrothermal, microwave, and solvothermal, at high temperatures and complex methods. So there is a requirement for simple and low-temperature method of preparation of CuO nanostructure.

Few reports are available on the conversion of spinel oxides to metal and metal oxide in which the spinel oxide can be considered as a precursor. Yang et al. reported on

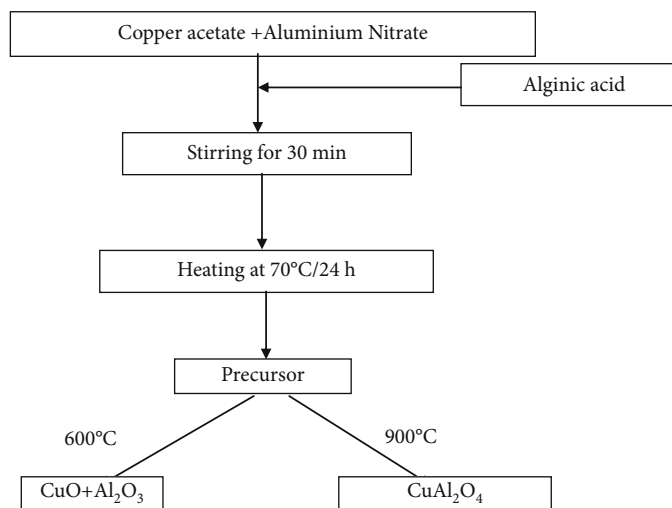


FIGURE 1: Experimental procedures for the synthesis of nano- CuAl_2O_4 .

the preparation of nanocrystalline “Cu” from rod-like CuFe_2O_4 [23]. Ribeiro et al. reported the formation of surface “Ni” nanoparticles from NiAl_2O_4 during CO_2 reforming of methane [24]. CuMn_2O_4 catalyst showed high reactivity in water gas shift reaction due to its reduction to Cu/MnO in the presence of H_2 atmosphere at 350-400°C [25]. Formation of “Cu” on the surface of CuCr_2O_4 makes the system an active catalyst for the selective hydrogenation of furfural to furfuryl alcohol [26]. Similarly, Ni metal dispersed on the surface of nickel spinel oxide catalyst results in stable performance in ethanol steam reforming [27]. Spinel CuFe_2O_4 has been studied as a precursor for copper catalyst by Kameoka et al. [28]. Nillohit et al. synthesized mesoporous CuO nanoparticles from $\text{Cu}(\text{OOCPh})_2\text{Lut}_2$ precursor complex by annealing at 450°C [29]. Precursors already reported for synthesizing CuO nanoparticles are $\text{Cu}_2(\text{OH})_3\text{Br}$, CuS, etc. [30, 31]. So far, no reports are available for the synthesis of CuO from CuAl_2O_4 precursor. However, the regeneration process of Cu or CuO from copper containing spinel oxides has not been investigated thoroughly.

Molten salt syntheses are effective low-temperature synthesis without using expensive precursors and toxic elements, and they do not require any specialized equipment for synthesizing metal oxides. Molten hydroxide synthesis is a type of molten salt synthesis in which hydroxides are used instead of salts which produces single-phase and controlled morphology [32, 33]. Due to its advantages, molten hydroxide synthesis is considered to be the most promising one, and hence, it is applied to prepare simple metal oxide from complex metal oxide.

The development of new methods for preparation of cupric oxide with various morphologies has always been important because cupric oxide is a significant metal oxide. From the literature reports, it was prominent that the synthesis will have an effect on size and morphology of the particles [34]. To the best of our knowledge, no work has been done to synthesize CuAl_2O_4 particles by polymeric precursor method using alginic acid as a complexing agent and its conversion to CuO by molten hydroxide method. There-

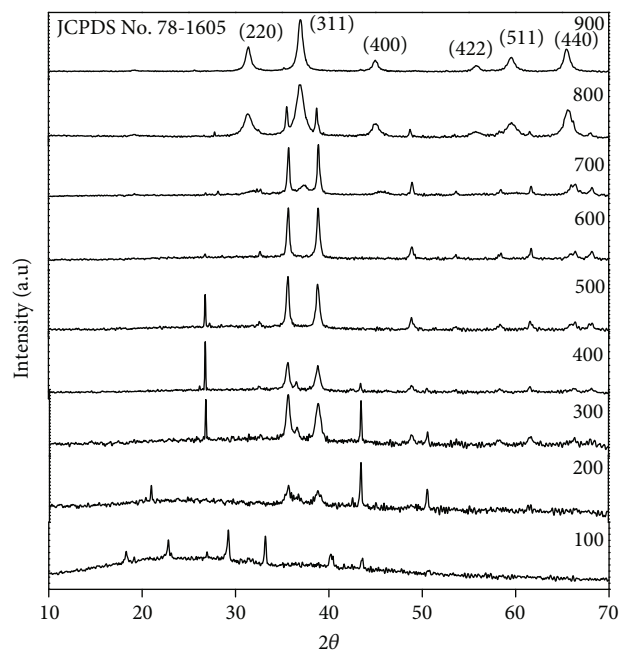


FIGURE 2: XRD pattern of CuAl_2O_4 powder obtained on heating the precursor from 100-900°C.

fore, the aim of this study is to prepare nanostructured CuAl_2O_4 powders and CuO nanopowder at low temperature and to calculate its band gap.

2. Experimental

2.1. Materials. The reagents used were of analytical grade. Aluminium nitrate (98%) and alginic acid (19-25%) were procured from SD Fine-Chemical Limited, India. Cuprous acetate (99%) was from Sisco Lab and NaOH from Qualigens.

2.2. Synthesis of CuAl_2O_4 by Polymeric Precursor Method. Nanosized copper aluminate spinel particles are synthesized

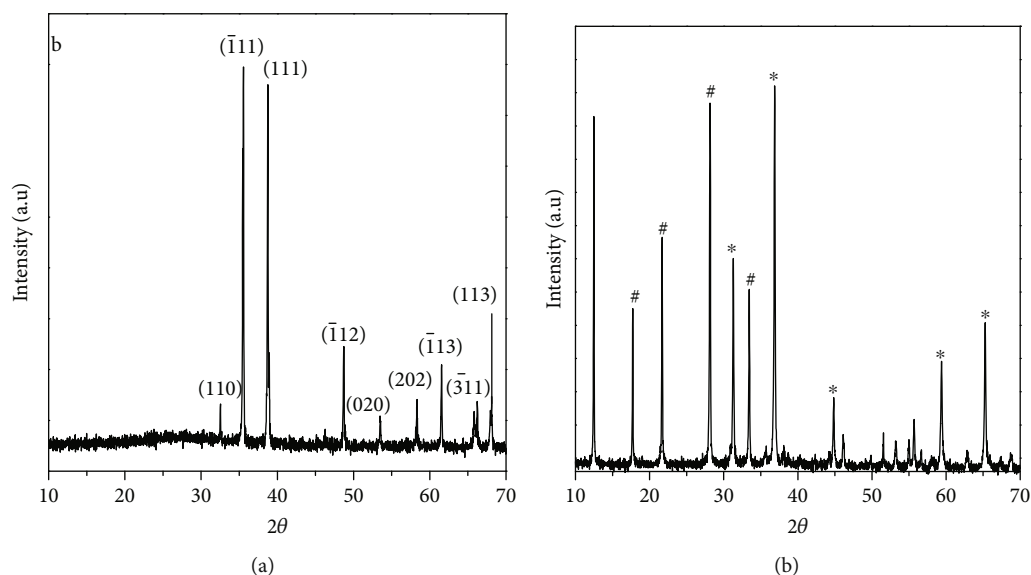


FIGURE 3: (a) XRD pattern of CuO (CAI). (b) XRD pattern of CAII: * indicates CuAl_2O_4 ; # indicates Al_2O_3 .

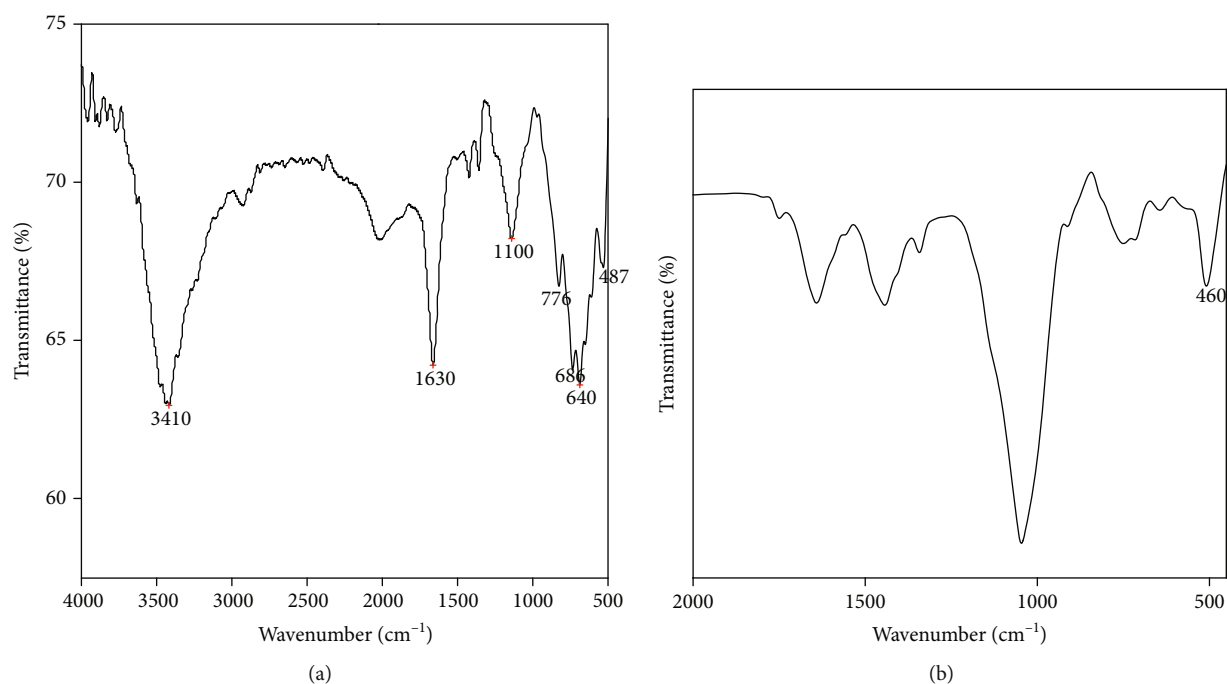


FIGURE 4: (a) FTIR spectrum of CuAl_2O_4 . (b) FTIR spectrum of CuO (CAI).

by polymeric precursor approach. The elaborate experimental procedure for the synthesis of CuAl_2O_4 is shown in Figure 1.

The synthesis of polymeric precursor was carried out as follows. The two solutions cuprous acetate and aluminium nitrate were stirred thoroughly to get a homogeneous solution. Secondly, 60 ml of 20% alginate acid is added and kept to stirring at 70°C for 24 h till a dark blue gel formed. The gel on continuous heating gets converted to black powder. The black powder or precursor was then calcined at different (100°C , 300°C , 500°C , and 700°C) temperatures for 12 h and $900^\circ\text{C}/5\text{ h}$ to produce nanosized CuAl_2O_4 particles.

2.3. Molten Hydroxide Synthesis. Synthesized CuAl_2O_4 nanomaterial was treated with NaOH (molten hydroxide) by two approaches

- (i) Solid state reaction
- (ii) Solution reaction method

2.4. Solid State Reaction. CuAl_2O_4 and alkali (NaOH) are mixed well in a mortar in the ratio of 1 : 10. After thorough grinding for 5 min, the slurry was immediately put into a

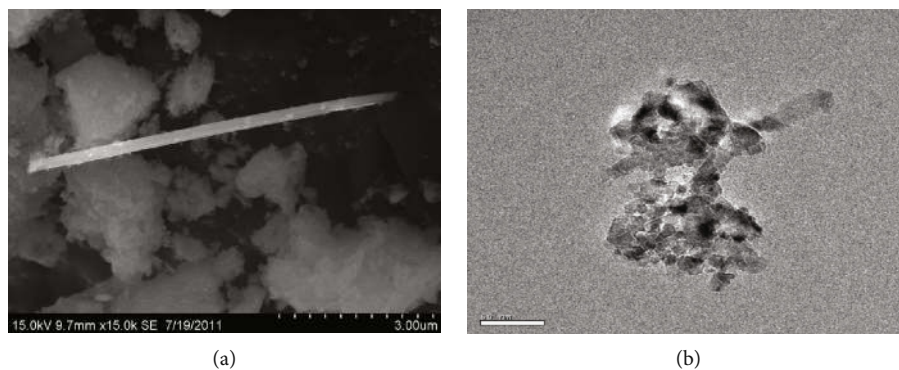


FIGURE 5: (a) SEM image of CuAl_2O_4 . (b) TEM image of CuAl_2O_4 .

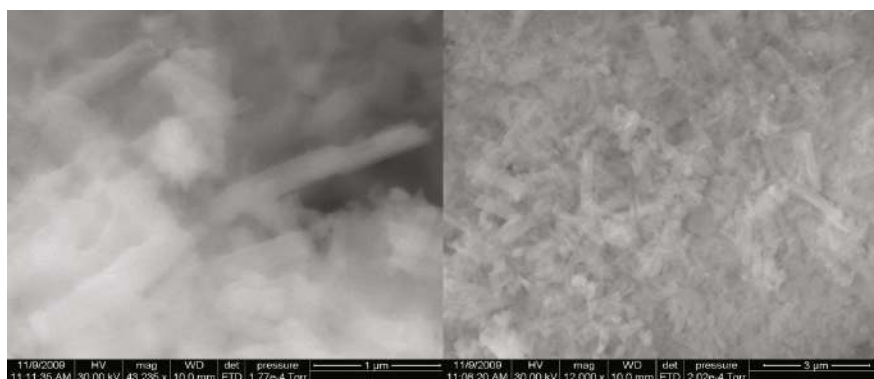


FIGURE 6: SEM images of CuO (CAI).

crucible and heated at 100°C for 24 hours. After 24 h, a dark blue-coloured layer formed on the substance. The product was then washed multiple times with water to eliminate any sodium aluminate that had generated in the process. The powder (CAI) is then dried and tested.

2.5. Solution Reaction Method. CuAl_2O_4 (0.235 g) is dissolved in 10 ml water and mixed thoroughly to get a homogeneous dispersion. The sodium hydroxide solution (10 ml, 2.35 g) is added to the dispersion and refluxed in an oil bath at 100°C for 24 hours. The mixture is then filtered, rinsed, and analyzed (CAII).

2.6. Characterization. Powder X-ray diffraction was used to describe the phase present in the CuAl_2O_4 precursor and alkali-treated copper aluminate (CAI and CAII) as manufactured powders at room temperature in a Bruker instrument (D8 Advance) using $\text{Cu K}\alpha$ radiation ($\lambda=1.54$). The Debye-Scherrer formula was used to calculate the average particle size of the final product. The KBr disc approach was used to record the infrared spectra (FTIR spectrometer, JASSCO Model 4100). The FEI QUANTA FEG 200 HR scanning electron microscope was used to perform scanning electron microscopic analysis on the sample. TEM pictures were captured using a Philips CM 200 with a 20-200 kV working voltage. The optical properties of the powders are measured using DR UV-VIS instrument.

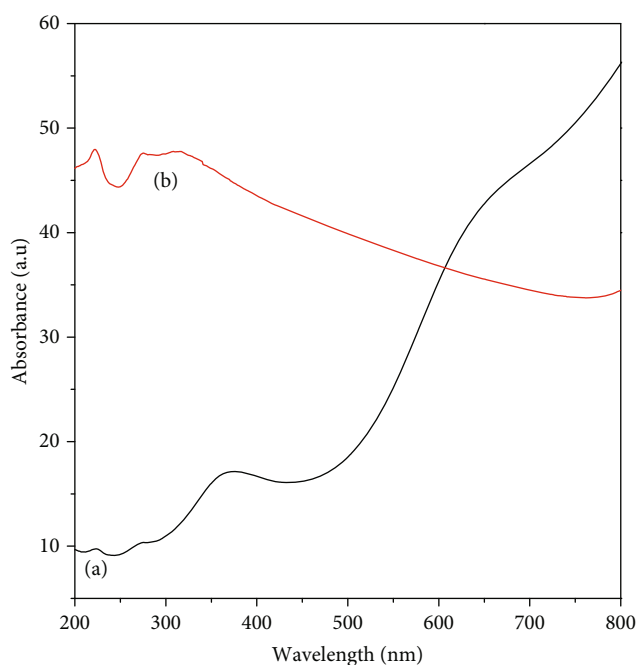


FIGURE 7: UV-DRS diffuse reflectance spectra of (a) CuAl_2O_4 and (b) CuO (CAI).

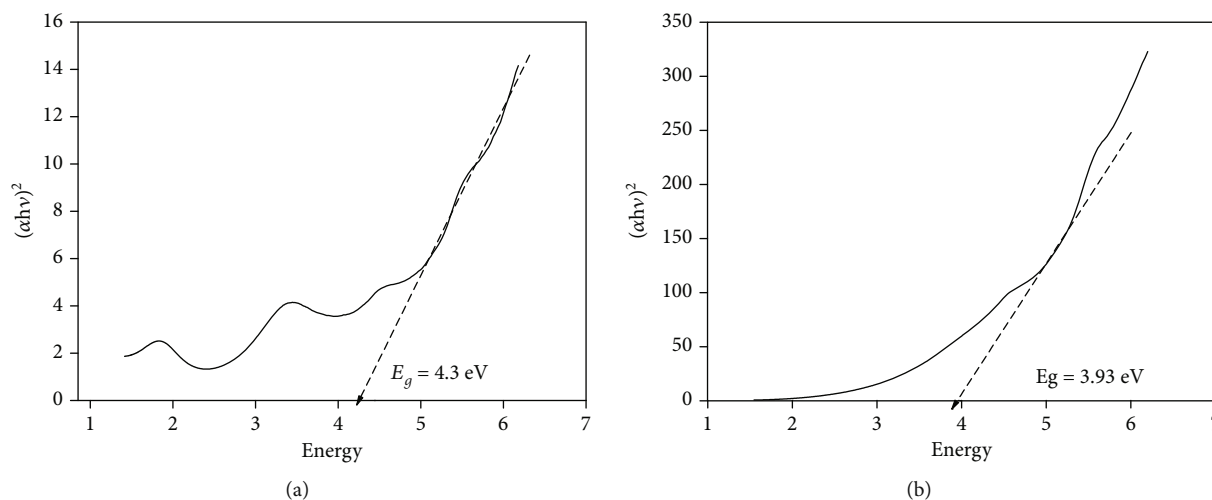


FIGURE 8: Tauc plot of direct allowed transition of (a) CuAl_2O_4 and (b) CuO .

3. Results and Discussion

The XRD pattern of CuAl_2O_4 precursor heated at different temperatures is shown in Figure 2. At each temperature, the sample is heated for 12 h in air to evaluate the formation of pure phase. The precursor on heat treated at $600^\circ\text{C}/12\text{ h}$ yields pure CuO phase with monoclinic structure in agreement with JCPDS No. 45-0397 [35]. On further heating to 700°C , weak intense CuAl_2O_4 peak and more intense CuO were obtained. The relative peak intensity of CuO decreased on further heating. On heating at $900^\circ\text{C}/5\text{ h}$, the precursor yields normal spinel CuAl_2O_4 . The XRD peaks of CuAl_2O_4 are in good agreement with JCPDS No. 78-1605. From the XRD data, the crystallite size of as-prepared CuAl_2O_4 was calculated to be 14 nm using the Debye-Scherrer equation

$$D = \frac{K\lambda}{\beta \cos \theta}, \quad (1)$$

where β is the full width maximum, K is the shape factor (0.9), and λ is the wavelength of X-ray source. CuAl_2O_4 is formed at higher temperature, and CuO is formed at 600°C . Niasari et al. synthesized nanocrystalline CuAl_2O_4 at 800°C by modified sol-gel method. Our results are in good agreement with their reports [10].

The XRD peaks of “CAI” (Figure 3(a)) are in good agreement to pure monoclinic CuO (JCPDS No. 45-0937) whereas the XRD peaks of “CAII” (Figure 3(b)) contain CuAl_2O_4 , Al_2O_3 , and AlOH . This shows that CuAl_2O_4 does not react with NaOH solution even when it was refluxed for 12 h.

FTIR analyses were used to identify the functional groups of nanosized spinel CuAl_2O_4 and interaction of CuAl_2O_4 with NaOH . The vibrations at 3419 cm^{-1} and 1641 cm^{-1} (Figure 4(a)) are due to the longitudinal and bending vibration of water. A broad peak centered at 640 cm^{-1} is due to the Cu-O, Al-O, and Al-O-Al longitudinal vibrations in CuAl_2O_4 [36, 37]. The IR absorption spectrum of NaOH -treated CuAl_2O_4 (Figure 4(b)) shows a different pattern from the spinel. On treatment with NaOH , a broad peak centered at 640 cm^{-1} dis-

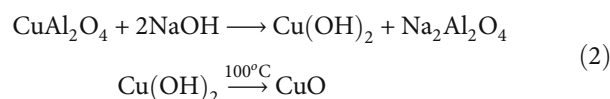
appears and a small peak appeared at 460 cm^{-1} which confirms the formation of Cu-O. Also, the vibrations due to alumina are not observed which further indicates the complete conversion of CuAl_2O_4 into CuO [38].

The size and the morphology of synthesized nanosized CuAl_2O_4 were examined by SEM and TEM techniques. Figures 5(a) and 5(b) show the SEM and TEM images of nanosized CuAl_2O_4 , respectively. The SEM image exhibits a variety of morphologies, including nanosized rod production and porous spherical particles. Thus, the homogeneity in shape is not achieved using alginate precursor. The surface area of the synthesized CuAl_2O_4 is $27.6\text{ m}^2\text{g}^{-1}$.

The TEM image (Figure 5(b)) was done by ultrasonication of the CuAl_2O_4 powder in acetone. The TEM image indicates that the particles are of diameter 50 nm. From the TEM image, we can further confirm that the obtained nanocrystals are not dispersed well and the cubes aggregated to form different shapes such as rods and triangles. Thus, the homogeneity in shape is not achieved using an alginate precursor.

The SEM image of CuO (CAI) formed from solid state reaction (Figure 6) shows the rod morphology which is observed in CuAl_2O_4 . The morphology of CuAl_2O_4 persists on further treatment with alkali. Similar to the spinel, the rods are agglomerated and the porosity gets reduced. Similar to the reported literatures, the surface area of the synthesized CuO is $3.59\text{ m}^2\text{g}^{-1}$.

With reference to the results obtained, the nano- CuAl_2O_4 is transformed to pure nano- CuO by solid state reaction with alkali. It is well known that CuAl_2O_4 on heating at higher temperature results in a mixture of CuAlO_2 and CuO [39]. The mechanism that exists in the formation of CuO from CuAl_2O_4 by alkali treatment is mentioned below in the form of equations.



CuAl₂O₄ on alkali treatment by solid state reaction forms a metastable phase copper hydroxide. The produced copper hydroxide decomposes at low temperature 100°C to form CuO and sodium aluminate. Since sodium aluminate is soluble in water, it is removed in washings with water and pure CuO nanorods obtained. Our reports are in good agreement with the result of Yannick et al. that Cu(OH)₂ easily undergoes dehydration on heating to form stable CuO [40].

3.1. Optical Properties of CuAl₂O₄ and CuO. The UV-DRS diffuse reflectance spectra of CuAl₂O₄ and CuO were measured in the wavelength range of 200-800 nm shown in Figure 7 to investigate optical properties. The UV-VIS absorption spectrum of the synthesized CuAl₂O₄ nanostructure is shown in Figure 7(a). There is an absorption band centered at 364 nm with two small shoulders at 269 and 224 nm. The absorption band for CuO is at 294 nm with a shoulder at 221 nm (Figure 7(b)) which was similar to the reported literature [41].

Tauc approach (Figure 8) was applied to calculate the band gap (E_g) of CuAl₂O₄ and CuO using the below equation

$$(ah\nu)^{1/n} = A(h\nu - E_g). \quad (3)$$

The optical band gap of CuAl₂O₄ nanoparticles annealed at 900°C was evaluated as 4.3 eV. Similarly, for CuO, it was estimated as 3.93 eV, respectively.

4. Conclusion

Nano-CuAl₂O₄ with a particle size of 20-50 nm was synthesized using the alginate precursor method. Various experimental techniques were used to characterize CuAl₂O₄ that was synthesized. CuAl₂O₄ has an optical band gap of 4.3 eV, whereas CuO has an optical band gap of 3.93 eV due to the absence of aluminium oxide. Molten hydroxide was used to transform CuAl₂O₄ into pure CuO nanorods at a lower temperature. This procedure can also be used to achieve controlled morphology. The activity of spinel CuAl₂O₄ as a precursor for the production of CuO is demonstrated in this study.

Data Availability

All data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

The authors thank VIT University for providing all required facilities to carry out the experiments.

References

- [1] M. L. Huggins, "Electronic Structures of the Spinel," *Physics Review*, vol. 21, no. 5, pp. 509–516, 1923.
- [2] E. J. W. Verwey and E. L. Heilmann, *The Journal of Chemical Physics*, vol. 15, p. 174, 1947.
- [3] Y. Yamaski, S. Miyasaka, Y. Kaneko, J.-P. He, T. Arima, and Y. Tokura, *Physical Review Letters*, vol. 96, 2006.
- [4] U. Lüders, G. Herranz, M. Bibes et al., "Hybrid perovskite-spinel magnetic tunnel junctions based on conductive ferrimagnetic NiFe₂O₄," *Journal of Applied Physics*, vol. 99, no. 8, article 08K301, 2006.
- [5] S. Satpathy and R. M. Martin, "Electronic structure of the superconducting oxide spinel LiTi₂O₄," *Physical Review B*, vol. 36, no. 13, pp. 7269–7272, 1987.
- [6] D. Segev and S.-H. Wei, "Structure-derived electronic and optical properties of transparent conducting oxides," *Physical Review B*, vol. 71, no. 12, article 125129, 2005.
- [7] J. Kim and A. Manthiram, "Low temperature synthesis and electrode properties of Li₄Mn₅O₁₂," *Journal of the Electrochemical Society*, vol. 145, L53, 1998.
- [8] L. Ji, S. Tang, H. C. Zeng, J. Lin, and K. L. Tan, "CO₂ reforming of methane to synthesis gas over sol-gel-made Co/γ-Al₂O₃ catalysts from organometallic precursors," *Applied Catalysis A: General*, vol. 207, no. 1-2, pp. 247–255, 2001.
- [9] M. H. Amin, A. Kazemzadeh, B. Arfaei, N. S. Chaudhury, and V. Sahajwalla, "Investigations of calcium aluminate slag penetration to MgO monolithic refractories in steelmaking process," *International Journal of ISSI*, vol. 3, no. 2, pp. 34–42, 2006.
- [10] M. S. Niasari, M. F. Khouzani, and F. Davar, "Bright blue pigment CoAl₂O₄ nanocrystals prepared by modified sol-gel method," *Journal of Sol-Gel Science and Technology*, vol. 52, pp. 321–327, 2009.
- [11] L. V. Weizhong, B. Liu, Q. Qiu et al., "Synthesis, characterization and photocatalytic properties of spinel CuAl₂O₄ nanoparticles by a sonochemical method," *Journal of Alloys and Compounds*, vol. 479, pp. 480–483, 2009.
- [12] K. Ajay, P. B. Chauke, S. Zahra et al., "Microwave-mediated fabrication of mesoporous Bi-doped CuAl₂O₄ Nanocomposites for Antioxidant and Antibacterial Performances," *Materials Today: Proceedings*, vol. 15, pp. 454–463, 2019.
- [13] R. G. Chaudhary, V. N. Sonkusare, and G. S. Bhusari, "Microwave-mediated synthesis of spinel CuAl₂O₄ nanocomposites for enhanced electrochemical and catalytic performance," *Research on Chemical Intermediates*, vol. 44, pp. 2039–2060, 2018.
- [14] F. Meyer, R. Hempelmann, S. Mathur, and M. Veith, "Microemulsion mediated sol-gel synthesis of nano-scaled MAl₂O₄ (M=Co, Ni, Cu) spinels from single-source heterobimetallic alkoxide precursors," *Journal of Materials Chemistry*, vol. 9, pp. 1755–1763, 1999.
- [15] L. Zou, F. Li, X. Xiang, D. G. Evans, and X. Duan, "Self-generated template pathway to high-surface-area zinc aluminate spinel with mesopore network from a single-source inorganic precursor," *Chemistry of Materials*, vol. 18, pp. 5852–5859, 2006.
- [16] Z. Chen, E. Shi, Y. Zheng, W. Li, N. Wu, and W. Zhong, "Synthesis of mono-dispersed ZnAl₂O₄ powders under hydrothermal conditions," *Materials Letters*, vol. 56, p. 601, 2002.
- [17] M. A. Valenzuela, J. P. Jacobs, P. Bosch, S. Reijne, and B. Zapata, "The influence of the preparation method on the

- surface structure of ZnAl_2O_4 ,” *Brongersma HH Appl Catal A Gen*, vol. 148, p. 315, 1997.
- [18] K. C. Patil, S. T. Aruna, and S. Ekambaram, “Combustion synthesis,” *Current Opinion in Solid State & Materials Science*, vol. 2, p. 158, 1997.
- [19] Y. Y. Jiang, J. G. Li, X. T. Sui et al., “ CuAl_2O_4 powder synthesis by sol-gel method and its photodegradation property under visible light irradiation,” *Journal of Sol-Gel Science and Technology*, vol. 42, pp. 41–45, 2007.
- [20] U. Kameswari and C. N. Pillai, “Reaction of piperidine with formaldehyde over alumina and spinel aluminates,” *Catalysis Letters*, vol. 38, pp. 53–56, 1996.
- [21] T. Mimani, “Instant synthesis of nanoscale spinel aluminates,” *Journal of Alloys and Compounds*, vol. 315, p. 123, 2001.
- [22] A.-m. Cao, J. D. Monnell, C. Matranga, J.-m. Wu, L.-l. Cao, and J. Di Gao, “Hierarchical nanostructured copper oxide and its application in arsenic removal,” *The Journal of Physical Chemistry C*, vol. 111, pp. 18624–18628, 2007.
- [23] S. C. Yang, W. N. Su, S. D. Lin et al., “Preparation of nano-sized Cu from a rod-like CuFe_2O_4 : suitable for high performance catalytic applications,” *Applied Catalysis B: Environmental*, vol. 106, pp. 650–656, 2011.
- [24] F. P. N. Ribeiro, R. C. R. Neto, S. F. Moya, M. V. M. Souza, and M. Schmal, “Synthesis of NiAl_2O_4 with high surface area as precursor of Ni nanoparticles for hydrogen production,” *International Journal of Hydrogen Energy*, vol. 35, pp. 11725–11732, 2010.
- [25] Y. Tanaka, T. Utaka, R. Kikuchi, T. Takeguchi, K. Sasaki, and K. Eguchi, “Water gas shift reaction for the reformed fuels over Cu/MnO catalysts prepared via spinel-type oxide,” *Journal of Catalysis*, vol. 215, no. 2, p. 271, 2003.
- [26] R. Prasad and P. Singh, “Applications and preparation methods of copper chromite catalysts: a review,” *Bulletin of Chemical Reaction Engineering & Catalysis*, vol. 6, no. 2, pp. 63–113, 2011.
- [27] H. Muroyama, R. Nakase, T. Matsui, and K. Eguchi, “Ethanol steam reforming over Ni-based spinel oxide,” *International Journal of Hydrogen Energy*, vol. 35, pp. 1575–1581, 2010.
- [28] S. Kameoka, T. Tanabe, and A. P. Tsai, “Spinel CuFe_2O_4 : a precursor for copper catalyst with high thermal stability and activity,” *Catalysis Letters*, vol. 100, pp. 89–93, 2005.
- [29] S. K. Maji, N. Mukherjee, A. Mondal, B. Adhikary, and B. Karmakar, “Chemical synthesis of mesoporous CuO from a single precursor: Structural, optical and electrical properties,” *Journal of Solid State Chemistry*, vol. 183, pp. 1900–1904, 2010.
- [30] J.-Y. Li, S. Xiong, B. Xi, X.-G. Li, and Y.-T. Qian, “Synthesis of CuO perpendicularly cross-bedded microstructure via a precursor-based route,” *Crystal Growth & Design*, vol. 9, no. 9, pp. 4108–4115, 2009.
- [31] C. Mu and J. He, “Confined conversion of CuS nanowires to CuO nanotubes by annealing-induced diffusion in nanochannels,” *Nanoscale Research Letters*, vol. 6, 2011.
- [32] T. Lusiola, F. Bortolani, Q. Zhang, and R. A. Dorey, “Molten hydroxide synthesis as an alternative to molten salt synthesis for producing $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ lead free ceramics,” *Journal of Materials Science*, vol. 47, pp. 1938–1942, 2012.
- [33] J. T. Zeng, K. W. Kwok, and H. L. W. Chan, “ $\text{K}_x\text{Na}_{1-x}\text{NbO}_3$ powder synthesized by molten-salt process,” *Materials Letters*, vol. 61, pp. 409–411, 2007.
- [34] S. A. Hassanzadeh-Tabrizi, “Optimization of the synthesis parameters of high surface area ceria nanopowder prepared by surfactant assisted precipitation method,” *Applied Surface Science*, vol. 257, no. 24, pp. 10595–10600, 2011.
- [35] D. Keyson, D. P. Volanti, L. S. Cavalcante, A. Z. Simoes, J. A. Varela, and E. Longo, “CuO urchin-nanostructures synthesized from a domestic hydrothermal microwave method,” *Materials Research Bulletin*, vol. 43, pp. 771–775, 2008.
- [36] J. Yanyan, L. Jinggang, S. Xiaotao, N. Guiling, W. Chengyu, and G. Xiumei, “ CuAl_2O_4 powder synthesis by sol-gel method and its photodegradation property under visible light irradiation,” *Journal of Sol-Gel Science and Technology*, vol. 42, pp. 41–45, 2007.
- [37] M. Salavati-Niasari, F. Davar, and M. Farhadi, “Synthesis and characterization of spinel-type CuAl_2O_4 nanocrystalline by modified sol-gel method,” *Journal of Sol-Gel Science and Technology*, vol. 51, pp. 48–52, 2009.
- [38] T. Sato, “Low-Frequency Vibration to aluminas,” *Shigen to Sozhai*, vol. 114, pp. 987–990, 1998.
- [39] C.-Y. Hu, K. Shih, and J. O. Leckie, “Formation of copper aluminate spinel and cuprous aluminate delafossite to thermally stabilize simulated copper-laden sludge,” *Journal of Hazardous Materials*, vol. 181, pp. 399–404, 2010.
- [40] Y. Cudennec and A. Lecerf, “The transformation of $\text{Cu}(\text{OH})_2$ into CuO, revisited,” *Solid State Sciences*, vol. 5, no. 11-12, pp. 1471–1474, 2003.
- [41] V. K. J. KavithaGanesan, A. Natarajan, A. Rajaram, S. Ravichandran, and SatishRamalingam, “Green synthesis of copper oxide nanoparticles decorated with graphene oxide for anticancer activity and catalytic applications,” *Arabian Journal of Chemistry*, vol. 13, pp. 6802–6814, 2020.