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Soft chemical approach for the synthesis and characterization of aluminium copper oxide ($CuAl_2O_4$) nanopowder

Taimur Athar*

Indian Institute of Chemical Technology, Hyderabad (A.P.), India

*Corresponding author: Tel:(+91) 40-27191677: E-mail: taimurathar2001@gmail.com

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ABSTRACT

With the help of facile single source molecular precursor the synthesis of $CuAl_2O_4$ nanopowder with well-defined structural framework was carried out via cost-effective soft–chemical approach with two and three coordination state around copper and Aluminum atom respectively. The synthesized nanoparticles were thoroughly characterized by using several physicochemical techniques such as XRD, SEM, TEM, thermal analysis, UV and FT-IR for structural, optical and morphological studies. With the adjustment of reaction parameters allows us for systematic tuning of particle size, shape as well as to control the other functional properties. It can be concluded that self-assembly is an integral part which take place by understanding the metal chemistry during synthetic approach and therefore help to opens a new exciting opportunities for better understanding the reaction conditions, growth and along its mechanistic approach which leads to fabrication of potential nanodevise in near future.

Keywords: Soft-chemical process; characterization; particle size; shape; surface area.

Taimur Athar, Ph.D. is working as a Principal scientist in Indian Institute of Chemical Technology, Hyderabad. My research interest as follows: My research interests focused both in fundamental and technological applications with the help of synthesis of multifunctional and crystalline nanomaterials with desired chemical–physical properties and help for better understanding the structural-electronic-property relationship at the micro to nanoscale via soft–Green chemical approach. With designing of novel single source soft molecular precursor and understanding the mechanistic approach to design multifunctional nanostructure materials with controlled size and shape with better understanding the surface morphology then integrate it into cost–effective nanodevices with high selectivity, accuracy and reproducibility.

Introduction

The synthesis of colloidal and monodisperable functional nanomaterials has attracted an increasing interest because of their scientific and potential applications due to their size effects and nucleation growth process. The design of novel versatile functional structure take place via self–assembly with well–defined morphologies is important both for fundamental and technological research which help to fabricate a new devise for its futuristic applications with reliable–reproducible results. The fundamental properties of metal oxide nanomaterials depend in its architectural framework with required geometry, morphology, shape and hierarchical nanostructure with size **[1-8]**. Metal alkoxides are very good single source molecular precursor act as a nanoblock for the synthesis of their corresponding metal oxides material via self-assembly. The presence of M-O-C bond polarities, size and shape of the alkyl group, atomic radius, coordination number around metal ion along with degree of polarization govern the solubility and volatility as a prime requirement in the molecular precursors. The metal derivative of functional alcohol have good hydrolysis tendency which changes into its metal oxide nanomaterial at moderate conditions **[9-12]**.

The chemical environment in the molecular precursor with desired structural framework helps in coding functional properties in Inorganic materials at nanoscale. The heterometallic oxide material was synthesized via cost effective wet chemistry with required functional properties to give a high crystalline nanostructure powder in good yield **[13-17].**The soft-chemical synthetic approach is a reproducible process takes minimum time by balancing thermodynamic–kinetic parameters for controlling a growth process. The metal ion plays a critical role due to their coordination behavior for controlling a functional behavior, the nucleation, growth, orientation and formation of nanostructure material with high performance which depends with the tuning of surface–morphology. The process is flexible, simple and novel for the preparation of homogenous, well dispersed colloidal functional nanomaterials with large surface area at the bench scale and

then processing it to a production level **[15-17]**. The tuning of physical-chemical properties in nanoscale materials is a major driving force for its application research.

Experimental

Materials

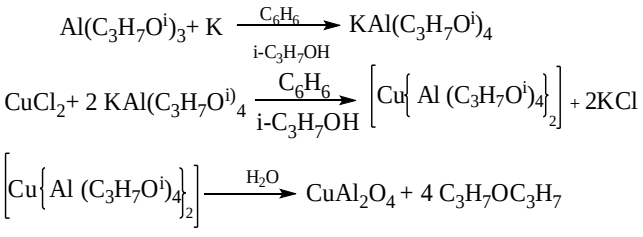
Anhydrous Copper chloride (98%), Potassium (99%), Aluminum isoproxide and organic solvents were purchased from Aldrich. Anhydrous Copper chloride was used without further purification. Organic solvents were further purified before use **[18, 19].** Aluminum isoproxide was distilled before use at 95^{o}C /0.6mm) .All operation was carried out under dry atmosphere with exclusion of dioxygen and moisture by using Schlenk vacuum line for the preparation of metal alkoxide. Considering the high reactivity of alkoxy–based metal derivative, the hydrolysis take place with water, which help to attains nucleation at moderate temperature to give a uniform particle size with its narrow distribution.

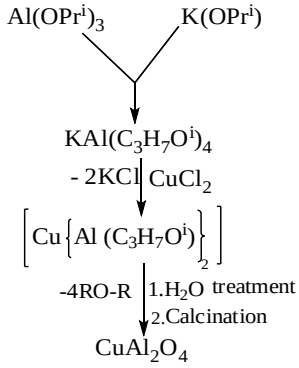
Synthesis of bimetallic oxide

A 2.51gm of K (63.94 mmol) was taken in C_6H_6 and then dry iso-C_3H_7OH was added into it. The iso-C_3H_7OH reacts with K, the exothermic reaction take place. Later on it was cooled to room temperature. It was refluxed and then stirred for another 30 minutes. To the same solution 13.04 gms Al $(OPr^i)_3$ (63.92 mmol) was added .The reaction mixture was refluxed for 4 hours. After cooling, it was filtered. In the filtrate, the 4.30gm of $CuCl_2$ (31.96 mmol) was added into it and then refluxed for another 6 hours. It was filtered in vacuo to separate out KCl. After drying the filtrate, brown solid alkoxide was obtained in good yield (80%). The bimetallic alkoxide was treated with de-ionized water. The resulting product were collected and washed several time by using iso-C_3H_7OH-de-ionized water mixture respectively and then dried at 70 ^{0}C for 6 hour in lab oven. After calcinations in dry air with the heating rate of 10 ^{o}C per minute from room temperature to 1000^{o}C.The cherry brown bimetallic oxide nanoparticle was obtained in good yield.

Characterization

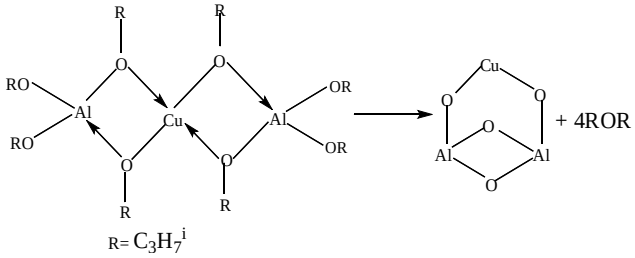
The spectroscopic data of H^1were recorded in $CDCl_3$ solvent on a Bruker AV-300MHz spectrometer and chemical shifts were reported in ppm. Elemental analysis was performed with the help of Vario EL analyzer. The optical properties were recorded by using GBC UV-vis Cintra spectrophotometer with wavelength ranging from 200-800 nm. FT-IR spectra was recorded in the range of 4000-400 cm^{-1} using KBr pellets in Perkin Elmer GX spectrometer with a wave number resolution of 4 cm^{-1}. Thermal analysis was carried out by heating the sample at the rate of 10 °C/minute from ambient to 1000 °C in dry air using Mettler Toledo star analyzer. X-ray powder diffraction patterns were taken in reflection mode of CuK_α (λ = 1.5406 Å) radiation in the range from 0θ to 80θ on a Siemens D5000 X-ray diffractometer by using continuous diffraction. Scanning microscope image was taken by using Hitachi S520 scanning electron microscope. EDX was done with the help of Oxford link ISIS-300 instrument. Philips Tecnai G^2 FEI F12 transmission electron microscope was operated at 80-100 kV and also for SAED. The samples were collected on a carbon holey copper grid to see morphology and particle size. The multi-point BET was acquired on QuadraSorb Station 3 under nitrogen atmosphere after degassing the sample at 200 °C for an hour.





R = $C_3H_7O^i$

Flow chart for the preparation of bimetallic oxide nanoparticle



Change from Bimetallic alkoxide to bimetallic oxide nanoparticle

Results and discussion

Metal alkoxide studies

FTIR spectroscopy: IR (Nujol) cm^{-1}, 1126 corresponds to the stretching vibration of iso-Proxy group, 1035 corresponds to the stretching vibration of C-O bond of the iso-proxy group. The presence of broad peaks at 620, 576 and 536 correspond to stretching vibration of Al-O-Cu, Cu-O and Al-O respectively **[20-23].**

^{I}H NMR: ^{I}H NMR in $CDCl_3$ was carried out at the room temperature. The double doublet peaks appears at δ1.21ppm (48H) which corresponds to the methyl group

present in the terminal and bridging alkoxy group and appearance of septet at δ4.46 ppm (8H) occurs due to methine protons. **[24-25].**

Elemental analysis

The calculated elemental value was less as compared to theoretical values as shown in the bracket, because hydrolysis takes place during sampling. C=48.27 (48.85), H= 9.07(9.49)

Molecular weight

The molecular weight of the bimetallic alkoxide was calculated with the help of cryoscopic method in dry benzene shows the dimeric nature due to the presence of Al^{3+} and Cu^{2+}.

Bimetallic oxide nanopowder studies

With the use of metal alkoxide as a single source molecular precursor (SSP), the synthesis of homogenous nanomaterials can be easily being carried out with correct stoichiometric ratio. The functional nanopowder obtained help to understand the relationship between structure-composition and along with other functional properties, which help to better understanding the chemistry of hierarchical structure for its effective applications to give reproducible with high accuracy-sensitivity-reliable results.

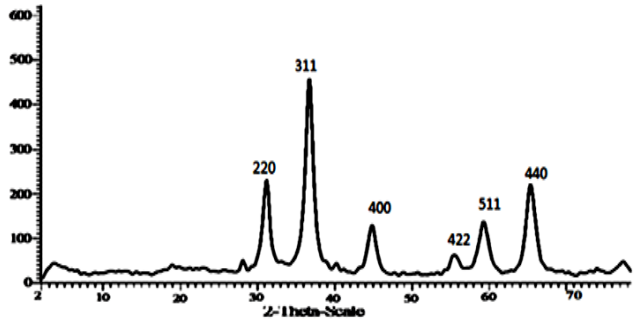


Fig. 1. X-ray diffraction pattern showing the reflection to crystallographic plane attributed to cubic phase**.**

XRD studies

The diffraction peaks show the tetragonal structure as illustrated in **Fig. 1** without the absence of any noticeable peaks for impurity and other side product. The presence of strong and sharp peaks suggests the formation of high crystalline particle with single phase. The crystal lattice increases with the change in atomic number. The average particle size was calculated by using Debye-Scherer equation. The average particle size was found to be 20.09 nm. The diffraction peaks match well with the database (JCPDS file #78-1605), which corresponds to tetragonal structure. EDX shows accurate stoichiometric ratio **[26-29]** .Calcinations plays an important role in the formation of crystalline phase with controlled particle size and narrow size distribution. It was concluded that the formation of the crystalline phases strongly depend with the types of molecular framework, the reaction time, temperature, solvent, synthetic methodology, heating rate and the type of molecular precursor used. The thermal and XRD analysis suggest the metal oxide nanopowder have high temperature and stability.

FT-IR studies

The broad peaks located at 592.25 and 685.7 can be attributed to the Al–O and Cu-O stretching and bending vibration present in the Inorganic network **[20 -23]**. Due to the surface vibration the change in surface structure takes place after calcination. With an influence of number of volume atoms present in framework help to decrease in lattice energy from the surface atoms which leads to tensile stress for renormalization of the surface atoms and to form a new vibration mode as illustrated in **Fig. 2.** Depending on the synthetic approach the crystalline nature increases due to Intra-intermolecular forces, which leads to the formation of self-assembled nanostructure powder as supported by thermal analysis and XRD studies. No change in vibration frequencies takes place even after ageing, which support the quantum size particle remains under control with no change in oxidation state of the metal ion. The symmetric broad band at 3444 cm^{-1} and deformation vibration of H-O-H at 1634.05 cm^{-1} support the presence of OH group due to absorption of moisture taking place during sample preparation from the atmosphere.

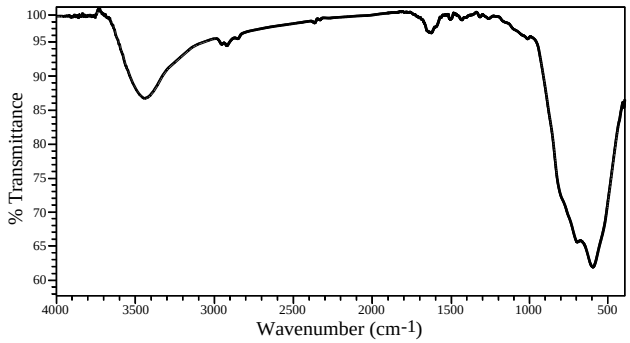


Fig. 2. FT-IR spectra of $CuAl_2O_4$ nanopowder**.**

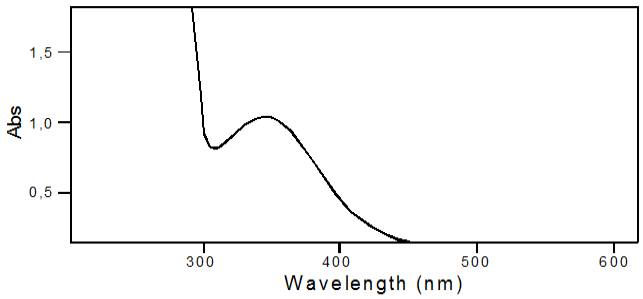


Fig. 3. UV-visible spectra of $CuAl_2O_4$ nanopowder**.**

UV-absorbance studies

UV–visible absorption of the nanostructured hierarchical $CuAl_2O_4$ architecture supports the exponential change occurs in the crystalline structure as shown in **Fig. 3**. It was observed that with linear increase in absorption help to enhance the photon energy in particle. The inclination of linear curve occurs due to UV interband absorption with charged transition take place from topmost occupied state

of valence band to the bottommost unoccupied state of the conduction band. The endo-exothermic absorption peaks centered at 315 nm and 350 nm corresponds to the Π- Π* transition with blue shift confirming the formation of monodisperse nanoparticle **[25].**

Thermal studies

The thermal studies show the loss occurs from 70 ^{o}C to 110^{o}C which can be attributed to the elimination of low boiling solvent along with dehydration. From 650 ^{o}C to 670 ^{o}C correspond to dehydroxylation and its conversion into metal oxide nanomaterials take place with change in phase purity. The DTA curve at 680^{o}C corresponds to the decomposition of impure fraction which leads to the purity of particle. The DTA curve shows the presence of broad endothermic peaks take place with the reduction in the surface area .The change at 190 ^{o}C refers to the weight loss along with the solvent evaporation and decomposition of material. The purity of the particle takes place at 680^{o}C after the complete removal of surface impurities as shown in **Fig. 4 [29-30].**

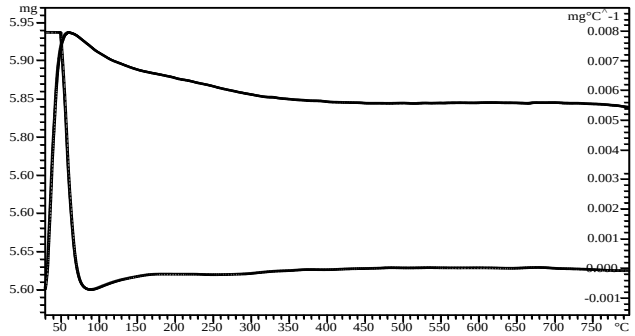


Fig. 4. Thermal Analysis of the $CuAl_2O_4$ nanopowder.

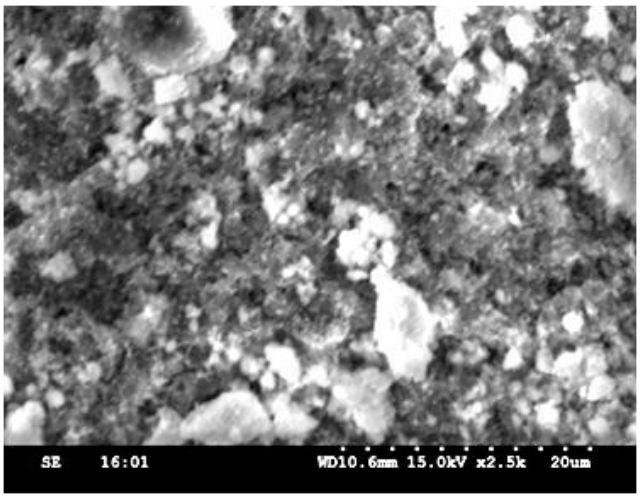


Fig. 5. SEM micrograph of the $CuAl_2O_4$ nanoparticles.

SEM and TEM studies

The surface morphology and average size of a bimetallic oxide nanomaterial was investigated with the help of SEM and TEM respectively as shown in the **Fig. 5** and **Fig. 6 [32-35].**

The morphology of the variable particle with high precision is not possible due to agglomeration taking place due to Oswald–ripening process as shown with SEM image in the **Fig. 5.** Micrograph shows the occurrence of agglomerated particle with few micrometers in size.
The appearance of an irregular particle size with dark and white patches shows the presence of intensity and size with limited saturation as shown in the **Fig. 5**. The present of substantial homogeneity reflect the relatively clean surface morphology, which depend with mass ratio of the reactant. With the careful observation shows the porosity occurs with an increase in surface area for future applications in nanodevices.

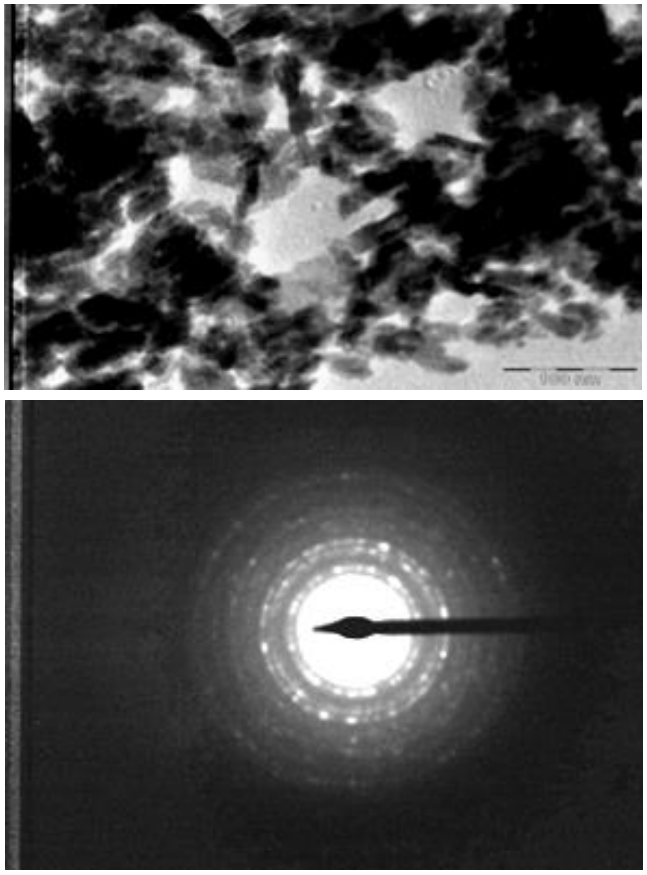


Fig. 6. TEM micrograph illustrate particle pattern with SAED for $CuAl_2O_4$ nanoparticles**.**

It is observed that the particles are distinguishable from each other with uniform size distribution. Analysis of image shows the particle size has a relatively good disparity which agrees support the formation of crystallite size. The nucleation and growth is controlled by the reaction parameters along with Oswald ripening mediated process which help to get a correct phase behavior and solubility based in good knowledge of surface chemistry. The mass ratio of the reactant plays a crucial role in defining the nature of the dispersion of the powder depends with synthetic methodologies.

The SAED pattern taken from an individual nanoparticle shows the presence of sharp diffraction spots along with connecting diffuse rings as illustrated in **Fig. 6**. The small size connects with rings in a short range. Thereby support the presence of well-defined single crystal.

The intensity of the diffraction rings indicates a formation of crystalline structure of the particle with its narrow distribution. It is concluded that the growth process can be co-related with colloidal interaction between the molecular templates as well as nucleation process during the synthetic approach.

BET studies

The surface area was found to be 4.95m^2/g. It supports that the formation of crystalline structure with limited porosity. The pore size requirement needs a better understanding to maximize the performance-property relationship. The size of the nanopowder can be controlled by changing the pore diameter. The average pore diameter lies in between 40-45 nm and pore volume with 0.05cm^3/g. With an increase in temperature both the pore diameter and pore volume of the sample decreases with surface area as shown in **Fig. 7 [36-38].**

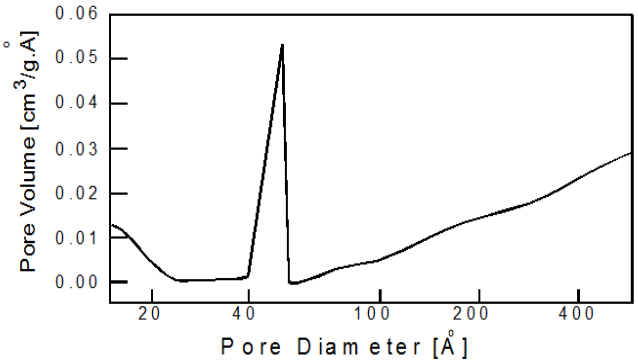


Fig. 7. Illustrating the relationship between pore diameter and its volume for the $CuAl_2O_4$ nanopowder**.**

Conclusion

Wet chemical green synthesis offers a high degree of flexibility with desired size, shape and morphology by retaining the stoichiometric ratio under control for the synthesis of functional nanomaterials from single source molecular precursor as metal alkoxide. With the help of physico-chemical properties in metal oxide nanopowder, it is easy to fabricate a device for use in future applications. The synthetic approach gives a favorable architectural framework for other types of functional nanomaterials with other materials, which help to design other multifunctional nano-object with high selectivity-reliability-reproducible results at the bench scale to scale up to the production scale. The nanostructured hierarchical $CuAl_2O_4$ architectural material with favorable structure, chemical and electrical properties is a promising candidate for the fabrication of sensor devices.

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