Synthesis And Characterization of Copper Titanium Oxide Nanomaterials

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***Abstract*—Copper Titanium Oxide nanocomposite have significant attention due to their promising applications in photocatalysis, gas sensing and optoelectronic devices. In this work, Copper Titanium Oxide nanocomposites are successfully prepared by using a combined sol-gel and mechano-chemical ball milling approach. Initially CuO nanoparticles were prepared via sole-gel method using Cupric Chloride dihydrate as the copper pre cursor, Sodium Hydroxide as precipitate agent and acetic acid as complexing agent. The obtained wet CuO nanoparticles were mixed with Titanium Oxide microparticles in 3 different weight ratios of 1:3, 1:4, and 1:5. Each mixture is subjected to high energy planetary ball milling using a ball-to-powder weight ratio of 10:1 which allowed effective mechanochemical interaction between CuO and TiO_2 and promoted the formation of Copper Titanium Oxide phases. Following ball milling process the obtained powder is calcinated at 450ºC for 8hours to enhance phase formation, improve crystallinity and reduce the particle size into the nanometer range.**

The structural, morphological and compositional characteristics of the synthesized nanocomposites were investigated by using X-ray diffraction (XRD), Raman spectroscopy, Scanning electron microscopy and Energy dispersive X-ray spectroscopy. these techniques are employed to analyze phase formation, crystalline size, morphology, and elemental composition of the $CuTiO_3$ nanocomposites.

***Index Terms*—Copper Titanium Oxide nanocomposites, Mechano-chemical synthesis, XRD, EDAX, SEM**

I. INTRODUCTION:

Transition Metal oxide nanocomposites have emerged as significant materials because of their tuneable physiochemical properties. They exhibit unique electrical, catalytic and optical properties. Particularly $CuTiO_3$ exhibits many favourable properties such as narrow band gap energy, high chemical stability, high surface area and enhanced charge carrier separation, making it suitable for the applications in photocatalysis, gas sensing and optoelectronic devices.

The incorporation of Cu^{2+} ions into TiO_2 lattice introduces defect states and oxygen vacancies, which plays an important role in absorption of visible light and surface reactivity. Compared to single phase oxides, $CuTiO_3$ nanocomposites demonstrate superior performance due to interfacial charge transfer and defect mediated catalytic activity.

At nanoscale, $CuTiO_3$ exhibit size dependent properties that are strongly influenced by morphology and degree of structural disorder. Nano structuring increases surface area and promotes efficient mass and charge transport. However, achieving phase-pure $CuTiO_3$ with controlled nano crystallinity remains challenging, as conventional synthesis routes often require high temperatures and prolonged processing times, which can lead to grain growth and secondary phase formation.

Mechano-chemical synthesis such as high energy ball milling, offers a cost-effective and scalable approach for producing oxide nanocomposites with controlled structural features. When combined with wet chemical methods with chemicals methods like sol-gel synthesis, mechano-chemical synthesis process enables mixing at the atomic level, promotes solid state diffusion and facilitates phase formation at relatively lower temperatures. This hybrid approach of synthesis

of $CuTiO_3$ nanocomposites beneficial in reduced crystalline size.

In this context, present work focuses on the synthesis of $CuTiO_3$ nano composites using sol-gel assisted high energy ball milling route, followed by controlled calcination. The influence of CuO: TiO_2 compositional variation on phase formation, crystallinity and morphology is systematically investigated. Structural and morphological characteristics are analysed using X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM) and Energy dispersive X-ray spectroscopy, providing insights into crystalline size, microstructural evolution and elemental analysis. The results are evident of the formation of nanocrystalline $CuTiO_3$ and its potential to be used in different applications.

II. MATERIALS AND REAGENTS

- Cupric chloride dihydrate ($CuCl_2 \cdot 2H_2O$) – Copper precursor
- Sodium hydroxide (NaOH) – pH adjusting agent
- Acetic acid (CH_3COOH) – Reaction stabilizing agent
- Deionized water – Solvent for all preparations

SYNTHESIS OF CUO NANOPARTICLES:

CuO nanoparticles were synthesized using a controlled wet-chemical precipitation route.

The aqueous solution (0.2M) was prepared by dissolving cupric chloride dihydrate in de-ionized water. NAOH pellets were dissolved in the de-ionized water to obtain NAOH solution (8M).

The prepared aqueous solution was mixed with glacial acetic acid to stabilize the reaction medium. The solution was under continuous magnetic stirring heated up to 80ºC temperature to achieve homogeneous ion distribution. The pH of the mixed aqueous solution was adjusted to approximately 7 by the dropwise addition of NaOH solution, promoting controlled nucleation and growth of CuO particles.

The resulting precipitate was collected by filtering through filter paper and washed repeatedly with deionized water to remove unreacted ions and by-products, followed by draining. The washed material was kept drained till wet CuO particles were obtained.

SYNTHESIS OF $CUTIO_3$ NANOCOMPOSITES:

Copper Titanium oxide nanocomposites were synthesized in 3 different ratios using Ball Milling method. The wet copper oxide nanoparticles synthesized by sol-gel method and titanium dioxide powders are taken in ratio of 1:3 i.e., 10 grams of CuO nanoparticles combined with 30 grams of TiO2 powders and subjected to mechano chemical synthesis using high energy ball milling equipment. This process was carried out for 36 hours. The powder then obtained is calcinated at 450ºC for 8 hours to remove any moisture present in the sample. The same process is used for the preparation of other two samples in the ratio of 1:4 and 1:5 i.e., 10 grams of wet copper oxide nanoparticles combined with 40 and 50 grams of titanium dioxide powders and ball milled for 42 and 48 hours. These samples are calcinated at 450ºC for 8 hours to remove any present. Then the samples are characterized to know the characteristics.

III.CHARACTERIZATION:

STRUCTURAL CHARACTERIZATION:

- X-ray Diffraction (XRD)

Purpose: Phase identification, crystallinity, crystallite size estimation

MORPHOLOGICAL AND ELEMENTAL ANALYSIS:

- Scanning Electron Microscopy (SEM)
  Purpose: Surface morphology and particle distribution
- Energy Dispersive X-ray Spectroscopy (EDS/EDAX)
  Purpose: Elemental composition and stoichiometry verification

VIBRATIONAL ANALYSIS

- Raman Spectroscopy
  Purpose: Phase confirmation and detection of secondary phases

STRUCTURAL CHARACTERIZATION

The crystalline structure and phase composition of the synthesized Copper Titanium Oxide were analyzed using X-ray diffraction (XRD) with Cu Kα radiation. Diffraction patterns were recorded over a broad 2θ range. Structural parameters including interplanar

spacing, average crystallite size, and dislocation density were calculated from the diffraction data to assess the influence of precursor composition on crystal growth and structural quality.

MORPHOLOGICAL AND ELEMENTAL ANALYSIS

Surface morphology and particle distribution were examined using Scanning electron microscopy (SEM). Elemental composition and stoichiometry were evaluated using energy-dispersive X-ray spectroscopy (EDS) attached to the SEM system, confirming the presence and relative distribution of Copper, Titanium and oxygen.

RAMAN SPECTROSCOPY

Raman spectroscopy was employed to confirm phase formation and assess the structural integrity of the $CuTiO_3$. Characteristic vibrational modes were analyzed to distinguish $CuTiO_3$ from possible secondary phases and to validate crystallographic consistency across different compositions.

IV. RESULTS:

X-RAY DIFFRACTION TECHNIQUE:

XRD patterns of the 3 synthesized $CuTiO_3$ samples recorded in the 2Θ range of 10-80°C using Cu Kα radiation (λ=1.5406 Aº) confirmed crystalline nature of the materials. All the 3 samples exhibited a prominent diffraction peak centered at 2Θ ≈ 25°, along with additional reflections in the range of 35-75°, indicating formation of a well-defined crystalline phase.

Crystalline size of the samples was calculated using Scherrer equation. For 1:3 ratio samples the crystallite size varied approximately from 15 to 58nm, for 1:4 ratio samples the crystallite size varied between 21 to 39 nm and for 1:5 sample it varied from 15-41nm. The variations in the crystallite sizes can be attributed to synthesis conditions, which influence nucleation and grain growth mechanism.

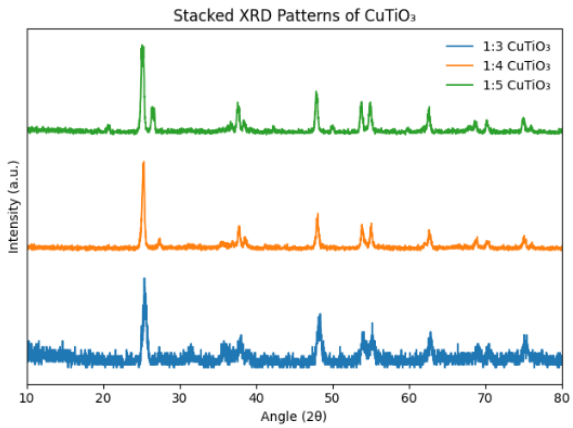
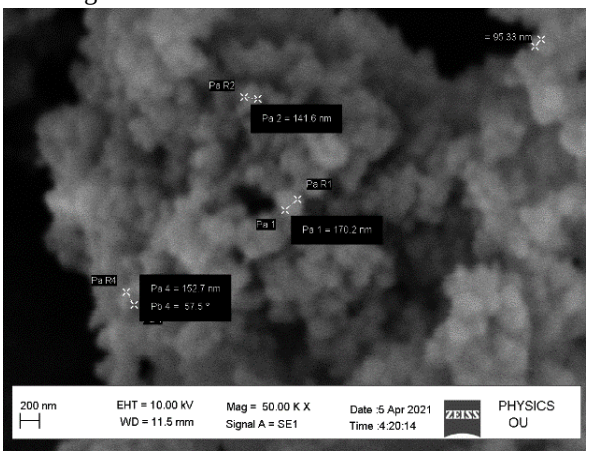


FIG. XRD PATTERNS OF 1:3,1:4,1:5 $CUTIO_3$ SAMPLES

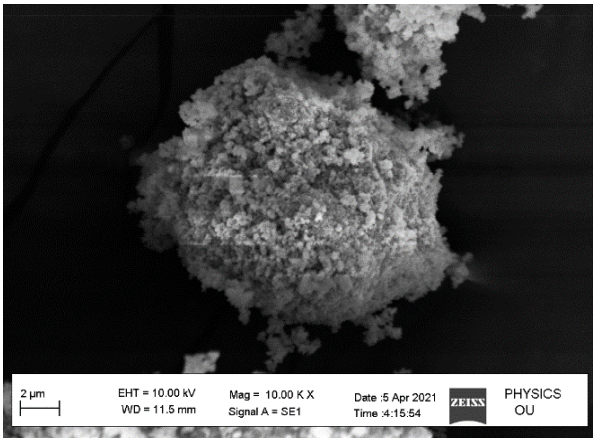
The strong peak at 2Θ ≈ 25° in all samples indicate that relatively larger FWHM values and compared to higher-angle reflections confirming the nanocrystalline nature of the synthesized $CuTiO_3$ samples.

SCANNING ELECTRON MICROSCOPY:

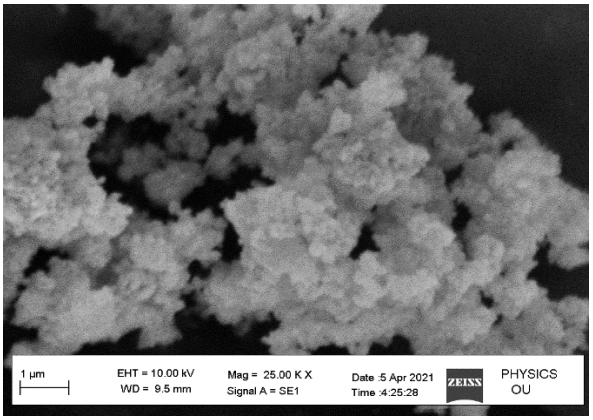
a. SEM image of 1:3 $CuTiO_3$ sample at 50000X magnification



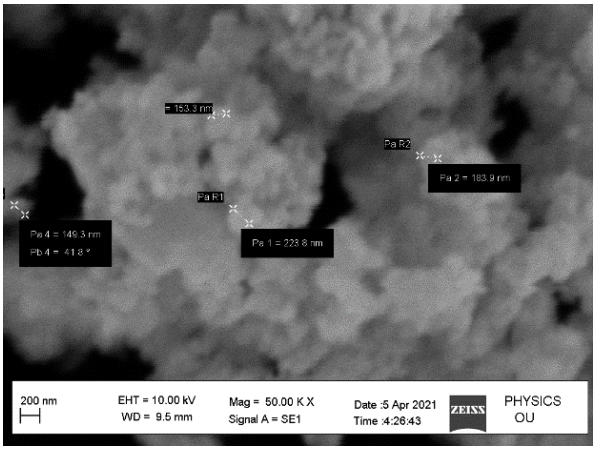
b. SEM image of 1:3 $CuTiO_3$ sample at 10000X magnification



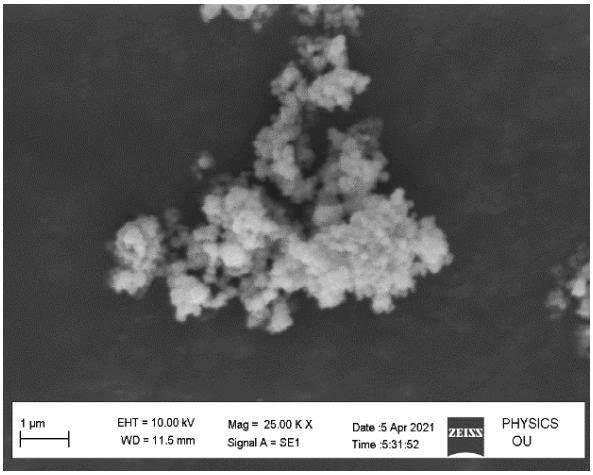
c. SEM image of 1:4 $CuTiO_3$ sample at 25000X magnification



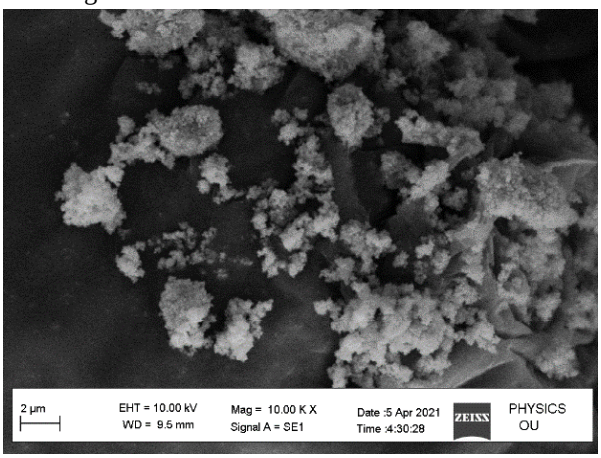
d. SEM image of 1:4 $CuTiO_3$ sample at 50000X magnification



e. SEM image of 1:5 $CuTiO_3$ sample at 25000X magnification



f. SEM image of 1:5 $CuTiO_3$ sample at 10000X magnification



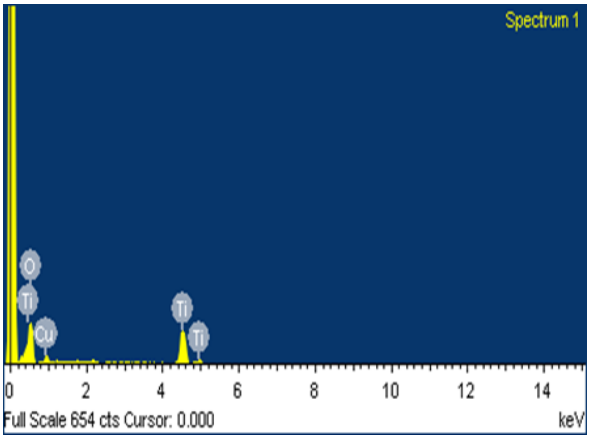
SEM was employed to determine the surface morphology, particle size distribution and agglomeration behavior of the synthesized nanomaterials. The SEM images at different magnifications were recorded to reveal the formation of nanostructured composites and varying degrees of agglomeration.

The sample 1:3 (fig.a) shows densely packed agglomerates composed of spherical shaped nanoparticles and individual particle size directly measured from image lies in the range of 130-170 nm, indicating the aggregation of smaller crystallites. The sample of ratio 1:4 consists of more uniformly distributed particles forming cauliflower like agglomerates composed of finer grains. It suggests improved nucleation and grain growth. The sample 1:5

at lower magnification revealed loosely packed agglomerates. Compared to the other two samples this exhibits relatively larger agglomerates. This porous and non-uniform morphology can be related to different synthesis conditions. Such porous advantageous for applications requiring high surface area including catalysis and sensing.

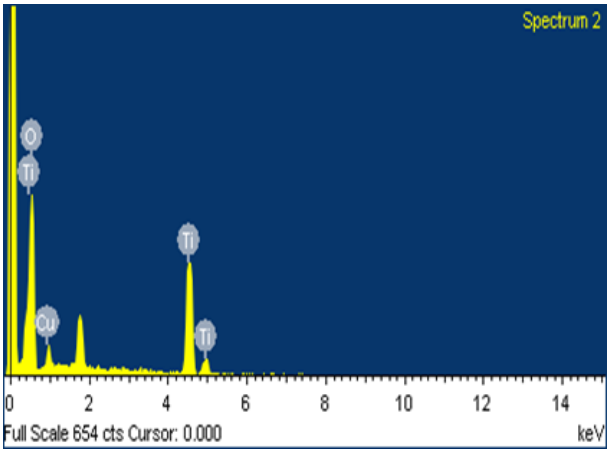
V.ENERGY DISPERSIVE X-RAY SPECTROSCOPY:

a. EDAX SPECTRUM OF 1:3 COPPER -Titanium Oxide Nanocomposites:



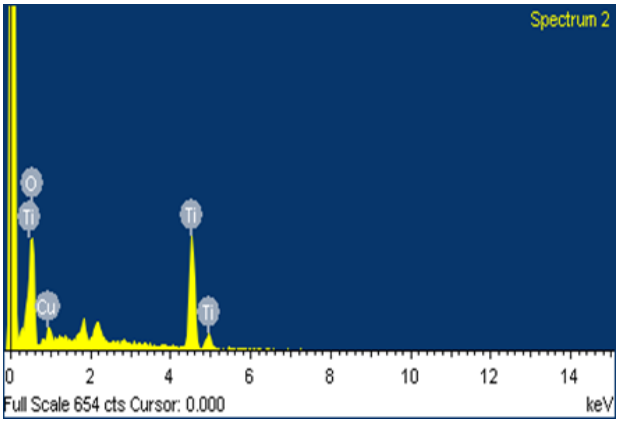
Element	Weight%	Atomic%
O K	34.63	61.72
Ti K	60.94	36.29
Cu L	4.43	1.99
Totals	100.00	

b. EDAX SPECTRUM OF 1:4 COPPER -Titanium Oxide Nanocomposites:



Element	Weight%	Atomic%
O K	37.49	64.76
Ti K	56.71	32.72
Cu L	5.80	2.52
Totals	100.00	

c. EDAX SPECTRUM OF 1:5 COPPER Titanium Oxide Nanocomposites:



Element	Weight%	Atomic%
O K	42.69	69.45
Ti K	52.85	28.72
Cu L	4.46	1.83
Totals	100.00	

EDAX was employed for the elemental analysis of the synthesized Copper Titanium Oxide nanocomposites. This analysis confirms the presence of Cu-Ti-O elements and no other detectable impurities are present in the samples, validating the successful synthesis of chemically pure Copper Titanium Oxide nanocomposites.

VI. RAMAN SPECTROSCOPY:

Raman spectroscopy was employed to further validate phase formation and structural integrity of the $CuTiO_3$ nanocomposites. The recorded Raman spectra show characteristic vibrational modes associated with $CuTiO_3$, confirming the formation of the desired phase. The absence of strong secondary-phase peaks

suggests the formation of single-phase Copper Titanium Oxide. Raman spectroscopy gives the graph between intensity and Raman shift. Raman spectra of all 3 samples exhibit multiple well defined vibrational modes within the 100-1000 cm^{-1}. The extracted spectra were studied for reliable comparison of peak positions and relative intensities. The 1:3 sample exhibited highest Raman intensities with particular strong modes observed near 770~795 cm^{-1} and 915-980 cm^{-1}. For 1:4 and 1:5 samples similar peak positions as 1:3 sample i.e., 720-795cm^{-} and 890-970 cm^{-1} can be seen but significantly reduced intensities and slightly broadening peaks were noted. The sharp and well resolved peak positions in1:3 sample indicates high degree of long-range structural order. The gradual reduction of peak sharpness from 1:3-1:4-1:5 indicates progressive structural degradation. Structural degradation caused likely due to difference in synthesis conditions such as precursor homogeneity, duration or calcination temperature.

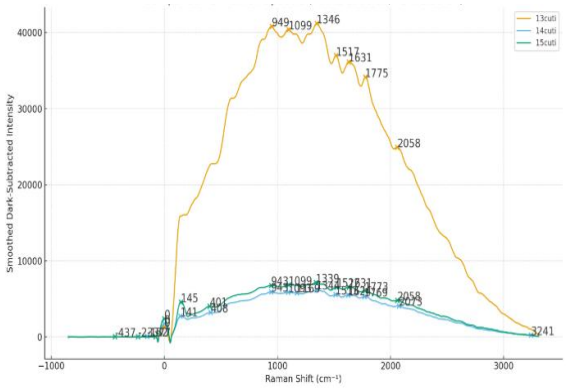


FIG. RAMAN SPECTRA OF 1:3,1:4,1:5 $CUTIO_3$ NANOCOMPOSITES

Raman spectroscopy confirms the synthesis of $CuTiO_3$ with no detectable secondary phases. Variation peak intensities and sharpness differ in degrees of crystallinity, with 1:3 sample showing superior structural order comparatively.

VII. CONCLUSION:

- Copper titanium oxide nanoparticles were synthesized using sol gel method for the CuO nanoparticles and high energy ball milling to synthesize copper titanium oxide using TiO2 powders.
- Through X-ray Diffraction technique crystalline size of the samples was calculated using Scherrer equation. For 1:3 ratio samples the crystallite size varied approximately from 15 to 58nm, for 1:4 ratio samples the crystallite size varied between 21 to 39 nm and for 1:5 sample it varied from 15-41nm.
- Raman spectroscopy was done for the 3 synthesized samples of different ratios and the peak intensity values of all 3 samples were almost similar to each other while 1:3 ratio sample shown superior crystallinity comparatively.
- EDAX was done for all the 3 samples and the elemental percentages of Copper, Titanium and Oxygen were determined.
- SEM analysis to know the morphology is done and it was observed that nanoparticles are agglomerated. In 1:3 Copper Titanium oxide typical nanoparticles clusters with clear boundaries are visible
- In 1:4 sample more sintered and denser aggregates are possibly due to high reaction sensitivity were visible.
- In 1:5 sample cauliflower like structure nanoparticles agglomerates were visible.

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