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SYNTHESIS AND CHARACTERIZATION OF NANO CuO/Al_2O_3 MIXED OXIDES BY CHEMICAL COPRECIPITATION WITHOUT USING ADDITIVES

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ABSTRACT

In this research, mixed oxides nanoparticles of CuO/Al_2O_3 were synthesized by chemical coprecitation without the use of additives (surfactants). The use of additives in the synthesis of nanoparticles by coprecipitation results in less aggregation and enhances finer nanoparticles. However, non use of surfactant in the nanoparticles synthesis of CuO/Al_2O_3 can be explore in the process eliminating the additional cost especially where the application of the particles is for reinforcement purposes if nanoscale particles can be achieved without additives as seen in this research. An average crystallite size of 92.12nm was achieved and the X-ray Diffraction (XRD) pattern shows a different combination of peaks produce from different phases which validates that produced particles is a mixture. Observation of the shapes in the micrograph of produced particles suggests spherical from CuO and spike from Al_2O_3 which further validates mixed components.

Keyword: *Characterisation, Coprecipitation, Mixed-oxide, Nanoparticles, Nanotechnology, Surfactant.*

INTRODUCTION

A nanoparticle (or nanopowder or nanocluster or nanocrystal) is a microscopic particle with at least one dimension less than 100 nm [9]. Nanoparticles are of great scientific interest because they are effectively a link between bulk materials and atomic or molecular structures [12]. Notably, the properties (especially surface area to volume ratio) of materials change as their size approaches the nanoscale and as the percentage of atoms at the surface of a material becomes significant. According to [9], Nanoparticles exhibit a number of special properties relative to bulk materials. For instance, Copper nanoparticles smaller than 50 nm are found to be super hard materials that do not exhibit the same malleability and ductility as bulk copper. Also, Nanoparticles have unexpected visible properties; for instance gold nanoparticles have been seen to appear deep red to black in solution, because they are small enough to confine their electrons and produce quantum effects.

After several years of intense research effort, it is apparent that a considerable numbers of synthesis approaches to a great variety of nanoparticles are available [13][5]. There are various methods that can be employed in the synthesis of nanoparticles, but these methods are broadly divided into two main classes [6][9] i.e. Bottom-up approach and Top-down approach. Various chemical, physical and biological synthetic methods have been used in production of metal nanoparticles [13] and the problems experienced are stability and aggregation of nanoparticles, control of crystal growth, morphology, size and size distribution [6][9]. Precipitation is defined as the process of forming a phase-separated solid from homogeneous solution, after supersaturation with respect to the precipitating solid has been achieved [4]. The process of solid formation can be induced by addition of an agent (additive) which initiates a chemical reaction or which reduces the solubility (antisolvent) of solid formed. Precipitation normally involves high supersaturation, and thus frequently amorphous intermediates are obtained as the first solids formed [4].

It is worthy of note that simultaneous precipitation of more than one component can occur from normally soluble components which is termed coprecipitation. When this happens in most cases, both components to be precipitated are essentially insoluble under precipitation conditions, although their solubility products might differ substantially. Hence, according to the IUPAC nomenclature, coprecipitation is the simultaneous precipitation of a normally soluble component with a macrocomponent from the same solution by the formation of mixed crystals, by adsorption, occlusion, or mechanical entrapment. Coprecipitation provides the possibility of creating very pure materials (Precipitate) and the flexibility of the process with respect to final product quality. However, there are factors that can affect the quality of precipitate and the final

product. These factors include; Nature of the raw materials, concentration and composition of components [16], used solvent, reaction temperature [4][7], Influence of pH, Aging time and Influence of Additives [14][3].
The use of additives or surfactants in coprecipitation synthesis of nanoparticles is seen in [14][3][17][18] and very fine particle sizes were achieved. Synthesis and characterisation of nano mixed oxides of CuO-Al_2O_3 by chemical coprecipitation is carried out in the presence of surfactant like Cetyltrimethylammonium bromide (CTAB) [17][19]. However, non use of surfactant can be explore thereby removing extra chemical presence and procurement cost in the process [20] and hence the need for synthesis without the use of surfactant. Moreover, feature size of 100nm can still produce strengthening and toughening properties likewise modify hardness and plasticity properties as discussed in [2].

Therefore, the aim of this work is to synthesize and characterise mixed oxides nanoparticles of CuO/Al_2O_3 by chemical coprecitation without the use of surfactant. Aluminium oxides and its hydrates have variety of useful physical and chemical properties like large hardness, insolubility in solvents and inertness to some chemical compounds [8]. Copper-oxides (Cu_2O and CuO) nanostructures likewise have drawn considerable research attention because of their many interesting physical and chemical properties, including thermal and electrical conductivities, semiconductor property, catalytic activity, anti-microbial activity, sensor property etc. [1].

MATERIALS AND METHODS

To synthesise CuO/Al_2O_3 nanoparticles by coprecipitation, solution of 0.1M Copper nitrate from Copper Nitrate trihydrate and 0.1M Aluminium nitrate from Aluminium Nitrate nonahydrate were prepared. Also, Solution of 0.2M Sodium hydroxide was prepared from flaked Sodium hydroxide. The solutions were prepared based on the required molarities. Equal volume ratio solution (mixture) of 0.1M copper nitrate and Aluminium nitrate was titrated against 0.2M sodium hydroxide solution. The end point was monitor using change of red litmus paper to blue. The obtained product was centrifuged (to ensure complete reaction and enhance separation of precipitate) at 2500r/min for 15min. Water bath was used to heat to 80°C which helps in separating more of the precipitate from the solution and further converting of intermediate product to end product. As shown in Figure 2a, colour change from deep blue is observed in the process until there is clear separation (Figure 2b) of precipitate from solution. The clear liquid is carefully decanted from the precipitate. The precipitate was filtered and washed with ethanol to cleanse precipitate of residue reactants. The black precipitate obtained was dried at 60°C to evaporate residue ethanol and moisture, followed by calcination at 600°C to convert the obtained hydroxide into Nano mixed oxide. The calcined mixed oxide was ball milled to obtain the nano mixed oxide powder.

Chemical Reaction Equations

$$Cu(NO_3)_2(aq) + 2NaOH(aq) \rightarrow Cu(OH)_2(s) + 2NaNO_3(aq) \quad (1)$$

$$Cu(OH)_2 \xrightarrow{heat} CuO + H_2O \quad (2)$$

$$Al(NO_3)_3(aq) + 3NaOH(aq) \rightarrow Al(OH)_3(s) + 3NaNO_3(aq) \quad (3)$$

$$2Al(OH)_3 \xrightarrow{heat} Al_2O_3 + 3H_2O \quad (4)$$

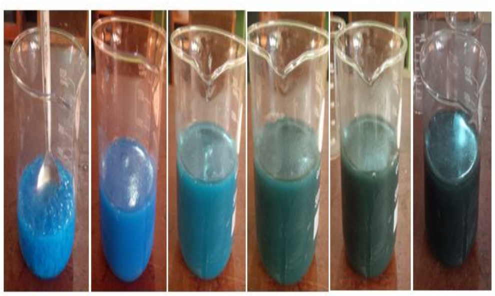

Figure 2a

Figure 2b.

Figure 2a: *Observe colour change in the reacted mixed of $Cu(NO_3)_2(aq)$ $Al(NO_3)_3(aq)$ solution with 3NaOH(aq) solution*.
Figure 2b: *Clearly separated precipitate of CuO/Al_2O_3*

X-ray diffraction (XRD) test was carried out on the produced powder using Empyrean X-ray Diffractometer, CuKα radiation, in the 2θ range 0 - 80° with a step of 0.026°. Also surface morphology of the produced powder was examined using Phenom ProX (by Phenomworld, Eindhoven Netherlands) scanning electron microscope, available in Ahmadu Bello university (ABU), Zaria, Nigeria. The scanning electron microscope (SEM) was operated at 15KV at various magnifications.

RESULTS AND DISCUSSION

X-ray diffraction analysis (XRD) pattern differs for different element/compound and crystallite sizes. X-ray diffraction analysis pattern of obtained mixed nano CuO/Al_3O_2 powder is presented in figure 3. The X-ray diffraction analysis pattern agrees with nano CuO/Al_3O_2 powder pattern as in [10] and also shows a different combination of peaks produce from different phases which validates that produced powder is a mixture [15]. Peaks from the X-ray diffraction pattern in Figure 3 were taken and crystallite size at each peak was calculated using the Scherrer's formula as presented in Table 1. The average particle size [Dp Average (nm)] was gotten from the calculated crystallite sizes of the peak lists in XRD pattern using Scherrer's formula [11]:

$$Dp = \frac{K\lambda}{(B\cos\theta)} \qquad (5)$$

Where Dp - Average crystallite size (nm), K - Scherrer constant, λ - X-ray wavelength, B - FWHM (Full Width at Half Maximum) of XRD peak and θ - XRD peak position, one half of 2θ. The average crystallite size of particles was calculated to be 92.12nm which is within the nanoscale range [9].

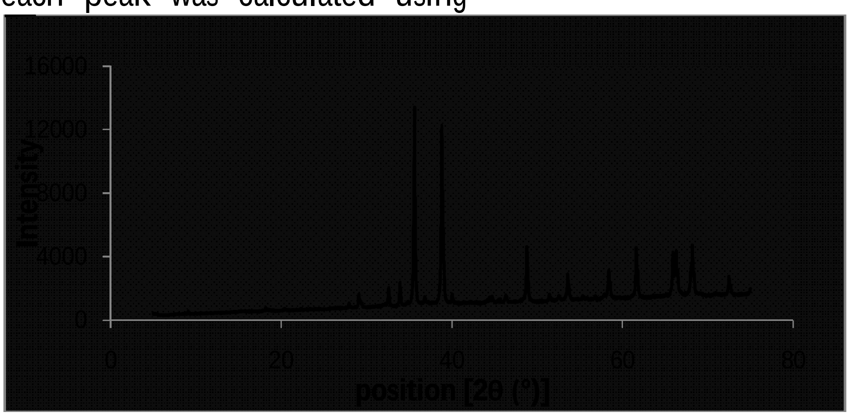

Figure 3: *XRD analysis pattern for mixed oxides of CuO/Al_3O_2 powder*

Table 1: *Table of Peak List from XRD pattern of mixed oxides of CuO/Al_3O_2 powder and crystallite size calculation*

S/No	Peak position 2θ (°)	Height [cts]	d-spacing [Å]	FWHM B_{size} (°)	Crystallite size Dp (nm)
1	29.0966	833.48	3.06906	0.1023	83.79
2	32.603	1126.59	2.74656	0.1023	84.51
3	33.9231	1434.52	2.64264	0.1023	84.80
4	35.6172	11283.2	2.52073	0.1279	68.14
5	38.8129	10354.3	2.31831	0.0936	93.99
6	38.9621	5591.69	2.31552	0.0624	141.05
7	48.7776	3400.9	1.86546	0.0936	97.33
8	53.5736	1604.34	1.70922	0.0936	99.30
9	58.3861	1756.07	1.57928	0.1248	76.16
10	61.6016	3147.63	1.50433	0.0936	103.20
11	65.903	2674.91	1.41618	0.0936	105.64
12	66.2874	2732.36	1.40889	0.1248	79.40
13	66.4766	1581.99	1.40883	0.0936	105.99
14	68.1875	3140.32	1.37419	0.0936	107.05
15	68.3922	1380.42	1.37398	0.1248	80.38
16	72.4736	1146.48	1.30311	0.1248	82.43

Observation of the surface morphology of the produced powder as seen in micrographs Figure 4a, 4b, 4c reveal produced powder constitutes mixture of different materials which validates the powder is a mixed oxides. Also, observation of the monographs (Figure 4a, 4b, 4c), particle size of nanoscale dimensions (<100 nm) are clearly noticeable. It equally suggests homogeneity of mixture of formed CuO/Al_3O_2 components and particles are irregularly shaped with the presence of nodular individual particles, with the rough surface morphology.

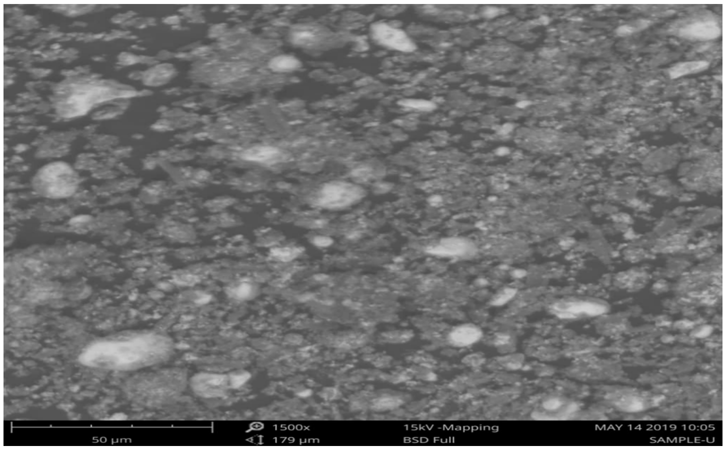

Figure 4a: *Micrograph of Nano CuO/Al_2O_3 powder (x1500)*

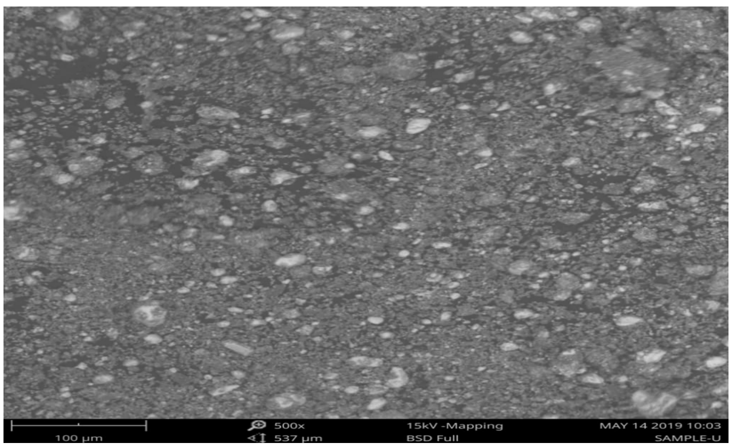

Figure 4b: *Micrograph of Nano CuO/Al_2O_3 powder (x500)*

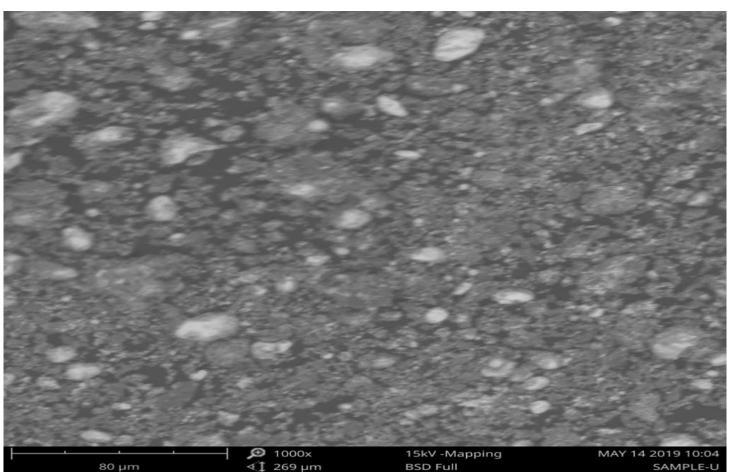

Figure 4c: *Micrograph of Nano CuO/Al_2O_3 powder (x1000)*

CONCLUSIONS

The characterization of the produced nano mixed oxide results show that mixed oxide of CuO and Al_2O_3 of nanoscale range (<100 nm) was achieved by coprecipitation even without the use of surfactants. Coprecipitation results in the formation of mixed crystal, by the results of X-ray Diffraction (XRD) pattern which shows a different combination of peaks produce from different phases. Observation of the shapes in the micrographs of produced particles suggest spherical from CuO and spike from Al_2O_3 which further validates mixed components by coprecipitation. The produced crystallite size of 92.12 nm mixed oxide of CuO and Al_2O_3 which was achieved can be a good reinforcement material especially for metal matrix.

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Conflict of Interests

The authors declared none.

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