Research Article

Synthesis and Characterization of CuO, TiO₂, and CuO-TiO₂ Mixed Oxide by a Modified Oxalate Route

Ekane Peter Etape,¹ Lambi John Ngolui,² Josepha Foba-Tendo,¹
Divine Mbom Yufanyi,³ and Beckley Victorine Namondo¹

¹Department of Chemistry, Faculty of Science, University of Buea, P.O. Box 63, Buea, Cameroon

²Department of Chemistry, ENS Yaoundé, BP 47, Yaoundé, Cameroon

³Department of Chemistry, Faculty of Science, The University of Bamenda, P.O. Box 39, Bambili, Bamenda, Cameroon

Correspondence should be addressed to Josepha Foba-Tendo; jnfoba@gmail.com

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Copper oxide (CuO), titanium oxide (TiO₂), and Cu-doped TiO₂ nanoparticles have been synthesized by pyrolysis of their corresponding precursors initially prepared by precipitation in aqueous solution using *A. carambola* fruit juice as a natural source of the precipitating agent (oxalate). The precursors were synthesized and characterized by FTIR, TGA, and PXRD. The results revealed that the precursors obtained were CuC₂O₄, TiO₂(OH⁻)₂C₂O₄, copper-doped titanium hydroxyl oxalate, and copper titanium hydroxyl oxalate. Complete decomposition for the as-prepared precursors containing titanium ions occurs at 600°C while impurity free copper oxalate decomposed at 450°C. The as-prepared precursors were decomposed and calcined at 600°C for 4 hours and the calcination products were characterized by XRD, SEM, and EDX. The results revealed the decomposition products to correspond to CuO, TiO₂, Cu_{0.131}Ti_{0.869}O₂, and CuO/TiO₂.

1. Introduction

Nanosized transition metal oxides, including copper oxide and titanium oxide (TiO₂), are the subject of sustained scientific interest, because of their potential applications in sensing, catalysis, cosmetics, optoelectronic devices, biomedical field, and magnetism [1, 2]. CuO is a narrow band-gap (1.2 eV) *p*-type semiconductor with photoconductive and photochemical properties and has found applications in gas sensing [3, 4], in catalysis [5–7], as antimicrobial agent [8–11], and in batteries [12], magnetic devices [13–15], super capacitors [16], and field emission [17]. TiO₂ is an *n*-type semiconductor with wide band gap ranging from 3.2 eV to 3.6 eV. It has found applications in cosmetics, paper and medical devices coating, and gas sensors [18–20]. A significant advantage of TiO₂ is the formation of a heterojunction on reaction with another material [21, 22]. In these applications, an important parameter is the specific surface area, which is strongly related to the nanostructured

morphology. Decreasing the size of materials to the nanometre scale may result in unique properties that are significantly different from those of the bulk material. The chemical and physical properties of CuO and TiO₂ depend on their microstructure, such as the morphology and the size and orientation of the constituent grains. To improve and extend the functions of these inorganic nanomaterials, one or more components are often combined to form nanocomposites for various applications in photocatalysis, electronics, and gas sensors [23, 24]. The unique properties of composite nanomaterials originate from their ability to combine the most desirable physicochemical properties of their constituents. Among these composites, CuO/TiO₂ nanocomposites have attracted interest due to their narrow band gap, stability, nontoxicity, and easy availability [21]. Preparation of high-quality nanocrystals of desired size is a prerequisite for investigating and utilising their size-dependent properties. Various approaches such as chemical precipitation [9], sol-gel method [10, 25, 26], hydrothermal method [6, 27],

TABLE 1: Combination volumes of the metal chloride and *A. carambola* fruit juice solutions.

Sample code	$V_{\text{Ti}^{3+}(\text{aq})}$ (mL)	$V_{\text{Cu}^{2+}(\text{aq})}$ (mL)	V_{juice} (mL)	V_T (mL)
E ₁	44	56	200	300
E ₂	100	—	200	300
E ₃	—	100	200	300
E ₄	13.1	86.9	200	300

microwave-assisted method [28], sonochemical synthesis [29], and solvothermal synthesis [30] have been reported for the synthesis of uniform-sized (or monodisperse) metal oxide and metal oxide nanocomposites with diverse morphologies.

Titanium oxide is found in three different crystalline forms: rutile, anatase, and brookite. The anatase phase has been reported to display higher photocatalytic activity than the others, owing to its higher density of localized states [31]. Different synthetic methods have been reported for the synthesis of anatase [31, 32], rutile [33], and brookite [34] phases. The precipitation of titanium by oxalate routes has been reported [35] with the precipitate formulated as $\text{TiO}(\text{C}_2\text{O}_4) \cdot n\text{H}_2\text{O}$ which has as complex isomer $\text{Ti}(\text{OH})_2(\text{C}_2\text{O}_4) \cdot (n-1)\text{H}_2\text{O}$, with $n \leq 3.5$ (in solid state the product might be polymeric or amorphous).

In spite of all the progress made, the synthesis of CuO, TiO_2 , Cu-doped TiO_2 , and CuO/ TiO_2 nanomaterials of controlled size and shape remains a challenge. Size and shape need to be tailored by an appropriate choice of the synthesis methods and conditions. Fine-tuning of the morphology is of key importance, since the surface energy, the electronic structure, bonding, and the chemical reactivity of nanomaterials are all directly related to surface morphology [36]. The purity and stoichiometry (quality of the nanoparticles generated) depend on the synthesis route. Synthesis of nanomaterials by thermal decomposition using cheap, readily available, nontoxic precursors emerges as the most suitable and cost-effective approach. We have been interested in investigating how selected thermal decomposition conditions can influence the nanoscale formation of first row transition metal oxide nanoparticles and their resulting physicochemical properties [22, 37]. In this paper we report on the synthesis of copper oxide (CuO), titanium oxide (TiO_2), and Cu-doped TiO_2 nanoparticles by a simple modified oxalate process (using *A. carambola* fruit juice as source of ligand to precipitate the metal oxalates). The influence of amount of dopant on the composition and morphology of precursor and calcined samples is investigated. This method has the advantage of mixing the component salt at microscopic level without the use of an additional solvent.

2. Experimental

2.1. Materials and Methods. Titanium trichloride (20% in 3% hydrochloric acid) (Alfa Aesar, Germany), calcium chloride (MERCK), copper chloride (Fluka), commercial oxalic acid, and potassium permanganate were of analytical grade and were used without further purification. HPLC *A. carambola* fruit juice (source of the precipitating agent) was also used.

2.2. Processing and Characterization of the Fruit Juice. The fruit juice was processed and characterized as previously reported by Nguimezong et al. [37].

2.3. Synthesis of Precursors. The oxide nanocomposites and the doped materials were both obtained in the same manner via two experimental steps. Solutions (0.04 M) of the various metal chlorides (Cu^{2+} and Ti^{3+}) were prepared in 200 mL of distilled water. The precursor was synthesized by coprecipitation in aqueous solution containing the metal chlorides using *A. carambola* fruit juice as the source of the precipitating agent. Using copper titanyl oxalate as an example, 200 ml portion of the juice extract was poured into a 400 mL round bottom flask at ambient temperature. The metal ion solutions (in the proportions specified in Table 1) were slowly and/simultaneously added to the juice while stirring. The mixture in each case was further stirred for 2 hours. The slurry obtained was aged for 8 hours. The precipitate obtained was filtered, washed successively with distilled water and ethanol, and dried in an oven at 80°C. The synthesis of the precursors and their thermal decomposition into the oxides are shown in Scheme 1.

2.4. Determination of Oxalate Ion Concentration. The concentration of oxalate ions in the fruit juice was determined by titration with permanganate solution. The permanganate solution was standardized using a standard solution of commercial oxalic acid.

2.5. Thermal Decomposition of the Precursors. The as-prepared precursor powders were calcined in a ceramic combustion boat holder at 600°C in a muffle oven (with temperature ramp of 10°C/min) for 4 hours under air flow.

2.6. Characterization Techniques. FTIR spectra were recorded from 4000 to 400 cm^{-1} on a PerkinElmer Spectrum Two Universal Attenuated Total Reflectance Fourier Transform Infrared (UATR-FTIR) spectrometer. Thermogravimetric analysis (TGA) was obtained using a Pyris 6 PerkinElmer TGA 4000 thermal analyzer. The TGA analysis was conducted between 30 and 900°C under nitrogen atmosphere at a flow rate of 20 mL/min and a temperature ramp of 10°C/min. The XRD diffractograms of the precursors and the decomposition products were recorded on a Bruker D8 Advance X-ray diffractometer, using a Cu K α radiation source ($\lambda = 0.15406$ nm, 40 kV, and 40 mA). Scans were taken over the 2θ range from 10° to 100° in steps of 0.01° at room temperature in open quartz sample holders. The phases were identified with the help of the Bruker DIFFRACplus evaluation software in combination with the ICDD powder

TABLE 2: Composition and colors of the precursor and decomposition products.

Sample code	Color of precursor	Color of decomposition product	Formula of decomposed product
E1	Greenish blue	Black	CuO/TiO ₂
E2	Greenish blue	Pale brown	TiO ₂
E3	Greenish blue	Black	CuO
E4	Greenish blue	Black	Cu-TiO ₂

SCHEME 1: Synthesis of the precursor complexes and metal oxides.

diffraction database (International Centre for Diffraction Data). The surface morphology of the samples was examined by a Scanning Electron Microscope (SEM) (JEOL JSM-5600 or TESCAN VEGA III XMU, Q150 T€). Prior to examination, samples were prepared by mounting about 0.5 mg of powder onto a 5 mm × 5 mm double sided carbon tape, on an aluminum stub. The powder was then sputter-coated for 40 seconds with carbon or gold.

3. Results and Discussion

Reaction of the metal salts with the *A. carambola* juice at ambient temperature generally led to colored complexes as shown in Table 2.

3.1. Oxalate Ion Concentration. The oxalate concentration in *A. carambola* fruit juice, determined by titration with standardized potassium permanganate, compared to that of 0.125 mole/L solution of commercial oxalic acid revealed that the concentration of oxalates in the juice was 78 mg/100 cm³. This concentration conforms to literature values which fall

in the range 76 mg/dL to 80 mg/dL [38]. The volume of permanganate required in each case is shown in Table 3.

3.2. FTIR Spectral Characterization. The formation of pure oxalate phases is indicated by FTIR analysis. Figure 1 shows the FTIR spectra of all four complexes (E1, E2, E3, and E4) synthesized using carambola juice as precipitating agent. They all exhibit similar characteristics and comparable patterns except for the broad band centered at 3250 cm⁻¹ present in E2 and E4 but less pronounced in E1 and E3. The broad band at 3250 cm⁻¹ is attributed to the stretching vibration of the O-H of (metal hydroxyl and/or the hydroxyl of water molecules of crystallization). The reduction in the intensity of the bands in E2 and E3 (copper dominated complexes) indicates the reduced amount of water of crystallization in these complexes. The strong band at 1580 cm⁻¹ can be attributed to the antisymmetric stretching vibration modes of the carboxylate groups C=O of oxalates. The three bands at 1487–1400 cm⁻¹, 1365–1337 cm⁻¹, and 1324–1292 cm⁻¹ are

TABLE 3: Volume of MnO_4^- required in the determination of oxalate in *A. carambola* fruit juice.

	Commercial oxalic acid			<i>A. carambola</i> fruit juice		
	Approx.	Accurate	Accurate	Approx.	Accurate	Accurate
2nd burette reading	47.2	46.6	46.6	6.6	12.4	18.2
1st burette reading	0.00	0.00	0.00	0.00	6.6	12.4
Titre/ cm^3	47.2	46.6	46.6	6.6	5.8	5.8
		46.6			5.8

FIGURE 1: FTIR spectra of the metal oxalate complexes.

FIGURE 2: PXRD patterns for the as-prepared precursors (E1 to E4).

attributed to the asymmetric and symmetric stretching modes of $\text{OC}=\text{O}$. These results are in conformity with literature [32]. The bands between 827 and 821 cm^{-1} are attributed to the bending vibrations of O-M-O . The bands between 750 and 490 cm^{-1} are characteristic M-O (Ti-O and Cu-O) vibrations. The absence of the free carbonyl, $\text{V}_{(\text{C}=\text{O})}$, vibration, expected at $1735\text{--}1705\text{ cm}^{-1}$, suggests that the entire carboxylate group is probably engaged in the formation of the coordination complex. These results suggest that the complexes represented by E2 and E4 contain the hydroxyl and oxalates ($\text{M}^{n+}(\text{OH})_{n-2}(\text{C}_2\text{O}_4^{2-})$) whereas E1 and E3 contain only the oxalate $[\text{Cu}(\text{C}_2\text{O}_4)^{2-}]$ as ligand (which is expected since the main titanium(IV) species in the titanyl oxalate solution is $\text{Ti}(\text{OH}^-)_2(\text{C}_2\text{O}_4)_2^{2-}$) as earlier reported in literature [33].

3.3. X-Ray Diffraction. The precursors E_1 , E_2 , E_3 , and E_4 and their decomposition products (ED_1 , ED_2 , ED_3 , and ED_4) obtained by pyrolysis of the precursors at 600°C for 4 hours in air were analyzed by X-ray powder diffraction (PXRD). The XRD patterns of the precursors are shown in Figures 2 and 3 while those of the decomposition products are shown in Figure 4. The PXRD patterns for the precursors are different from those of the corresponding decomposition products. The patterns for the decomposition products were indexed with ICDD files for TiO_2 anatase phase and CuO tenorite phase.

FIGURE 3: XRD pattern of E2 and E4 showing masked peaks.

The XRD pattern obtained for the decomposition product ED_3 reveals crystallinity with major peaks at 2θ values 35.52 , 38.72 , 48.82 , 61.34 , and 68.08 corresponding to the database 2θ values of JCPDS card number 48-1548 exhibiting copper(II) oxide (tenorite phase). On the other hand, the XRD pattern obtained for the decomposition product ED_2 reveals crystallinity with major peaks at 2θ values 25.3 , 37.88 , 47.98 , 55.28 , and 62.78 corresponding to the database 2θ

TABLE 4: Average crystallite sizes of the as-prepared nanosized metal oxides.

Sample	Plane (hkl)	FWHM	Bragg's angle (θ)	Crystallite size (d_{RX})/nm	Average (d_{RX})/nm
E1 (CuO/TiO ₂)	101	0.0058	12.65	24.3	25.43
	002	0.0058	17.76	25.3	
	110	0.0055	19.36	26.7	
E2 (TiO ₂)	101	0.0088	12.65	16.1	16.1
E3 (CuO)	002	0.0024	17.76	60.4	61.25
	111	0.0024	19.42	62.1	
E4 Cu-doped TiO ₂	101	0.0082	12.67	17.3	17.3

FIGURE 4: PXRD patterns of the decomposition products (ED1, ED2, ED3, and ED4).

values of JCPDS card number 21-1272 exhibiting titanium oxide (anatase phase). The structural properties of Cu-doped TiO₂ (ED4) and 0.56 CuO/0.44 TiO₂ (ED1) as-prepared were characterized by PXRD in the range 20° to 80°. Diffraction peaks in the pattern obtained were indexed, respectively, to titanium oxide (anatase phase) and CuO (tenorite phase). The values for ED4 were in good agreement with the database 2θ values of TiO₂ with lattice planes (101, 004, 200, 105, 211, and 204). The values for ED1 show partial agreement with each of the titanium oxide (anatase phase) (2θ value, 25.36, and lattice plane (101)) and CuO (tenorite phase) (2θ values, 35.54 and 38.82, and lattice planes (002, 111)). The results obtained from powdered XRD can be put under two categories (Figure 4): one which indicates just a single phase in each case corresponding to the decomposition products ED2 and ED3, and the other which indicates the presence of two phases ED1 and ED4. CuO (tenorite phase) ED3 was obtained from E3, while the mixed phase, ED1, was identified as CuO/TiO₂ (obtained from E1). The absence of any copper phase (copper metal or CuO) in the PXRD pattern for decomposition product ED2 can be explained by the fact that during pyrolysis Cu was incorporated into the TiO₂ crystal structure by substituting Ti. This is possible because the ionic radii of Cu²⁺ and Ti⁴⁺ (0.72 pm and 0.68 pm) are very close. The decomposition product ED4 corresponds

to Cu_{0.15}Ti_{0.85}O₂ while ED1 corresponds to 0.56 CuO/0.44 TiO₂. The crystallite sizes (d_{RX}) for the as-prepared samples were determined (by measuring the broadening of the most intense peak of the phase in a diffraction pattern for the as-prepared samples) according to Debye-Scherrer equation as follows:

$$d_{RX} = \frac{k\lambda}{\beta \cos \theta}, \quad (1)$$

where d_{RX} is the crystallite size, $k = 0.9$ is a correction factor which accounts for the particle shape, β is the full width at half maximum (FWHM) of the most intense diffraction plane, λ is the wave length of Cu target (0.15406 nm), and θ is the Bragg's angle. The results obtained are summarized in Table 4.

3.4. Thermogravimetric Analysis. The thermogravimetric and differential thermograms are presented in Figure 5. The thermograms for E2 and E4 are very similar. They each present three weight loss steps. The first occurs between 90 and 280°C, showing a weight loss of 26.3% (cf. 26.2% theoretically determined from the formula of the as-prepared precursor) which is attributed to the loss of water of crystallization. The second weight loss portion between 280 and 350°C shows a weight loss of 13.19% (cf. 13.6%) attributed to the elimination of one mole of carbon monoxide. The last weight loss portion occurs between 350 and 600°C, which shows a weight loss of 13.19% (cf. 23%) which can be attributed to partial decomposition of the intermediate. These results suggest that total decomposition of the reaction intermediate requires prolonged heating (calcinations for longer period). E1 also presents three weight loss steps but different from E2 and E4. The first portion between 90 and 270°C shows a weight loss of 12.87% (cf. 13.15%) attributed to the loss of water of crystallization. The second step between 270 and 370°C shows a weight loss of 33.66% (cf. 30%) attributed to the loss of carbon monoxide and partial elimination of carbon dioxide. The final weight loss of 9.0% (cf. 11.03%) can be attributed to the complete decomposition of the carbonate intermediate. In the case of E3, there is a relatively weak weight loss portion between 30 and 400°C corresponding to 8% by weight of the initial weight which can be attributed to water present in the matrix of the sample, though the relatively low representation indicates that the amount of water in E3 complex is greatly reduced. This is in agreement with FTIR results which indicated the absence of the O-H stretching vibration band characteristic

TABLE 5: EDX results for ED1, ED2, ED3, and ED4.

Sample code	Ti content (%)	Cu content (%)	Ti/Cu atomic ratio observed	Ti/Cu atomic ratio expected
ED1	44.0	56.0	0.79	0.81
ED2	100	—	0	0
ED3	—	100	0	0
ED4	86.95	13.05	6.66	6.69

FIGURE 5: TGA/DTG of the metal oxalate precursors (E1, E2, E3, and E4).

of water of crystallization. The second weight loss in the E3 sample corresponding to 46.12% can be attributed to the decomposition of the oxalate to the corresponding oxide.

The reaction pathway for E4 is the sum of reaction equation 1 and reaction equation 3 to give the product CuO/TiO_2 as shown in Scheme 2.

3.5. SEM and EDX Analyses. The elemental composition was obtained using EDX while the morphologies and microstructures of ED1, ED2, ED3, and ED4 were studied by SEM. Figures 6(a)–6(h) show the SEM/EDX results of the samples. As evident from the micrographs, the polycrystalline nature of the ED2 and ED4 residues is obvious with well-defined

polyhedral particles with grain sizes of $2\ \mu\text{m}$ whereas the ED1 and ED2 residues show less-defined grain sizes. The agglomeration of particles into larger sizes as the impurity of Ti into the sample occurs is also evident. The level of agglomeration in the copper-doped anatase appears to be lower than for the pure phase. This observed agglomeration could play a vital role in the properties of the target materials such as variation in electrical conductivity due to the change in specific surface area.

The results of semiquantitative analysis performed by EDX on the decomposition products ED1, ED2, ED3, and ED4 are summarized in Table 5. The Ti/Cu atomic ratios for E1 and E4 were, respectively, 0.79 (cf. 0.81 expected) and 6.66

FIGURE 6: (a) SEM of CuO/TiO₂ (ED1), (b) EDX of CuO/TiO₂ (ED1), (c) SEM of TiO₂ (ED2), (d) EDX of TiO₂ (ED2), (e) SEM of CuO (ED3), (f) EDX of CuO (ED3), (g) SEM of Cu-doped TiO₂ (ED4), and (h) EDX of Cu-doped TiO₂ (ED4).

SCHEME 2: Proposed reaction pathways for the formation of the products (E1 to E3).

(cf. 6.69 expected). The slight differences observed between the expected and obtained values can be explained by the limitation of EDX analysis as a quantitative method.

Nanoregimes of the sample were analyzed by SEM and Scherrer formula. The results of the structural studies revealed that all samples had crystallites in the nanosize range; Cu^{2+} addition into the TiO_2 increases the crystallite size which may be due to the replacement of Ti^{4+} ions by Cu^{2+} ions which have a higher ionic radius. Increase in crystallite size leads to weaker quantum confinement and modification of structure.

Figures 6(a)–6(h) show SEM images of the as-prepared TiO_2 , Cu-doped TiO_2 , CuO, and CuO/ TiO_2 nanosized particles. It shows that pure and doped TiO_2 nanosized crystallites agglomerate into porous polyhedral particles which measure

10–20 μm in size while CuO and CuO/ TiO_2 present as coarsening particles with low level of agglomeration.

4. Conclusion

We have been able to synthesize pure CuO, TiO_2 , $\text{Cu}_{0.131}\text{Ti}_{0.869}\text{O}_2$, and CuO/ TiO_2 nanoparticles by a modified oxalate process using *A. carambola* fruit juice as the source of the precipitating agent. Particle sizes of 61.25 nm for CuO, 17.3 nm for Cu-doped TiO_2 , 16.1 for TiO_2 , and 25.43 for CuO/ TiO_2 were obtained from calculations as confirmed by PXRD analysis. Introduction of Cu^{2+} impurities into the microstructure of TiO_2 increases the crystallite size which may be due to the replacement of Ti^{4+} ions by Cu^{2+} ions which have a higher ionic radius. Increase in

crystallite size leads to weaker quantum confinement but the doping fraction was too small to reflect modification in the structure. Decomposition of copper oxalate to copper oxide occurred at 450°C while decomposition of Ti and Ti/Cu oxalate to corresponding metal oxides (pure, doped, and composites) occurred at a later temperature 600°C. The purity of both our precursors was justified from the FTIR while EDX results indicated the elemental representation of the decomposition products. SEM results revealed that the nanoparticles agglomerated to crystallites which are about 2 μ in width. Our results demonstrate that the proposed modified coprecipitation technique by using a precipitating agent extract from *A. carambola* juice is simple and presents as an environmental friendly, low cost, and controllable method, which can also be applied to prepare a wide variety of mixed metal oxides of interest.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this article.

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