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

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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 hydroxyloxalate. 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, Cu₀.₁₃₁Ti₀.₈₆₉O₂, 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],
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 TiO(C\(_2\)O\(_4\))\(_n\)H\(_2\)O which has as complex isomer Ti(OH)\(_2\)(C\(_2\)O\(_4\))(\(n - 1\))H\(_2\)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 Nguimezon 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 Kα 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>
<thead>
<tr>
<th>Sample code</th>
<th>(V_{Ti^{3+}(aq)}) (mL)</th>
<th>(V_{Cu^{2+}(aq)}) (mL)</th>
<th>(V_{juice}) (mL)</th>
<th>(V_T) (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E(_1)</td>
<td>44</td>
<td>56</td>
<td>200</td>
<td>300</td>
</tr>
<tr>
<td>E(_2)</td>
<td>100</td>
<td>—</td>
<td>200</td>
<td>300</td>
</tr>
<tr>
<td>E(_3)</td>
<td>—</td>
<td>100</td>
<td>200</td>
<td>300</td>
</tr>
<tr>
<td>E(_4)</td>
<td>13.1</td>
<td>86.9</td>
<td>200</td>
<td>300</td>
</tr>
</tbody>
</table>
**Table 2: Composition and colors of the precursor and decomposition products.**

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Color of precursor</th>
<th>Color of decomposition product</th>
<th>Formula of decomposed product</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1</td>
<td>Greenish blue</td>
<td>Black</td>
<td>CuO/TiO₂</td>
</tr>
<tr>
<td>E2</td>
<td>Greenish blue</td>
<td>Pale brown</td>
<td>TiO₂</td>
</tr>
<tr>
<td>E3</td>
<td>Greenish blue</td>
<td>Black</td>
<td>CuO</td>
</tr>
<tr>
<td>E4</td>
<td>Greenish blue</td>
<td>Black</td>
<td>Cu-TiO₂</td>
</tr>
</tbody>
</table>

**Scheme 1: Synthesis of the precursor complexes and metal oxides.**

**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...
attributed to the asymmetric and symmetric stretching modes of OC=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, \(V(C=O)\), vibration, expected at 1735–1705 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 (\(M^{n+}(OH)_{n-2} (C_2O_4^{2-})\)) whereas E1 and E3 contain only the oxalate \([Cu(C_2O_4)^{2-}]\) as ligand (which is expected since the main titanium(IV) species in the titanyl oxalate solution is Ti(OH\(^+\))\(_2(C_2O_4)^{2-}\)) 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.

The XRD pattern obtained for the decomposition product ED3 reveals crystallinity with major peaks at 2\(\theta\) values 35.52, 38.72, 48.82, 61.34, and 68.08 corresponding to the database 2\(\theta\) 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 ED2 reveals crystallinity with major peaks at 2\(\theta\) values 25.3, 37.88, 47.98, 55.28, and 62.78 corresponding to the database 2\(\theta\)
The decomposition product ED4 corresponds to CuO/TiO$_2$ while ED1 corresponds to 0.56 CuO/0.44 TiO$_2$. 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:

$$d_{RX} = \frac{k \lambda}{\beta \cos \theta},$$

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

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>Plane (hkl)</th>
<th>FWHM</th>
<th>Bragg’s angle (°)</th>
<th>Crystallite size ($d_{RX}$/nm)</th>
<th>Average ($d_{RX}$/nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1 (CuO/TiO$_2$)</td>
<td>101</td>
<td>0.0058</td>
<td>12.65</td>
<td>24.3</td>
<td>25.43</td>
</tr>
<tr>
<td></td>
<td>002</td>
<td>0.0058</td>
<td>17.76</td>
<td>25.3</td>
<td>25.43</td>
</tr>
<tr>
<td></td>
<td>110</td>
<td>0.0055</td>
<td>19.36</td>
<td>26.7</td>
<td>26.7</td>
</tr>
<tr>
<td>E2 (TiO$_2$)</td>
<td>101</td>
<td>0.0088</td>
<td>12.65</td>
<td>16.1</td>
<td>16.1</td>
</tr>
<tr>
<td>E3 (CuO)</td>
<td>002</td>
<td>0.0024</td>
<td>17.76</td>
<td>60.4</td>
<td>61.25</td>
</tr>
<tr>
<td></td>
<td>111</td>
<td>0.0024</td>
<td>19.42</td>
<td>62.1</td>
<td>62.1</td>
</tr>
<tr>
<td>E4 Cu-doped TiO$_2$</td>
<td>101</td>
<td>0.0082</td>
<td>12.67</td>
<td>17.3</td>
<td>17.3</td>
</tr>
</tbody>
</table>

![Figure 4: PXRD patterns of the decomposition products (ED1, ED2, ED3, and ED4).](image-url)
Table 5: EDX results for ED1, ED2, ED3, and ED4.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Ti content (%)</th>
<th>Cu content (%)</th>
<th>Ti/Cu atomic ratio observed</th>
<th>Ti/Cu atomic ratio expected</th>
</tr>
</thead>
<tbody>
<tr>
<td>ED1</td>
<td>44.0</td>
<td>56.0</td>
<td>0.79</td>
<td>0.81</td>
</tr>
<tr>
<td>ED2</td>
<td>100</td>
<td>—</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>ED3</td>
<td>—</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>ED4</td>
<td>86.95</td>
<td>13.05</td>
<td>6.66</td>
<td>6.69</td>
</tr>
</tbody>
</table>

![Figure 5: TGA/DTG of the metal oxalate precursors (E1, E2, E3, and E4).](image)

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 $2\mu m$ 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/TiO$_2$ (ED1), (b) EDX of CuO/TiO$_2$ (ED1), (c) SEM of TiO$_2$ (ED2), (d) EDX of TiO$_2$ (ED2), (e) SEM of CuO (ED3), (f) EDX of CuO (ED3), (g) SEM of Cu-doped TiO$_2$ (ED4), and (h) EDX of Cu-doped TiO$_2$ (ED4).
Scheme 2: Proposed reaction pathways for the formation of the products (E1 to E3).

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$_2$, Cu$_{0.131}$Ti$_{0.869}$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 oxide to copper oxide occurred at 450°C while decomposition of Ti and Ti/Cu oxide 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 2μ 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.

**References**


