Green Synthesis and Pinning Behavior of Fe-Doped CuO/Cu$_2$O/Cu$_4$O$_3$ Nanocomposites

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Abstract: Egg white-induced auto combustion has been used to synthesize undoped and Fe-doped CuO/Cu$_2$O/Cu$_4$O$_3$ nanocomposites in a soft, secure, and one-pot procedure. X-ray powder diffraction (XRD) and Fourier transform infrared (FTIR) investigations have been used to identify functional groups and the structural properties of crystalline phases present in the as-synthesized composites. Scanning Electron Microscopy/Energy Dispersive Spectrometry (SEM/EDS) elemental mapping analyses and Transmission Electron Microscopy (TEM) techniques were used to explore the morphological and compositional properties of these composites. N$_2$-adsorption/desorption isotherm models have been used to examine the surface variables of the as-prepared systems. Based on the Vibrating Sample Magnetometer (VSM) technique, the magnetic properties of various copper-based nanocomposites were detected due to being Fe-doped. XRD results showed that the undoped system was composed of CuO as a major phase with Cu$_2$O and Cu$_4$O$_3$ as second phases that gradually disappeared by increasing the dopant content. The crystalline phase’s crystallographic properties were determined. The average particle size was reduced when the synthesized systems were doped with Fe. The construction of porous and polycrystalline nanocomposites involving Cu, Fe, O, and C components was confirmed by SEM/EDS and TEM measurements. In terms of the increase in magnetization of the as-manufactured nanocomposites due to Fe-doping, oxygen vacancies at the surface/or interfacial of nanoparticles, while also domain wall pinning mechanisms, were investigated. Finally, employing the investigated production process, Fe doping of CuO/Cu$_2$O/Cu$_4$O$_3$ nanocomposite resulted in the development of a single phase (CuO) exhibiting “pinned” type magnetization. This is the first publication to show that CuO/Cu$_2$O/Cu$_4$O$_3$.

Keywords: CuO/Cu$_2$O/Cu$_4$O$_3$ NPs; XRD; FTIR; SEM; TEM; EDS and VSM

1. Introduction

One of the most essential approaches that has a clear and significant impact on the diverse properties of various materials is the doping process. Doping in a lattice involves the introduction of a few foreign atoms that have a minor impact on the lattice’s thermal conductivity. The climb frequency of the complex Fe impurity vacancy may be estimated from the deviation of self-diffusion anisotropy at 1313 K [1–3]. The doping procedure can significantly influence the physical and chemical properties of materials. Environmental remediation, pollution sensing, energy production, conversion, and storage essentially require metal oxides. They have a wide range of functional qualities that are influenced
by the crystal structure, morphology, composition, intrinsic flaws, doping, and other factors [4–7]. Among these oxides is copper oxide, which has special interest due to its many applications, such as catalysis, superconductors, sensors, energy storage systems, spintronic, anticancer, and antimicrobial agents [8–13].

Many modern applications, such as nanoscale electronic components, incorporate magnetic metal nanowire arrays with variable aspect ratios. Electrochemical processing has been used to deposit Ni nanowires on through-pore alumina membranes. New nanostructured composite materials based on nanoscale structural features, such as nanopillars, nanotubes, nanowires, or nanodots, are being explored to ensure such properties. Technology for making composite materials with Ni nanopillars (Ni NPS). The unusually well-organized cellular structure of porous anodic alumina (PAA) has piqued interest. Thermodynamic and chemical properties of nickel nanowires (NWs) electrochemically deposited in the pores of anodic aluminum oxide membranes, as well as the framework synthesis approach’s synthesis of a significant number of novel nanoelements [14–16].

The structural, morphological, electrical, and magnetic characteristics of copper oxides have all been modified by doping [17]. CuO thin films prepared by spray pyrolysis demonstrated a significant increase in crystallinity, optical band gap, and conductivity, while conserving the inherent monoclinic structure [18]. This behavior could be attributed to the presence of Fe in substitutional and/or interstitial positions within the CuO lattice. Spintronic devices might be constructed using transition metal-doped wide bandgap semiconductors, such as ZnO or GaN. In Co or Mn doped materials, room-temperature ferromagnetism has been demonstrated, but the origin of the reported magnetic properties in Tm-doped ZnO materials is still a topic of controversy, and more research concerning charge and spin transport in these materials is required. Doping of copper oxide with different elements (Mn, Zn, Ga, Ni, and Co) enhanced ferromagnetism at room temperature, which is an important property of diluted magnetic semiconductors [19–24]. Indeed, diluted magnetic semiconductors have potential applications in spintronics [25].

Recently, various reports on the preparation and characterization of Fe-doped CuO nanoparticles have been determined [26–28]. Synthesis of this system involved different routes, such as sol-gel, hydrothermal, co-precipitation, and ceramic methods. Among these methods, the urea-assisted auto-combustion route was used for the synthesis of pure and Fe-doped CuO without any impurity phases [29]. On the other hand, some studies could not avoid the presence of impurity phases as secondary phases [30–33]. When the combustion method relies on naturally occurring biomaterials such as egg white, it becomes safer, simpler, and inexpensive compared with conventional methods. We did not acquire copper oxide (CuO) as a single-phase in our recent research on the preparation of undoped copper oxides, but instead obtained a series of copper oxide-based nanocomposites (Cu2O/CuO and Cu2O/Cu) depending on the amount of egg white employed [34]. Egg white was used as a water-soluble polymeric matrix for the entrapment of copper ions, yielding a gelled precursor followed by the formation of nanosized copper particles. This behavior depends on gelling, foaming, and emulsifying characteristics and the binding adhesion of egg white [35].

Indeed, cupric oxide (CuO, tenorite), cuprous oxide (Cu2O), and cupric-cuprous oxides (Cu4O3, paramelaconite) are three distinct phases of copper oxides with different oxidation states [36,37]. The crystals of CuO, Cu2O, and Cu4O3 are monoclinic, cubic, and tetragonal structures, respectively. This difference in the crystal symmetries of these oxides resulted in a diversity of their properties and applications. The presence of all of these oxide combinations, or the exclusion of one or two of them, is predicted to have a significant impact on the final product’s qualities [34]. Many factors, including doping, the preparation process, and the composition of the pre-cursors, play a role in this involvement. [34,38]. CuO/Cu2O/Cu nanocomposites were formed using a glycine-assisted auto-combustion approach, whereas Cu2O/CuO and Cu2O/Cu nanocomposites were generated using an auto-combustion technique based on egg white [34,38]. In this work, pure and iron-doped ternary copper oxide systems containing CuO, Cu2O, and Cu4O3 were prepared...
using the egg white mediated auto-combustion method. Various methodologies were used to characterize the systems as they were prepared. These systems’ morphological and magnetic properties were discussed. This paper intends to contribute to a better understanding of the mechanism of phase transformation or phase stability in copper oxides, as well as the pinning influence of grain boundaries on the magnetic characteristics of iron-doped ternary copper oxide systems.

2. Materials and Methods

2.1. Materials

Copper (II) nitrate trihydrate and ferric nitrate hydrate, with linear formulas Cu(NO$_3$)$_2$.3H$_2$O and Fe(NO$_3$)$_3$.9H$_2$O, respectively, were used as chemical materials. Sigma-Aldrich Company (Darmstadt, Taufkirchen, Germany) provided these ingredients. These were quantitative reagents that were applied without further refining. Raw egg white from surrounding chickens was used to extract the egg white.

2.2. Preparation Route

Four Fe-doped copper oxide samples (C1, C2, C3, and C4) were synthesized by mixing calculated proportions of copper nitrate (2.426 g) and a specified amount of egg white (7 mL) with ferric nitrate (0.0080, 0.0242, and 0.0484 g), respectively [34]. The homogeneous precursors were concentrated for 5 min, mixed well with egg whites before being placed on really warm plates in a Pyrex beaker (Paul Marienfeld, Lauda-Königshofen, Germany) at 350 °C for 15 min. When the beaker temperature exceeded 350 °C, the crystal water was smoothly evaporated, a lot of foams were generated, and a spark occurred at one edge, spreading through the bulk, producing a massive and bulky substance within the jar. Table 1 provides the dopant percentages in the C1, C2, C3, and C4 samples.

Table 1. Weight and weight percentages for various samples.

| Sample | C1   | C2   | C3   | C4   |
|--------|------|------|------|------|
| Weight g | 2.426 | 0.0080 | 0.0242 | 0.0484 |
| wt.%    | 100% | 0.198% | 0.599% | 1.198% |

2.3. Characterization Techniques

The crystallite size ($d$), dislocation density ($\delta$), stress ($\varepsilon$), and strain ($\sigma$) of CuO, Cu$_2$O, and Cu$_4$O$_3$ existent in the composites investigated were computed using Equations (1)–(4) based on X-ray diffraction peak broadening. The X-ray investigation was performed using the BRUKER D8 advance diffractometer (Bruker, Karlsruhe, Germany). XRD patterns were run with Cu Kα radiation at 40 kV and 40 mA with scanning speeds of 2° per min [39,40]:

\[ d = \frac{0.89 \lambda}{\beta \cos \theta} \]  
\[ \delta = \frac{1}{d^2} \]  
\[ \varepsilon = \frac{\beta \cos \theta}{4} \]  
\[ \sigma = \varepsilon Y \]

where $d$ is the phase’s average crystallite size, 0.89 is the Scherrer constant, $\beta$ is the complete breadth at half the height of the peaks in radians, $\theta$ is the diffraction angle in radians, $Y$ is Young’s modulus, and $\lambda$ is the X-ray wavelength in nanometer scale.

Simultaneous thermogravimetry–derivative thermogravimetry (TG-DTG) measurements were taken using a thermal analyzer, the Nietzsche 449 Jupiter design (NETZSCH-Gerätebau GmbH Wittelsbacherstraße 42, 95100 Selb, Germany). The experiments were carried out in a nitrogen gas atmosphere with a gas flow rate of 40 mL min$^{-1}$ at temperatures ranging from 25 to 900 °C. The experimental sample was heated at a rate of 10 °C per minute.
A PerkinElmer Spectrophotometer was used to measure the examined solid’s Fourier-transform infrared spectrum (FTIR), type 1430, (PerkinElmer, Buckinghamshire, England). The IR spectra were collected at wavelengths ranging from 4000 to 400 cm\(^{-1}\). Two milligrams of solid samples were combined with 200 milligrams of vacuum-dried potassium bromide (KBr). After being dispersed for 3 min in a vibrating ball mill, the mixture was formed into a 13 mm diameter disk in a steel die and subjected to 12-ton pressure. The sample disk was placed in the holder of the IR spectrometer with two gratings.

The specimens were diffused in ethanol and then treated ultrasonically for a few minutes to dissipate individual particles over the mount setup and Copper grids, using JEOL JAX-840A and JEOL Model 1230 (JEOL, Tokyo, Japan) scanning electron microscopes (SEM) and transmittance electron microscopes (TEM) operating at 25 and 100 Kev, respectively.

Energy dispersive X-ray spectroscopy (EDS with Mapping) was performed using a Delta kevex device (JEOL, Tokyo, Japan) attached to an electron microscope, the JED-2200 Series (JEOL, Tokyo, Japan). The following settings were used: 25 kV accelerating voltage, 120 s accumulation duration, and 6 mm window width. The Asa approach, Zaf-correction, and Gaussian approximation were used to determine the surface molar composition.

Specific surface area (SBET), statistical thickness surface area (St), total pore volume (VP), and mean pore radius (r) of various samples were determined from nitrogen adsorption isotherms at 77 K using a conventional volumetric apparatus (Brunauer Emmett Teller method) using Micrometrics’ Gemini VII 2390 V1.03 series of surface area analyzers (Microtrac, Alpharetta, GA, USA). Each sample was out-gassed for 2 h at 200 °C at a reduced pressure of 10\(^{-5}\) Torr. before the measurements.

Using a vibrating sample magnetometer (VSM), the magnetic properties of the materials were investigated under a maximum field of 20 kOe (9600-1 LDJ, Weistron Co., Ltd., West Hollywood, CA, USA). Hysteresis loops, Saturation magnetization (Ms), remanence magnetization (Mr), and coercivity (Hc) were all reported.

3. Results

3.1. XRD Analysis

Investigation of the structural characteristics of the synthesized crystalline solids (C1, C2, C3, and C4) can be achieved using XRD measurement. The XRD spectra of pure or undoped copper oxide and doped copper oxide with various Fe concentrations are shown in Figure 1. A closer examination of this figure revealed some of the following results: (i) various reflections were observed for monoclinic CuO, cubic Cu\(_2\)O, and tetragonal Cu\(_4\)O\(_3\) phases according to PDF Files 801917, 782026, and 831665, respectively. The miller indices, two thetas (2\(\theta\) observed and calculated), and the differences between the values of two thetas for the C1 sample are tabulated in Table 2, which is the representative table for the other samples.

This table confirms the presence of previous copper oxides, indicating the formation of CuO/Cu\(_2\)O/Cu\(_4\)O\(_3\) composite. Furthermore, the majority of the observed peaks were strong and sharp, confirming the crystalline nature of the composite as constructed. Since this CuO phase’s peaks are significantly greater than those of the Cu\(_2\)O and Cu\(_4\)O\(_3\) phases, the eventual composite is composed primarily of CuO. The C1 sample’s XRD pattern revealed that it was completely fabricated of copper-based heterostructures with CuO as the primary phase and Cu\(_2\)O and Cu\(_4\)O\(_3\) as minor phases. This finding suggests that by employing an egg white-mediated combustion technique, CuO/Cu\(_2\)O/Cu\(_4\)O\(_3\) nanoparticles could be synthesized. (ii) As seen in the XRD pattern of the C2 sample, doping the C2 sample with a minor amount of ferric nitrate (0.198 wt.%) resulted in a decrease in the height of the peaks of both Cu\(_2\)O and Cu\(_4\)O\(_3\). (iii) Interestingly, the increase in the amount of dopant to 0.599 wt.% led to the complete disappearance of all peaks related to the Cu\(_2\)O phase as shown in the XRD spectrum of the C3 sample. In addition, the treatment of CuO/Cu\(_2\)O/Cu\(_4\)O\(_3\) nanocomposite 1.198 wt.% ferric nitrate brought about a specified solid containing CuO as a single phase with very small traces Cu\(_4\)O\(_3\) at 2\(\theta\) equal to 44.41.
Figure 1. The C1, C2, C3, and C4 samples’ X-ray Diffraction (XRD) patterns.

Table 2. Miller indices, two theta values (observed and calculated), and the discrepancies between the two theta values for various samples.

| 2 Θ Calc. | C1 2 Θ Obs. | Diff. | C2 2 Θ Obs. | Diff. | C3 2 Θ Obs. | Diff. | C4 2 Θ Obs. | Diff. | h | k | l |
|-----------|-------------|-------|-------------|-------|-------------|-------|-------------|-------|---|---|---|
| 32.18     | 32.4609     | −0.2809 | 32.4817     | 0.1083 | 32.4669     | 0.1231 | 32.5161     | 0.0739 | 1 | 1 | 0 |
| 35.26     | 35.3798     | −0.1198 | 35.4735     | 0.0065 | 35.4828     | −0.0028 | 35.5464     | −0.0664 | 0 | 0 | 2 |
| 36.27     | 36.442      | 0.172   | 36.442      | 0.172  | -           | -      | -           | -      | 1 | 1 | 1 |
| 38.53     | 38.6807     | −0.1507 | 38.7153     | 0.0347 | 38.7036     | −0.0036 | 38.7308     | −0.0308 | −1| 1| 1 |
| 42.29     | 42.22       | 0.109   | -           | -      | -           | -      | -           | -      | 2 | 0 | 0 |
| 44.41     | 44.146      | −0.264  | 44.146      | 0.424  | 44.146      | −0.264 | 44.57       | 0.16   | 2 | 1 | 3 |
| 46.21     | 46.1327     | 0.0773  | -           | -      | -           | -      | -           | -      | −1| 1| 2 |
| 48.66     | 48.5869     | 0.0731  | 48.6777     | 0.0423 | 48.6896     | 0.0304 | 48.756      | 0.084  | −2| 0| 2 |
| 51.39     | 51.3039     | 0.0861  | -           | -      | -           | -      | -           | -      | 1 | 1 | 2 |
| 53.25     | 53.3673     | −0.1173 | 53.4211     | 0.0389 | 53.3808     | 0.0792 | 53.465      | −0.005 | 0 | 2 | 0 |
| 56.67     | 56.5976     | 0.0724  | -           | -      | -           | -      | -           | -      | 0 | 2 | 1 |
| 58.06     | 58.2274     | −0.2124 | 58.3234     | −0.0134 | 58.3271     | −0.0171 | 58.3276     | −0.0176 | 2 | 0 | 2 |
| 61.33     | 61.373      | −0.043  | 61.5353     | 0.0447 | 61.5426     | 0.0374 | -           | -      | −1| 1| 3 |
| 65.62     | 65.6686     | −0.0486 | 65.7755     | −0.1555 | 65.7459     | −0.1259 | 65.8059     | 0.0541 | 0 | 2 | 2 |
| 66.03     | 66.1        | −0.07   | 66.1404     | −0.1104 | 66.1369     | −0.1069 | 66.2657     | −0.0157 | −3| 1| 1 |
| 67.89     | 67.827      | 0.063   | 67.9609     | −0.0709 | 67.9631     | −0.0731 | 68.1016     | 0.0584 | 1 | 1 | 3 |
| 71.58     | 71.4887     | 0.0913  | -           | -      | -           | -      | -           | -      | −3| 1| 2 |
| 72.43     | 72.3356     | 0.0944  | 72.3549     | 0.0751 | 72.347      | 0.083  | 72.4318     | −0.0018 | 3 | 1 | 1 |
| 72.94     | 72.8446     | 0.0954  | -           | -      | -           | -      | -           | -      | 2 | 2 | 1 |
| 75.03     | 74.8512     | 0.1788  | -           | -      | -           | -      | -           | -      | −2| 2| 2 |
| 75.15     | 75.0387     | 0.1113  | 75.1539     | −0.0039 | 75.0985     | 0.0515 | 75.2513     | −0.1013 | −2| 2| 2 |
| 79.71     | 79.905      | −0.195  | 79.7296     | 0.0774  | -           | -      | -           | -      | 0 | 2 | 3 |
The authors believe that this result is new and no discovered in the kinds of literature before this study. The last treatment will lead to the distinctive properties of the CuO-based product. (iv) Fe-doping of CuO/Cu2O/Cu4O3 nanocomposite brought about a slight shift in all diffraction lines of its constituents, indicating incorporation of iron ions in the crystal lattice of all or some contents of this composite. (vi) No one can dispute the presence of carbon ash arising from the combustion of egg white, which won’t show up in XRD measurements due to its insignificant quantity [41]. This will be clarified and confirmed by FTIR and EDS analyses.

The C1, C2, C3, and C4 samples’ crystal parameters, identified phases, and PDF files, the crystal parameters’ lattice constants (a, b, and c), angles (α, β, and γ), unit cell volume, X-ray density (Dx), and space groups are shown in Table 3. Based on XRD measurements, Table 4 illustrates the expected crystallite size (d), dislocation density (δ), strain (ε), and stress (σ) of CuO, Cu2O, and Cu4O3 crystallites in various samples. We were able to determine all prior crystallographic parameters using FullProf software [42]. Inspection of these tables revealed that: (i) Fe-doping of the CuO/Cu2O/Cu4O3 nanocomposite resulted in a decrease in the values of both β and the unit cell dimensions of CuO, with a subsequent decrease in its unit cell volume. This behavior could be attributed to the incorporation of Fe ions into the CuO yielding contracted lattice because the ionic radii of Fe ions (0.064 nm and 0.076 nm for Fe3+ and Fe2+, respectively) is smaller than that of Cu ions (0.069 nm and 0.096 nm for Cu2+ and Cu1+, respectively [43,44]). On the other hand, Fe-doping did not result in any change in these values for Cu4O3 and Cu2O. (ii) Doping the investigated composite brought about an increase in the crystallite size of both CuO and Cu2O and also a decrease in the crystallite size of Cu4O3. Opposite behaviors were observed in the values of δ, ε, and σ for these oxides.

Table 3. The C1, C2, C3, and C4 samples, crystal parameters, identified phases, and their PDF files.

| Sample | a (Å)   | b (Å)   | c (Å)   | α (°)  | β (°)  | γ (°)  | Volume (Å³) | Dx (g/cm³) | Space Group | Phases          |
|--------|---------|---------|---------|--------|--------|--------|-------------|------------|-------------|----------------|
| C1     | 4.6981  | 3.4336  | 5.1471  | 90     | 99.65  | 90     | 81.85       | 6.499      | Monoclinic  | CuO (PDF 801917) |
| C2     | 4.2667  | 4.2667  | 4.2667  | 90     | 90    | 90     | 77.67       | 6.117      | Cubic       | Cu2O (PDF 782026) |
| C3     | 5.837   | 9.932   | 9.932   | 90     | 90    | 90     | 338.39      | 5.930      | Tetragonal  | Cu4O3 (PDF 831665) |
| C4     | 4.6970  | 3.4304  | 5.1331  | 90     | 99.59  | 90     | 81.85       | 6.499      | Monoclinic  | CuO (PDF 801917) |

3.2. TG/DTG Analyses

The thermal behavior of pure and Fe-doped samples was investigated. Thermo gravimetric analysis and differential thermal analysis (TGA/DTGA) were used to determine the thermal behavior of the prepared pure and Fe-doped copper oxides (CuO/Cu2O/Cu4O3, CuO/Cu2O/Cu4O3, CuO) in the range of ambient temperature to 900 °C. Figure 2 illustrates the TGA/DTGA patterns of the examined systems. The TG curve of prior copper oxide systems can be seen in this figure as containing five phases of disintegration with sequential
weight losses in the temperature ranges of 25–200 °C, 250–360 °C, 373–425 °C, 450–650 °C, and above 650 °C.

Table 4. CuO, Cu2O, and Cu4O3 crystallites sizes, dislocations, stress, strain, and identified phases.

| Sample | d (nm) | δ (Lines/nm²) | ε | σ (N/m²) | Phases |
|--------|--------|---------------|---|----------|--------|
| C1 | 54.30 | 3.39 × 10⁻⁴ | 6.38 × 10⁻⁴ | 0.06095452 | CuO (PDF 801917) |
| C1 | 62.92 | 2.53 × 10⁻⁴ | 5.51 × 10⁻⁴ | 0.05430656 | Cu2O (PDF 782026) |
| C1 | 104.50 | 9.16 × 10⁻⁵ | 3.32 × 10⁻⁴ | 0.038844 | Cu4O3 (PDF 831665) |
| C2 | 56.89 | 3.09 × 10⁻⁴ | 6.09 × 10⁻⁴ | 0.05818386 | CuO (PDF 801917) |
| C2 | 84.88 | 1.39 × 10⁻⁴ | 4.08 × 10⁻⁴ | 0.04021248 | Cu2O (PDF 782026) |
| C2 | 85.64 | 1.36 × 10⁻⁴ | 4.05 × 10⁻⁴ | 0.047385 | Cu4O3 (PDF 831665) |
| C3 | 56.89 | 3.09 × 10⁻⁴ | 6.09 × 10⁻⁴ | 0.05818386 | CuO (PDF 801917) |
| C3 | 85.84 | 1.36 × 10⁻⁴ | 4.04 × 10⁻⁴ | 0.047268 | Cu4O3 (PDF 831665) |
| C4 | 59.64 | 2.81 × 10⁻⁴ | 5.81 × 10⁻⁴ | 0.05550874 | CuO (PDF 801917) |

Indeed, the weight loss of different systems observed in the temperature range of 25–200 °C was about 0.8–1.8%. The C1, C2, and C3 samples also displayed weight losses of about 1.9–2.8% and 0.9–2.6% in the temperature ranges of 250–360 °C and 373–425 °C, respectively, according to two minor endotherm peaks on the DTG curves in this region. These losses could be attributed to the conversion of Cu4O3 to Cu2O and CuO and/or the removal of organic moieties that remained in the biosynthesized NPs [43–46]. The weight losses of the C1, C2, and C3 samples due to the transformation of Cu4O3 increased as the Fe-dopant content increased. Indeed, the XRD results confirm that the content of Cu4O3 decreases by increasing the concentration of dopant and disappears in the C4 sample. The weight loss observed at 450–650 °C was about 9.5–18.5%, which corresponds to the partial conversion of CuO to Cu2O. This observation confirms that oxygen escapes from the prepared samples during the thermal treatment [47]. On the other hand, the noticeable loss of weight at above 600 °C also confirms the release of oxygen from the samples. Moreover, this weight loss above 600°C could be attributed to the elimination of carbon traces and/or formation of CuFe2O4 or CuFeO2 which was synthesized with a theoretical weight loss of 5.26% [30]. The XRD results in this study refer to the possibility of copper ferrite formation depending on the decrease in the height of the peak of both Cu2O and Cu4O3 crystallites that disappear in the C4 sample. Finally, the total weight loss of different samples increased by increasing the dopant content. The total weight loss values of the C1, C2, C3, and C4 samples were 20.1, 23.5, 29.5, and 26.5%, respectively. This increase in the total weight loss can be interpreted in terms of the formation of copper ferrite, which is the pinning center in doped systems.

3.3. FTIR Analysis

Figure 3 depicts the FTIR spectra of the C1, C2, C3, and C4 samples in the range between 4000 and 400 cm⁻¹. This figure consists entirely of various bands related to different functional groups. Some of these bands are strong and sharp in the range of 478–475 cm⁻¹, 1105–1101 cm⁻¹, and 1180–1177 cm⁻¹ while the other bands were weak. The bands located at 478–475 cm⁻¹, 431–421 cm⁻¹, 528–520 cm⁻¹ and 585–590 cm⁻¹ could have been attributed to the Cu(II)-O stretching of CuO nanoparticles [44]. In addition, the bands at 618–616 and 699–640 cm⁻¹ are also due to Cu (I)-O stretching of Cu2O nanoparticles [45–47]. The bands located at 1366–1352 cm⁻¹ and 1586–1537 cm⁻¹ are due to the C-O-H stretching of carbon traces [48,49]. The detected bands observed at 3730–3318 cm⁻¹, 1105–1101 cm⁻¹ and 1180–1177 cm⁻¹ could be attributed to the stretching and bending vibrations of the hydroxyl groups (O-H) for the adsorbed water molecules on the surface the as-prepared solids blended with KBr [50–52]. Fe doping resulted in a
change in the positions and intensities of the observed bands, especially the bands related to Cu-based nanoparticles.

Figure 2. TG-DTG patterns of the C1, C2, C3, and C4 samples.

3.4. Morphological Properties

SEM/TEM can be used to analyze the surface morphology of the systems under investigation. SEM images of the C1, C2, C3, and C4 samples are shown in Figure 4. The synthesized samples were composed of numerous nanosized particles, as can be seen in this diagram. The SEM images of various samples indicate that most particles are heavily agglomerated, resulting in diverse levels. On the uppermost surface layers, semi-spherical particles can be observed. The particle size of both agglomerated particles and those on the surface of the layers was reduced as a result of Fe doping. Figures also show the elemental analysis (EDS) of the C1, C2, C3, and C4 samples. It can be seen from this figure that the C1, C2, C3, and C4 samples consisted entirely of Cu, O, and C elements (inset tables in Figure 4).
The presence of the C element is due to the use of egg white in the synthesis process. In addition, the C2, C3, and C4 samples contained Fe elements as additional elements due to the doping of these samples by iron. The distribution of previous elements in various samples was determined using the elemental mapping method. This method depends on accumulating extremely precise elemental composition data over the surface of samples to provide high-resolution imaging via elemental composition data. The mechanism of this method can be discussed in terms of every pixel in the digital image being scanned to maintain the existing elemental spectrum, and then transforming the relative intensity into computed colorization layers with color code. Finally, the layers and sites of elemental compositional information were determined.

EDS mapping analyses of the various samples are presented in Figures 5 and 6. The elemental composition analysis was achieved concerning different positions from the SEM images presented in Figures 5a and 6a. Figures 5b–d and 6b–d display the homogeneity of distribution of the Cu, C, and O elements in the C1, C2, C3, and C4 samples. It can be seen from these figures that the whole body of the prepared samples is built from the Cu and O elements. In addition, we can observe that the concentration of distributed Cu elements increases as the dopant content increases due to the escape of the oxygen from the sample with the formation of copper ferrite, especially CuFeO$_2$ crystallites. Figures 5e and 6e show the homogeneity of the distribution of the Fe element in the C2, C3, and C4 samples. Based on the elemental mapping investigation, it can be seen that elements are properly distributed in the aggregated pure and doped CuO/Cu$_2$O/Cu$_4$O$_3$ nanocomposites.

The transmission electron microscopy (TEM) technique enabled us to study some specified morphological properties, such as the morphology, crystallization, particles sizes, and size distribution of the investigated samples. Figure 7 (left of Figure 7) displays TEM images of the C1, C2, C3, and C4 samples. This figure shows the presence of some agglomerated particles in different samples. The C1 and C2 samples contain many spherical and monoclinic-like structures with moderate sizes. The particles of the C3 and C4 samples have many spherical-like structures with high sizes due to the high agglomeration of nanosized particles. Figure 7 (right of Figure 7) also depicts the histogram for the particle size distribution of the C1, C2, C3, and C4 samples with an average size of the order of 20, 20, 24, and 55 nm, respectively. This indicates that Fe-doping stimulates the agglomeration of nanosized particles, yielding an increase in the grain size of the as-prepared solids. This behavior is comparable to that obtained from the XRD measurements.
the left of Figure 7) shows a set of concentric rings for the C1, C2, C3, and C4 samples, indicating the polycrystalline structure. These rings connected with well-defined spots, which emphasized the formation of highly crystalline particles.

Figure 4. Cont.
3.5. Surface Properties

The surface parameters of the C1, C2, C3, and C4 samples, namely SBET, VP, and \( \bar{r} \), were measured using \( \text{N}_2 \)-adsorption/desorption isotherms done at 77 K. Figure 8 depicts several isotherms of the as-prepared systems. These isotherms belong to type-II with a type H3 hysteresis loop, according to this figure. Furthermore, the surface area can be calculated using another method known as the t-method, which is based on t-curves. Furthermore, the surface area can be calculated using another method known as the t-method, which is based on t-curves. We were able to calculate the statistical thickness surface area (St) using this method, which is equal to the slope of a plot of the volume of adsorbate (Vl) vs. the statistical thickness adsorbed film (t). In Figure 8, Vl-t plots are shown. Due to the upward deviations that happen when the multilayers’ adsorption begins to be increased by capillary condensation in a porous material, these plots demonstrated that the as-constructed systems contain broad pores. The values of SBET, St, VP, and, \( \bar{r} \), are listed in Table 5. Fe-doping copper-based nanocomposites resulted in minor changes in SBET and St. On the other hand, this treatment increased the analyzed system’s total pore volume and mean pore radius. Fe-doping copper-based nanocomposites resulted in minor changes in SBET and St. On either token, this treatment led to an increase in the total pore volume and mean pore radius in the investigated systems.
Figure 5. Energy dispersive spectrometry (EDS) elemental mapping analyses of the samples C1 and C2: (a) SEM, (b) Copper distribution, (c) Oxygen distribution, (d) Carbon distribution, and (e) Iron Fe K.
Figure 6. Energy dispersive spectrometry (EDS) elemental mapping analyses of the samples C3 and C4: (a) SEM, (b) Copper distribution, (c) Oxygen distribution, (d) Carbon distribution, and (e) Iron Fe K.
Figure 7. Cont.
Figure 7. Transmission electron micrograph (TEM) images and particle size distribution of the C1, C2, C3, and C4 samples.

Table 5. Surface properties of the C1, C2, C3, and C4 samples.

| Samples | SBET (m$^2$/g) | St (m$^2$/g) | Vp (cc/g) | $\bar{r}$ (nm) |
|---------|----------------|--------------|-----------|-----------------|
| C1      | 8.867          | 14.219       | 0.0526    | 23.298          |
| C2      | 7.834          | 10.353       | 0.0430    | 21.932          |
| C3      | 9.836          | 12.254       | 0.0750    | 30.495          |
| C4      | 8.768          | 11.058       | 0.0843    | 38.454          |

3.6. Magnetic Properties

The magnetization (M-H) curves of the undoped and Fe-doped CuO/Cu$_2$O/Cu$_4$O$_3$ nanocomposites were determined at room temperature with an applied field in the range of ±20,000 Oe as shown in Figure 9. As seen from this figure, Fe-doping of the as-prepared system affects the shape of magnetization curves. The different magnetic parameters (Ms, Mr, Mr/Ms, and Hc) of the investigated nanocomposites are tabulated in Table 6. It can be seen from this table that doping of the CuO/Cu$_2$O/Cu$_4$O$_3$ system with iron increased the magnetic parameters studied. This increase is proportional to the content of the dopant. Therefore, the maximum increase in various magnetic parameters of our nanocomposite is more pronounced with the presence of 1.198 wt.% Fe, as shown in the case of the C4 specimen.

Table 6. The magnetic properties of the C1, C2, C3, and C4 samples.

| Samples | $M_s$ (emu/g) | $M_r$ (emu/g) | $M_r/M_s$ (emu/g) | $H_c$ (Oe) |
|---------|--------------|--------------|------------------|------------|
| C1      | 0.0146       | 0.0020       | 0.1370           | 106.63     |
| C2      | 0.5556       | 0.1408       | 0.2534           | 125.24     |
| C3      | 1.1248       | 0.3308       | 0.2941           | 122.28     |
| C4      | 2.3890       | 0.6307       | 0.2650           | 86.25      |
Figure 8. N$_2$-adsorption/desorption isotherms and $V_{14}$ plots of the C1, C2, C3, and C4 samples.
Figure 9. M-H curves at room temperature for C1, C2, C3, and C4 samples.
4. Discussion

This study acquires special importance due to its interest in obtaining CuO/Cu$_2$O/Cu$_4$O$_3$ nanocomposite, in addition to addressing the effect of Fe-doping on the stability of this compost. As a result of this importance, structural, morphological, and magnetic properties have been studied.

4.1. Formation of Pure CuO/Cu$_2$O/Cu$_4$O$_3$ Nano Composite

XRD measurements confirmed that the auto-combustion for a mixture of copper nitrate and egg white at 350 °C for 15 min resulted in the formation of copper-based multiple oxides that crystallized as CuO, Cu$_2$O, and Cu$_4$O$_3$. Moreover, one of our previous studies of the same precursor without using different concentrations of egg white 300 °C for 10 min resulted in the formation of both Cu$_2$O/CuO and Cu$_2$O/Cu [34]. These results strongly illustrate the effect of the preparation method on the stability and/or phase transformation of CuO crystallites. The stabilizing and controlling role of egg white in the synthesis of CuO/Cu$_2$O/Cu$_4$O$_3$ nanocomposite using the combustion method can be summarized as follows [53–59]: (i) egg white is a biological and natural fluid containing high levels of amino acids and proteins such as albumin and lysozyme. However, it has binding adhesion, gelling, foaming, and emulsifying characteristics. In addition, it can be associated with metal ions due to its easy solubility in water. All of these characteristics qualified the egg white to be a matrix for entrapment of metal ions to generate a gelled precursor to prepare size-controlled particles. (ii) Egg white leads to a fast thermal decomposition of the precursor through the self-combustion process. (ii) Egg white provides a reducing atmosphere for the reduction of some or all metal ions through the gases released during the combustion process. In addition, the burning of egg white produces a very small amount of carbon, which facilitates the reduction process of metal ions as follows [57]:

$$4\text{CuO} + \text{C} \rightarrow 2\text{Cu}_2\text{O} + \text{CO}_2$$  \hspace{1cm} (5)

On the other hand, the increase in both the heat temperature and the heat time (350 °C/15 min) compared with the previous work (350 °C/15 min) stimulates the solid-state reaction between some CuO and Cu$_2$O crystallites to form Cu$_4$O$_3$ nanoparticles as following:

$$2\text{CuO} + \text{Cu}_2\text{O} \rightarrow \text{Cu}_4\text{O}_3$$  \hspace{1cm} (6)

4.2. Formation of Pinning Materials within the Synthesized Doped Systems

Iron doping had clear effects on the stability and various properties of multiple copper oxides. The doping of pure CuO/Cu$_2$O/Cu$_4$O$_3$ nanocomposite with 1.198, 0.599, and 0.198 wt.% Fe resulted in the formation of doped CuO nanoparticles and both doped CuO/Cu$_4$O$_3$ and doped CuO/Cu$_2$O/Cu$_4$O$_3$ nanocomposites, respectively. The effects of Fe-doping on some structural properties of CuO/Cu$_2$O/Cu$_4$O$_3$ composite can be summarized in the following points: (i) The iron ions become mobile and either contribute to form a solid solution with copper oxides via an incorporation process and/or start producing seeds of the CuFe$_2$O$_4$ and/or CuFeO$_2$ crystallites that are not observable by XRD technique due to their small quantities and also a small amount of the dopant. Evidence for these contributions is summarized in the slight shift in diffraction peaks of the crystalline phases and/or the observed decrease in the unit cell volume, with a subsequent decrease in the height of the peaks of such phases. (ii) In the Fe-deficient doped sample, the C2 sample, the strongest possibility will be the formation of a solid solution by incorporation of iron ions in the crystal lattices of copper oxides. This speculation could be attributed to the ionic radius difference between Cu$^{1+}$ (0.096 nm), Cu$^{2+}$ (0.069 nm) and Fe$^{2+}$ (0.076 nm) or Fe$^{3+}$ (0.064 nm). However, a slight increase in the magnetism of the C2 sample compared to the undoped specimen indicates the incorporation process. (iii) In richly doped samples (C3 and C4), no one can ignore the possibility of dissolving some Fe ions in copper crystals to form a solid solution (Cu$_{1-x}$Fe$_x$O) and/or occurrence of an additional reaction in the solid-state between other Fe ions and copper ions to form CuFe$_2$O$_4$ and/or CuFeO$_2$. The
complete disappearance of all peaks of both Cu₂O and Cu₄O₃ phases, as shown in the C₄ sample, confirms the solid-state reaction between copper oxides and iron oxide yielding CuFe₂O₄ and/or CuFeO₂. Based on all of the above, we can conclude that Fe-doping of CuO/Cu₂O/Cu₄O₃ nanocomposite prepared by using a 7 ml egg white-assisted auto combustion route resulted in the formation of a pinned type composite containing magnetic copper nanoparticles [30]. The formation of CuFe₂O₄ and CuFeO₂ as pinning nanoparticles within the matrix of CuO/Cu₂O/Cu₄O₃ nanocomposite is as follows:

\[ \text{CuO} + \text{Fe}_2\text{O}_3 \rightarrow \text{CuFe}_2\text{O}_4 \quad (7) \]

\[ \text{Cu}_2\text{O} + \text{Fe}_2\text{O}_3 \rightarrow 2\text{CuFe}_2\text{O}_2 \quad (8) \]

Indeed, the functional molecular groups, that are present on the surface of the studied materials, can be determined by FTIR spectroscopy. In this study, FTIR analysis has contributed to providing important information about the identification of the material’s phase composition. However, this analysis emphasized the existence of some functional groups (O-H and C-O-H) that confirm the advantages of the prepared materials. The presence of hydroxyl groups at 4000–3300 cm⁻¹ and 1180–1100 cm⁻¹ due to the adsorption of water molecules by humidity indicates the formation of nanosized systems [60,61]. On the other hand, using the egg white-mediated approach to prepare the materials led to their contamination by some carbon ash [60]. The observation of C-O-H groups around 1355 cm⁻¹ and 1550 cm⁻¹ confirms the presence of carbon traces, which led to the reduction of some CuO to form Cu₂O with subsequent formation of CuO/Cu₂O/Cu₄O₃ nanocomposite.

FTIR study provides us with important information about the material’s phase composition as follows: (i) The characteristic stretching vibrations of the Cu(II)-O bond in monoclinic CuO along (202), (−202), and (−111) directions were located at 430, 475, and 525 cm⁻¹, respectively [55–57]. However, most researchers confirm that the bands located in the range between 600 cm⁻¹ to 700 cm⁻¹ are corresponding to Cu(I)-O stretching of Cu₂O nanoparticles [61,62]. In addition, some authors have observed at 640 cm⁻¹ on FTIR spectra of copper-based materials related to the M-O-M stretching mode [61]. These observations speculated about the formation of multiple oxide-based nanostructures. (ii) As shown from FTIR spectra, the positions and intensities of the bands are affected slightly by Fe-doping, and also these intensities significantly increased by increasing the dopant content. This indicates that Fe ions are incorporated in the crystal lattices of CuO, Cu₂O, and Cu₄O₃ with subsequent formation of some ferrites containing CuFeO₂ and/or CuFeO₃. These ferrites exhibit two fundamental IR active modes around 600 cm⁻¹ and 400 cm⁻¹, which overlap with the modes of metal oxide investigated [63].

Fe-doping of CuO/Cu₂O/Cu₄O₃ nanocomposite resulted in various changes in its different structural and morphological properties. On the other hand, this treatment brought about a slight modification in the textural properties of the nanocomposite studied. The surface areas of different specimens varied between 7.834 and 9.836 m²/g with an increase in the values of Vp and t from 0.0526 cc/g and 23.298 nm to 0.0843 cc/g and 38.454 nm, respectively [60]. These findings are in agreement with the results of XRD, SEM, and TEM in terms of increasing the crystallite size and particle size. However, Fe-doping of CuO/Cu₂O/Cu₄O₃ nanocomposite did not change the nature of its wide pores but maintained the type of these pores with metacharacter. However, the micropores are present in the as-prepared samples, depending on the observed jump in all isotherms at low relative pressure. The comparison between the values of SBET and St indicates that these values are close to each other, which justifies the choice of the t-curve for the surface area analysis and also reveals the absence of ultramicropores.

4.3. Magnetization of Pure CuO/Cu₂O/Cu₄O₃ Nano Composite

First, paramelaconite (Cu₄O₃) is a derivative of melaconite CuO (today tenorite). It is a mixed valences oxide (Cu₂2⁺Cu₂1⁺O₃) because it is an intermediate copper oxide [62]. Indeed, the bulk of both CuO and Cu₂O display an antiferromagnetic (AFM) nature at room temperature. Consequently, Cu₄O₃ demonstrates AFM at room temperature. Despite
this, the nanosized particles of these oxides have magnetic properties due to the presence of room temperature ferromagnetism (RTFM) and/or paramagnetism/superparamagnetism associated with the AFM of these particles. In addition, we could also observe nonsaturation of the M-H curve for the C1 sample (right inset of Figure 9) with the presence of a superparamagnetic-like behavior. This finding demonstrates the exchange bias depending on the presence of a mixture of AFM and superparamagnetic-type compounds.

On the other hand, the origin of the superparamagnetic character in previous oxides could be attributed to different effects, such as the double exchange interaction, superexchange interaction, and pinning behavior at the interface or the surface [30,34]. These effects depend entirely on both the localized carrier at oxygen vacancy (Vo) and the valence of copper ions at the surface of CuO, which is composed of “+1” and “+2” valence states [34,64]. Therefore, the key factors that govern the magnetic properties of pure CuO/Cu$_2$O/Cu$_4$O$_3$ nanocomposites, are intra- and interphase exchange coupling interactions according to (Cu$^{2+}$-Vo-Cu$^{2+}$) and (Cu$^{1+}$-Vo-Cu$^{2+}$), respectively [34]. In other words, the RTFM of pure CuO/Cu$_2$O/Cu$_4$O$_3$ nanocomposites could be attributed to super- and double exchange interactions. These interactions demonstrate the mobility of the electrons between the Cu ions via Vo, yielding a ferromagnetic alignment.

4.4. Magnetization of Doped Systems Studied

The M-H curve for the C2, C3, and C4 samples displayed contributions from ferromagnetic and superparamagnetic components depending upon these samples consisting of Fe-doped CuO/Cu$_2$O/Cu$_4$O$_3$, Fe-doped CuO/Cu$_4$O$_3$, and Fe-doped CuO phases, respectively. Moreover, we could also observe saturation of the M-H curve for the C2, C3, and C4 samples (right inset of Figure 9). The origin of the RTFM character of the doped copper oxides could be attributed to domain wall pinning effects. Indeed, domain wall pinning is the main mechanism responsible for the observed magnetic behavior of doped samples. The domain wall motion can be discussed by combining the interface random walk approach and ideas from the Zener pinning model, which describes the interaction between the grain boundary and the pinning particles within the framework of the interface random walk approach [64–66].

In this study, the pinning centers can be raised from the formation of Cu–Fe–O solid solution formed within the sample apart from the composite-like behavior of superparamagnetic copper oxides dispersed, especially in the case of the C2 and C3 samples. One cannot also ignore the formation fraction of soft magnetic CuFe$_2$O$_4$ and/or CuFeO$_2$ nanoparticles as pinning sources. Similar results were investigated in the case of nanocrystal line and bulk samples of Fe-doped CuO were prepared by coprecipitation and ceramic methods [34].

Although the solubility of “Fe” in CuO is very much limited, a very small quantity of any immiscible component will always dissolve in and/or react with other components, such as Cu$_2$O and Cu$_4$O$_3$ yielding CuFe$_2$O$_4$ and/or CuFeO$_2$. Based on the XRD results, the decrease followed by the disappearance of the peak height of Cu$_2$O and Cu$_4$O$_3$ phases confirms this observation.

The strength, density, and dimensionality of the pinning centers can affect the value of coercivity. The value of coercivity decreases as the dopant concentration increases with a subsequent increase in squareness and magnetization. These findings were supported by increasing the crystallite size of both CuO and Cu$_2$O with a subsequent decrease in the values of $\delta$, $\epsilon$, and $\sigma$ for these oxides. However, these results confirm that the Fe-doped CuO/Cu$_2$O/Cu$_4$O$_3$ nanocomposites tend toward a “soft” nature. Although wall pinning is one of the impediments to wall motion, the pinning centers in our case as soft magnets do not impede because their magnetic properties are similar to those of the matrix.

Finally, this study confirms the formation of single-phase doped CuO, which is desirable for device fabrication, from CuO/Cu$_2$O/Cu$_4$O$_3$ nanocomposites by using egg white mediated auto-combustion route as follows: (i) it could be stabilized in a single-phase Cu–Fe–O solid solution without any ferrite formation. (ii) It could be prepared as a sample with homogenously dispersed CuFe$_2$O$_4$ and/or CuFeO$_2$ in CuO.
5. Conclusions

Based on the main objective of this study and the included analyses, we can summarize the conclusions of this study and come out with a recommendation for future research in this regard, as follows:

Undoped and Fe-doped CuO/Cu2O/Cu4O3 nanocomposites had been synthesized successfully by using a step-based auto combustion route. To make the green synthesis of our composite, we used egg white as a natural substance with special features.

Doping of CuO/Cu2O/Cu4O3 nanocomposites with 0.198, 0.599, and 1.198 wt.% Fe led to the formation of three doped systems; (i) the first system consisted of CuO, Cu2O, and Cu4O3 crystallites due to the doping with 0.198 wt.% Fe. (ii) The second system is composed of CuO and Cu4O3 due to doping with 0.599 wt.% Fe. (iii) 1.198 wt.% Fe-doping resulted in information about the third system, which contains CuO as a single phase.

Fe-doping of the synthesized composites brought about different modifications in various structural properties of composite constituents, namely CuO, Cu2O, and Cu4O3. Because of doping with iron oxides, the total pore volume and mean pore radius of the as-prepared system increased. Due to the doping, the as-synthesized nanocomposite was found to have slight changes. In several isotherms of the systems studied, Type II hysteresis loops with H3 were identified.

Unsaturation of the M-H curve was observed for the C1 sample in the presence of superparamagnetic-like behavior. Saturation of the M-H curve was observed for the C2, C3, and C4 samples with contributions from ferromagnetic and superparamagnetic components.

The magnetization and the squareness of the synthesized systems increased as the dopant concentration increased, while the coercivity of these systems decreased due to the domain wall pinning effect.

Doping of CuO/Cu2O/Cu4O3 nanocomposites with 1.198 wt.% Fe resulted in the formation of single-phase magnetic CuO nanoparticles, which is desirable for device fabrication.

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