Enhancement the larvicidal activity of nanostructure copper oxide against Culex pipiens mosquito by yttrium replacement based on crystallite size reduction and topographic surface nature

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Abstract
The current work aims to improve the metal oxide characteristics for mosquito control. Un-doped and Y-doped CuO have been synthesized by simple chemical route. Structural, composition, and morphological properties were characterized by XRD, Raman spectra, EDX, SEM, and TEM techniques. The obtained results revealed that CuO was strongly affected by Y3+ support, in which the crystallite size decreased, and the surface area increased. Larvicidal performance was assessed against Culex pipiens suggesting that the nanocomposite CuO/Y of higher efficiency (LC50 = 7.67 mg/l, \( R^2 = 0.977 \)) compared with pure CuO. Light microscopy and SEM images exhibited larvae malformations owing to using the fabricated nanomaterials.

1. Introduction
Mosquitoes are the main vector of severe diseases and risks including malaria, dengue, and filariasis which are the reason for death about two million people annually [1]. Culex pipiens (Diptera: Culicidae) is defined as the major vector of filarial nematode, Wuchereria bancrofti [2]. Filariasis is one of the most dangerous neglected diseases prevalent over the urban and semi-urban areas [3]. Due to the passive effect on environment and human public health, several studies have been investigated by the scientific community for reducing the blood-sucking mosquito populations [4–7]. It was found that, persistence using of traditional insecticides increase mosquito resistance. So, alternative techniques with novel strategies became necessary for mosquito control. Synthesis of the nanomaterials using different routes could be effective to overcome this threat. Metal oxide nanoparticles are set of these materials that possess special physical and chemical aspects. Recently, transition metal oxides have been used in various technological applications because of their tremendous advantages. For instance, zinc oxide (ZnO), titanium dioxide (TiO2), and manganese oxide (MnO) were successfully used as anti-larvicidal agents to control the growth of mosquito populations [8–11]. Naik et al. [12] have reported the larvicidal activity of pristine \( \alpha \)-MnO2 nanoparticles (NPs) combating mosquito (Diptera: Culicidae). Moreover, zinc oxide (ZnO) was used to control Aedes aegypti, which considered main source for malarial disease in tropic and subtropics regions [13, 14]. Nanosized copper oxide (CuO) of narrow band gap, p-type semiconductor, and good electrical conductivity plays an imperative role in chemical engineering and biological fields such as biosensing, biomedical, antibacterial, and implants [15, 16]. Copper oxide NPs were used as mosquitoicides [17], provided less toxicity toward the environment than with metal nanoparticles [11, 18]. Besides, rare-earth (RE) elements have much attention in the past few decades owing to their physical and chemical properties like rich absorption and emission spectra. Combination of appropriate amount of trivalent yttrium ions into metal oxide lattice will produce nanocomposite of small particle size, strong electronic transition and high photoluminescence [18–20]. There are several reports on tuning the properties of nonmetal oxides by RE elements. For example, induce cerium ions inside manganese oxide led to the phase transition from \( \beta \)-MnO2 to \( \alpha \)-MnO2 [21, 22]. Further,
Darwish et al. [23] have developed the nanocomposite Ag3VO4 decorated by Y2O3 for bactericides and larvicides. Numerous routes have been carried out to fabricate metal oxide nanostructures such as sol gel, hydrothermal treatments, chemical reduction, spray pyrolysis, and microwave assisted method [24–27]. Amid aforementioned methods, simple, low cost, large yield, and rapid chemical precipitation method has been used to fabricate fine nanoparticles. The present study refers to use the nanotechnology to overcome the drawbacks and obstacles of conventional mosquitocides. In this work, structural and surface morphological properties of CuO have been improved by Y3+ replacement for using as anti-larvicidal agents.

2. Experimental section

2.1. Fabrication of CuO and CuO/Y (30 wt%) nanomaterials
The nanopowder samples have been synthesized according to the following chemical reactions:

\[
(C_2H_3O_2)_2Cu \cdot H_2O + 2NaOH \rightarrow 2(NaC_2H_3O_2) + Cu(OH)_2 + H_2O
\]

\[
Cu(OH)_2 \rightarrow CuO + H_2O
\]

\[
YCl_3 + 3NaOH \rightarrow Y(OH)_3 + 3NaCl
\]

\[
2Y(OH)_3 \rightarrow Y_2O_3 + 3H_2O
\]

Firstly, CuO precursor solution was stoichiometry prepared by dissolving 12.50 g copper (II) acetate dehydrate Cu(CO_2CH_3)_2.2H_2O in 60 ml distilled water. Besides, 5 g sodium hydroxide (NaOH) was separately dissolved in 60 ml distilled water after that added drop by drop to the above solution with continuous stirring at a constant speed 500 rpm for 3 h. The product precipitate was formed at pH value of 9–10. Then filtered and thoroughly washed by distilled water to remove the unreacted salt ions. The final product was dried at 70 °C for 5–6 h in an oven and finally calcined in a muffle furnace at 500 °C for 2 h. The nanocomposite CuO/Y was produced by adding 3.25 g yttrium chloride (YCl3) to copper acetate solution with continuous stirring at room temperature. NaOH solution was wisely added to the mixture and the precipitate was filtered, washed, dried, and eventually annealed at the same conditions of pure CuO.

2.2. Instruments and characterization
The prepared powders were identified at room temperature by means of powder x-ray diffractometer (XRD; Rigaku Smart Lab.) operating at 40 kV, CuKα radiation (\(k = 1.5418 \text{ Å}\)) with a step size 0.2. The molecular structure and dopant ions of the nanopowders have been examined by Raman (Horiba Lab RAM HR Evolution) with 514.5 nm laser excitation. In order to prepare the thin films, 0.02 g of the nanostructures have been dissolved into 10 ml of ethanol solution under sonication then deposited onto p-type silicon and were left for drying. The films have been coated by thin conductive iridium layer using imaging sputter coater (Model, EMS 150T ES) for measuring the topological properties. Surface morphology and elemental chemical composition have been defined under scanning electron microscopy (SEM, Helios Nanolab. 400) attached with energy dispersive spectroscopy (EDX). Transmission electron microscopy (TEM) on (Hitachi-H-7500) was employed to visualize the mean size and particle’s distribution.

2.3. Mosquito rearing
Larvae of Cx. pipiens were reared in the Entomology laboratory, Zoology Department, Zagazig University, Egypt under conditions 26 ± 2 °C, 80 ± 5% relative humidity (R.H.) and photoperiod 14 l: 10D. The adult mosquitoes were kept in cages (40 × 40 × 40 cm) and fed 10% glucose solution; the females lay eggs two days after a blood meal. Egg rafts were hatched in a plastic tray containing water. Larvae were reared in plastic trays (30 × 25 × 5 cm) and fed on fish food.

2.4. Toxicity effect of nanoparticles on Cx. pipiens larvae
The Cx. pipiens larvicidal test was done by following the steps of the WHO protocol (2005), CuO and CuO/Y NPs were tested at concentrations (1, 5, 10, 15 and 20 mg l⁻¹). Twenty of 3rd larval instars were taken in a 500-ml glass beaker containing 250 ml of double distilled water with each of the NPs. For each concentration, five replicates were performed. The death was noted after 48 h of treatment and determined by the immobility of the larvae, even after light touch with a glass rod [28]. The control group was kept in double distilled water. The mortality rate was determined from the average of 5 replicates.

2.5. Light microscopy
After 48 h of treatment, the dead larvae were washed in 95% alcohol and examined using a light microscope (CXL Binocular compound microscope optic).
2.6. Scanning electron microscopy (SEM)
To stabilize the structure of samples, the treated larvae were prefixed in 2.5% glutaraldehyde (Sigma) about 2 h, washed with 0.1 M cacodylate buffer (pH 7.2) for about 15 min and used osmium tetroxide (OsO₄) to post-

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![Figure 1](image_url)

**Figure 1.** (a) XRD, (b) Raman, and (c), (d) EDX spectra of un-doped and Y-doped CuO nanopowders annealed at 500 °C.
fixation for 2 h. The specimens washed with buffer, dehydrated in ethanol dilution series (35%, 50%, 75% and 95%), embedded in an acetone solution, coated with iridium by an imaging sputter coater (Model, EMS 150T ES), and finally examined using a SEM (Model, Helios Nano-lab. 400) at 10 KV.

2.7. Statistical analysis
The mortality data were analyzed with SPSS version 14; using one-way analysis of variance (ANOVA) followed by pairwise comparisons based on Tukey’s HSD tests. The mean rates of larval mortality were subjected to probit transformation analysis to estimate LC50 and other statistics at 95% fiducial limits. All differences were considered significant P ≤ 0.05. The activity of nanomaterials against the larvae was obtained from the formula [29]:

\[
\text{Larvicidal activity (LA, %)} = \left( \frac{M_{\text{Test}} - M_{\text{Control}}}{\left(100 - M_{\text{Control}}\right)} \right) \times 100
\]

where, \(M_{\text{Test}}\) and \(M_{\text{Control}}\) according to the percent of the observed death rate of larvae in the tested and the control cup, respectively.

3. Results and discussions

3.1. Analysis of microstructure and surface morphology of polycrystalline nanopowders
Figure 1(a) provides XRD pattern of the samples. As described, the diffraction peaks at 2θ positions 32.72°, 35.73°, 38.82°, 48.87°, 53.56°, 58.48°, 61.71°, 66.25°, 68.28°, 72.62°, 75.35° correspond to (110), (−111), (111), (−202), (020), (202), (−113), (−311), (220), (311), (004), planes are ascribed to base centered monoclinic copper oxide, consistent with the standard card (JCPDS # 048-1548) [30–33]. No peaks for any traces such as Cu(OH)2 or cubic Cu2O are observed in the spectrum [32, 33]. Further, the sharp lines reveal the well crystallinity of pure CuO, whereas doped CuO displays low intensity peaks related to small grain size. The CuO spectra was changed by doping indicating more characteristic reflected peak at 2θ = 29.20° associated with yttrium oxide [34, 35]. When Cu was replaced by Y3+ ion inside the copper oxide framework, lattice disorder and strain are produced which result in phase segregation.

There are many factors and conditions effect on the crystallographic properties of the nanoparticles. Babu et al [36] have reported the impact of Mn dopants on bond length, crystal size, surface morphology and optical properties of CuO [37–39]. Jassem et al [40] have also reported the influence of pH values and calcination temperature on the microstructure of manganese oxide nanoparticles. The crystallite size (D) has been estimated by Debye’s Scherrer formula applied on the preferential orientation peak (111) [30, 31] given by:

\[
D = \frac{K\lambda}{\beta \cos \theta}
\]

Here, \(\beta\) is the line broadening at FWHM, \(\lambda\) the wavelength of the x-ray, \(k = 0.94\) the shape factor, and \(\theta\) the diffraction angle. The lattice strain (\(\varepsilon\)), dislocation density (\(\delta\)), and degree of crystallinity (\(X_c\)) were defined from the following expressions [31, 33]:

\[
\varepsilon = \frac{\beta \cos \theta}{4}
\]

\[
\delta = \frac{1}{D^2}
\]

\[
X_c = 0.24 / \beta
\]

The specific surface area was expressed as [41, 42]:

\[
S_a = \frac{6}{\rho \times D}
\]

where, \(\rho\) is the density of CuO = 6.31 g cm\(^{-3}\). The XRD parameters are estimated and summarized in table 1. As presented in table 1, D and \(X_c\) were decreased however, \(\varepsilon\) and \(\delta\) increased by yttrium doping. The reduction of crystallite size is attributed to the dissimilar ionic radii of Y3+ (1.02 Å) to Cu2+ (0.71 Å) that make crystal growth restriction. The increase of strain can be explained by the big difference in the electronegativity

| Metal oxide NPs | D (nm) | \(\varepsilon \times 10^{-3}\) | \(\delta \times 10^{-4}\) (nm\(^{-2}\)) | \(X_c\) | \(S_a \times 10^{-4}\) (cm\(^2\) g\(^{-1}\)) |
|----------------|--------|-----------------|-----------------|---------|-----------------|
| CuO            | 21.33  | 4.60            | 22.00           | 41.00   | 53.00           |
| CuO/Y          | 16.83  | 6.00            | 35.00           | 31.00   | 67.00           |

Table 1. XRD parameters of un-doped and Y- doped CuO nanomaterials.
between yttrium 1.22 and copper 1.90 [35, 43] in addition to high Y$^{3+}$ concentration (30 wt%) [44]. It was observed that, doping of Y interstitial will influence on copper, oxygen vacancies, and copper vacancies concentration [12, 38, 45]. The findings refer to that the nanocomposite copper yttrium oxide of large specific surface area which is so effective for mosquito control. To define the phase contents and doping elements, Raman spectra were done at room temperature. As illustrated in figure 1(b), host CuO exhibits three bands related to Cu-O vibrations, a strong peak at wave number 282 cm$^{-1}$ and another two weak peaks at 620 and 1087 cm$^{-1}$. Moreover, the doped sample shows three Raman active modes assigned to Cu-O-Y stretching frequency. The CuO/Y peaks are weak and broad owing to the change of energy levels inside the band gap [46–48].

The chemical composition and purity of the nanomaterials were recorded by EDX spectra. Figure 1(c) describes the pure CuO consists of Cu and O elements of average atomic percentage 72.64 and 27.36 respectively. The peak appears at 2.01 eV attributed to the presence of yttrium ions (figure 1(d)) [48–50]. For further microstructure analysis, surface nature and particle size distribution were characterized by SEM and TEM micrographs. Figure 2(a) displays CuO NPs uniformly distributed in hexagonal shapes [51]. Whereas the particles of CuO/Y nanocomposite are agglomerated in different needle shapes and volumes with high surface to volume area (figure 2(b)) [52–54]. It is clearly observed that, the surface morphology of un-doped CuO highly affected by Y$^{3+}$ generating free charge carriers and new active sites [12, 55]. It was found that, the SEM results of copper yttrium oxide is consistent with literature [56] who suggest that the microstructure and morphology strongly affected by doping ions. According to figure 2(c), pure CuO appears in nanospheres linked with hexagonal shapes. Furthermore, the particles of CuO/Y are aggregated together in sphere and rod shapes, figure 2(d) [57]. Where, the nanospheres ascribed to CuO while the nanorods attributed to Y$_2$O$_3$. It is worthy to note that, the average particle size of CuO nanospheres was decreased from 80 nm to approximately 50 nm by Y dopants [58, 59].
3.2. Larvicidal performance of the nanoparticles on *Cx. pipiens* larvae

The larvicidal activity was executed to examine the bio-influence of pure and doped CuO on the *Cx. pipiens* larvae. Third larval instar of *Cx. pipiens* have been subjected to the prepared nanostructures and the death rate was evaluated by a little amount of the nanostructures (1, 5, 10, 15 and 20 mg l\(^{-1}\)). Un-doped CuO showed mortality rates of 12.6 ± 0.478 to 76.8 ± 0.645% and from 24.2 ± 0.408 to 100% for the nanocomposite CuO/Y (table 2). The mortality probability of the nanopowder on *Cx. pipiens* mosquito larvae was distributed in figures 3(a), (b). It was observed that the larvicidal activity has been achieved by utilizing a small amount of the nanomaterials [60]. Moreover, LC\(_{50}\) of pure and Y-doped CuO against the larvae (*Cx. pipiens*) was 11.657 mg l\(^{-1}\) and 7.647 mg l\(^{-1}\), respectively (table 2). As described in table 2, the toxic effect of the nanoparticles against the tested larvae dependent on the concentrations. Owing to the habitation of *Cx. pipiens* larvae make it close to water surface to breathe through their long siphon and hence the large area of the larvae body is subjected to the nanopowder suspension. [61]. Limited studies have been reported to control mosquito larvae using nanometal oxides and rare-earth elements. In these studies, semiconducting materials involve zinc oxide, bismuth oxide, magnesium oxide, titanium oxide, silver oxide, and cerium oxide. Benelli [62] are examined against the mosquito vectors which are responsible for the transmission of life-threatening diseases. In addition, various LC\(_{50}\) of the nanomaterials are recorded against mosquito dependence of the tested species and their life stage. 100% mortality was evaluated upon the 1st larval instar of *Aedes aegypti* at concentration 0.250 mg l\(^{-1}\) after 24-h of CeO\(_2\) treatment [63].

The nanostructure Fe\(_2\)O\(_3\) achieved LC\(_{50}\) range from 4.5 ppm for 1st larval instar to 22.1 ppm for pupae. LC\(_{50}\) of ZnO rod shape against *Ae. aegypti* was ranged from 3.44 (1st larva) to 14.63 ppm (pupa) with high larvicidal efficiency. Further, nanostructured zinc oxide exhibits 100% mortality of mosquito (larva IV) for (Anopheles stephensi), and (Culex quinquefasciatus) at 8 and 10 \(\mu\)g ml\(^{-1}\). [64]. CuO NPs exhibits high larvicidal activity against the larvae of *Anopheles subpictus* with LC\(_{50}\) (32 ppm) at 48 h. post treatment [60, 65]. In literatures, the

| Table 2. Dose-dependent larvicidal activity against *Cx. pipiens* species. |
|-----------------|-----------------|--------------------|-----------------|-----------------|-----------------|
| Metal oxide NPs | Conc., mg l\(^{-1}\) | Mortality% mean ± SE | LC\(_{50}\) mg l\(^{-1}\) | (96% LCL–UCL) mg l\(^{-1}\) | Slope | Regression equation |
| CuO            | 1               | 12.6 ± 0.478        |                  |                  |                  |                  |
|                | 5               | 34.7± 0.645         |                  |                  |                  |                  |
| CuO/Y         | 10              | 51.5 ± 0.478        | 11.657           | 7.965–16.959     | 0.10            | \(Y = 0.1X + 1.257\) |
|                | 15              | 61.5 ± 0.478        |                  |                  |                  |                  |
|                | 20              | 76.8 ± 0.645        |                  |                  |                  |                  |
|                | 1               | 24.2 ± 0.408        |                  |                  |                  |                  |
|                | 5               | 42.0 ± 0.478        |                  |                  |                  |                  |
|                | 10              | 64.2 ± 0.645        | 7.647            | 4.176–11.410     | 0.116           | \(Y = 0.116X + 0.75\) |
|                | 15              | 80.0 ± 0.853        |                  |                  |                  |                  |
|                | 20              | 100' ± 0.000        |                  |                  |                  |                  |

LC\(_{50}\), lethal concentration that kills 50% of the exposed larvae; UCL, upper confidence limit; LCL, lower confidence limit; Significant at \(P \leq 0.05\); SE: stander error. Letters indicate degree of significant based on Tukey’s HSD tests between concentrations.

Figure 3. (a)–(b) Probability analysis of mortality of *Cx. pipiens* mosquito larvae by CuO and CuO/Y nanopowders.
availability, cost-effective production, co-friendly nature of the nanoparticles, and their low toxicity to human cells make it proper to heal some fungal and germ diseases in joints, intestines, and urinary tract moreover, it is considered an effective larvicidal agent [8, 66]. In the present work, pure and doped CuO have been used as anti-larvicides thank to small particle size, dispersion, and excellent surface to volume area [67, 68].

3.3. Histopathological investigation of treated larvae
To estimate the destructive effect of the fabricated nanoparticles on Cx. pipiens larvae and the ability to change their morphology are inferred by histopathological studies after a 48 h of exposure time at 20 mg l⁻¹, as observed in (figures 4, 6, 7). Light microscope images of treated larvae with synthesized samples revealed the damage and malformation in several body parts. Similar observation has been seen using cadmium nanometal and zinc oxide nanopowder against mosquito larvae, respectively [69, 70]. The damaged tissues suffer major changes involving rupture, and epithelial layer vanishing and aggregation of the nanostructure in the abdomen and respiratory opening as shown in figure 4. The presented results are matched with the literatures [62, 65, 71] who reported that CuO NPs possess anti-larvicid activity on Anopheles subpictus result in damage in the digestive canal,

Figure 4. Light microscope photographs of body parts (head, abdomen, and respiratory opening) of the 3rd larval instars of Cx. pipiens treated with CuO NPs. (a), (c), (e) and Y-doped CuO nanocomposite (b), (d), (f) (10 × 150).
Figure 5. The SEM micrographs of the untreated third larval instar of mosquito Cx. pipiens, (a) whole larval body; (b), (c) head capsule and mouth parts; (d), (e) abdominal segments; (f), (g) respiratory gills and siphon.
Figure 6. The SEM micrographs of third larval instar of mosquito Cx. pipiens larvae treated by CuO NPs for 48 h incubation period, (a)–(c) head capsule and mouth parts; (d), (e), Abdominal segments; (f), (g) respiratory gill and siphon.
Figure 7. The SEM micrographs of third larval instar of mosquito *Cx. pipiens* larvae treated by CuO/Y NPs for 48 h incubation period, (a)–(c) head capsule and mouth parts; (d)–(f) Abdominal segments; (g)–(i) respiratory gill and siphon.
siphon, and gills of mosquito larvae. On the other side, SEM microscopy images of untreated third larval instar are described in (figure 5), the body of the larvae is covered with many hairs in the dorsal region showed normal morphological features without any malformation (figure 5(a)). The head of the larvae has a typical, rounded, hardened capsule (SC) having chewing mouthparts (CM) and mouth brushes (MB) (figures 5(b), (c)). The muscles of larval midgut are arranged as a grid-like network (figures 5(d), (e)). The final segment of an untreated larvae of mosquito (figures 5(f), (g)) exhibit normal anal papilla (Ap), siphon (S), pectin teeth (Pt), saddle (Sa) and comb scale (CS). All these hallmarks of mosquito larvae have been described in previous studies [72, 73]. After exposed mosquito larvae to CuO, the nanoparticles were observed in the mouthparts, their brushes and vanishing of larval antennae, (figures 6(a)–(c)).

The larval body is entirely thinned, and the particles adhered to its cuticle (figure 6(d)) with high shrinkage of the abdominal muscles (AbdM) (figure 6(e)). The larval respiratory opening is significantly malformed, and the siphon is blocked with NPs (figures 6(f), (g)). Upon treatment by CuO/Y NPs, malformations are produced in different parts of the larval body, (figure 7), there was large amounts of the nanocomposite on the head, particularly mouth brushes and chewing mouthparts causing damage of antennae (figures 7(a)–(c)). The larval muscularis is extensively demolished and the particles distributed in the abdominal cuticle causing abdominal segments damage as demonstrated in (figures 7(d)–(f)). Also, the larval respiratory gills and the siphon were plugged with NPs result in suffocation (figures 7(g)–(i)) [2, 23, 74, 75].

4. Conclusions

CuO and Y-doped CuO nanopowders were successfully prepared by co-precipitation method. The prepared samples were identified using different techniques belong to base centered monoclinic structure in nanoscale size. The surface topography was significantly modified by Y3+ doping concentration, suggesting that the fabricated nanocomposite possess unique physical and chemical properties enable it to be used as larvicidal at different concentrations. On the other side, nanomaterials have a biotoxic impact at amounts under the levels that are registered to be toxic to humans. The images obtained from the scanning and optical microscopy confirmed that nanomaterials are considered a favorable choice as an effective anti-larvicidal agent. The outcomes indicate that CuO/Y nanocomposite of higher performance compared to pure CuO based on special structural and morphological aspects.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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