Synthesis, characterization, and interaction studies of uncapped, PVP, and CTAB capped CuO nanorods with aldicarb and chlorpyrifos

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Abstract

Uncapped copper oxide nanorods (CuOnrs), capped with cetyltrimethylammonium bromide (CTAB-CuOnrs), and polyvinyl pyrrolidine (PVP-CuOnrs) were utilized for the interaction study of the carbamate (Aldicarb (A.D.)) and organophosphate (Chlorpyrifos (C.P.)) pesticides. These nanorods were synthesized using the co-precipitation method, followed by calcination at 350 °C for 2 hr. X-ray diffraction study confirmed the monoclinic structure of the CuOnrs without any impurities with average crystallite size in the range of 10-12 nm. Field emission scanning and transmission electron microscopy (FE-SEM & TEM) studies confirmed the nanocrystalline structure of CuOnrs, CTAB-CuOnrs, and PVP-CuOnrs having rod-like structures. The contact angle study showed the hydrophilic nature of the uncapped CuOnrs and PVP-CuOnrs with a contact angle of 51 ° & 57 °, respectively. While CTAB-CuOnrs exhibited hydrophobic nature with a contact angle of more than 90 °. Interaction study of CuOnrs, CTAB-CuOnrs, and PVP-CuOnrs with A.D. and C.P was conducted using U.V.- vis absorption study (in the 250 - 400 nm region). Uncapped CuOnrs have shown the specific detection with A.D., while CTAB-CuOnrs have shown with C.P. without using any bio-recognition elements. PVP-CuOnrs did not show systematic change with both pesticides confirming the capping agent-dependent specific interaction of the pesticides.

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Keywords: Aldicarb, Chlorpyrifos, CTAB, PVA, CuO nanorods, co-precipitation method

Introduction

Metal oxides have been considered for several potential applications in various fields, including nanodevices, nanoelectronics, optoelectronics, nanobiosensor or sensor, photochemical catalysis and gas sensor, etc. (Ahamed et al., 2014; Aslani and Oroojpour, 2011; EmanAlzahrani and Ahmed, 2016) Copper oxide (CuO) nanostructures are one of the very smart transition metal oxides among other metal oxides with small bandgap (2.4 eV), and at nanoscale having specific features as good electrochemical activity and stability in the solution. (Giri and Sarkar, 2016; Khan et al., 2014; Mudunkotuwa et al., 2012; Xu et al., 2004) Besides these characteristics, nanostructured CuO shows functional physical properties such as high surface-to-volume ratio, photochemical and thermal stability, high-temperature superconductivity, biocompatibility, less toxicity, etc. (El-Trass et al., 2012; Nowack and Bucheli, 2007). These properties of CuO has also attracted the attention of biomedical research area and have been heavily used in glucose sensing, immuno-sensing, dopamine sensing, pharmaceutical activity, tumor therapy, and antifungal agent. (Verma et al., 2019; Yang et al., 2017) U.S. Environmental Protection Agency (EPA) has recognized CuO as an antimicrobial nanomaterial. After the declaration, CuO received much attention from biomedical devices to prevent bacterial infection. (Meghana et al., 2015) However, CuO nanomaterials are not much explored for environmental applications.

Copper is a micronutrient for plant growth and is involved in several processes like lignin synthesis, enzyme system, photosynthesis, plant respiration, and plant metabolism of carbohydrates and protein. (Sommer, 1931) It is found that transformations of CuO nps can be influenced by soil characteristics through the dissolution process. (Keller et al., 2017) Ionic copper can be both highly toxic in the presence of higher concentrations for soil microorganisms and act as a significant micronutrient for biological growth at low concentrations. (Arguello et al., 2013) CuO nps have been extensively used for gram-positive and gram-negative bacteria for antimicrobial activity because CuO is relatively cheaper than other metal oxides. (Ahamed et al., 2014; Germi et al., 2014; Nowak et al., 2014) CuO can be easily functionalized with other molecules, including polymers, due to its flexible nature, mixed easily with polarized liquids (e.g., water), and polymers lead to stabilizing its chemical and physical properties. (Ren et al., 2009) In this context, polyvinylpyrrolidone (PVP) and cetyltrimethylammonium bromide (CTAB) polymers were used as a capping agent for several metal oxides nanomaterials. (Briffa et al., 2017) The PVP and CTAB capped CuO nps were used to determine the antibacterial, fungal agent, and interaction with di-thiocarbamate pesticides. (Chen et al., 2006; Javed et al., 2017; Shahmiri et al., 2013) Di-thiocarbamate shows strong bonding with metals (Sn, Cu, Bi) due to a sulphur group in the molecule. This property affects biological capability inhibiting the growth of bacteria, and also having a wide application in uses as anticancer, antibacterial and antifungal. (Adeyemi and Onwudike, 2018; Athawale et al., 2005; Awang et al., 2011; Katari and Srinivas, 2014) Thus, interaction studies of uncapped CuO nps and capped PVP and CTAB with pesticides will provide promising results that could be utilized for device fabrication based on simple observation based on the alteration in absorption peaks. Pesticides are mainly used in agriculture to protect plants from unwanted life forms or organisms like pests, weeds, insects, or diseases. They include rodenticides, herbicides, fungicides, insecticides, and fumigants. (Hoffman et al., 2000; Organization, 1990; Stoytcheva, 2011) The most commonly used pesti-
cides belong to carbamate, organochlorine, organophosphate & organophosphorus groups. Aldicarb (A.D.), DDT, Chlorpyrifos (C.P.), monocrotophos, and methyl parathion are a few examples. These pesticides are highly toxic and are exposed to the human through ingestion, eating, drinking, lungs, and dermal absorption. (Deziel et al., 2015) Therefore, rapid detection of these pesticides led to a significant research in this area. The interaction study of CuO nanomaterial with pesticides is very limited, providing a lot of scope to explore.

In the present work, Uncapped copper oxide nanorods (CuOnrs), capped with cetyltrimethylammonium bromide (CTAB-CuOnrs), and polyvinyl pyrrolidine (PVP-CuOnrs) were synthesized by the chemical co-precipitation method. Efforts were made to explore the interaction of these UC-CuOnrs, PVP-CuOnrs, and CTAB-CuOnrs, with two pesticides, A.D. and C.P., through changes in UV-Visible absorption. Interestingly, it was found that UC-CuO and CTAB influence the specific interaction with different pesticides. U.C.- CuOnrs interacted specifically with A.D. In contrast, the CTAB-CuOnrs interacted with C.P., and PVP-CuO did not interact with either of the two. These results infer the effect of capping agents on the specific interaction that can be used to develop a specific detection system, i.e., sensor.

Material and Methods
Copper oxide (uncapped CuOnrs) nanostructure, cetyltrimethylammonium bromide (CTAB-CuOnrs), and polyvinyl pyrrolidine (PVP-CuOnrs) were synthesized by the co-precipitation method as described in literature elsewhere. (Das et al., 2013, Dhiman et al., 2020) The precursor used was high purity copper sulphate (Merck), and the reducing agent was sodium hydroxide (NaOH). Using these precursors, 0.25 M of copper sulphate and 0.1 M of NaOH solutions were prepared. Copper sulphate was taken in a 250 ml beaker and dissolved in D.I. water. For UC-CuOnrs, NaOH was directly added drop by drop to the copper sulphate solution. While for CTAB-CuOnrs and PVP-CuOnrs, before adding NaOH, 0.05 gm of CTAB and PVP were first added into two separate copper sulphate solutions and dissolved using a magnetic stirrer. Then NaOH was added to it drop by drop using a burette until the solution’s pH reached pH~12. After this step, the precipitates were filtered out using the Whatman filter paper and dried in an oven at 80°C for 12 h. The obtained dried powders were calcined at 350°C for 2 h to obtain the dark brown color powder of UC-CuO, CTAB-CuO, and PVP-CuO. Aldicarb (A.D.) and chlorpyrifos (C.P.) were procured from Sigma-Aldrich and used without further purification.

X-ray diffraction (XRD) analysis was performed to examine the phase and structure of the sample. Rigaku MiniFlex 600 X-Ray Diffractometer with CuKα radiation (λ=1.54Å) operating at 40 kV and 15 mA was used to obtain the sample XRD pattern. XRD data were recorded in the range of 20°-80° with a scan rate of 3° and a step size of 0.02°. The shape & structure of the material were examined by transmission electron microscopy (TEM) (JEOL-TEM-2100F). The detection of Aldicarb (A.D.) and Chlorpyrifos (C.P.) was performed with UC-CuO, CTAB-CuO, and PVP-CuO nanorods using UV-vis absorbance spectroscopy. The concentration for Aldicarb & Chlorpyrifos was in the range of 50 pM to 5 nM and 0.1 nM to 100 nM, respectively. For each of the UV-Vis studies, 3 ml of CuO solution was taken mixed with 500 μl of pesticide. Then for each of the samples, UV-Vis spectra were recorded in the range of 300-450 nm. FTIR was also performed to confirm the binding of A.D. & C.P. with CuO samples.

Results and Discussion
X-ray diffraction analysis
XRD profiles of UC-CuO, CTAB-CuO, and PVP-CuO nanostructures are shown in Figure 1. The peaks were sharp with slightly broad FWHM, confirming the nanocrystalline nature of the material with a small size. The observed peaks were indexed using JCPDF-895899 with a monoclinic structure and space group of C2/c. (Wang et al., 2012) The Scherer equation estimated the average crystallite size. (Christy et al., 2013, Singh et al., 2020 and Verma et al., 2020)

\[ D = \frac{K \lambda}{\cos(\theta)} \] (i)

where K~0.9; wavelength (λ) = 1.5406 Å; full width at half maximum (FWHM) of the diffraction peaks
is $\beta$, and the Bragg’s diffraction angle is $\theta$. The average crystallite size was in the range of 10-12 nm for UC-CuO, CTAB-CuO, and PVP-CuO nanorods. The peaks were indexed as (110), (-111), (111), (-202), (020), (202), (-113), (-311), (220), (311) and (-222) for the corresponding peaks to the monoclinic structure of CuO nanostructure. (Cheng et al.) All the samples have shown a clean phase without any impurity, thus making all the samples suitable for further studies.

UV-Vis absorbance study

Figure 2 shows the UV-Vis absorbance spectra of UC-CuO, CTAB-CuO, and PVP-CuO. The prominent absorption peak can be seen around 380 nm in all three samples with variation in the absorption intensity. (Liu et al., 2012) This peak is the surface plasmon absorption peak of the CuO nanomaterials, which depends on the size and surrounding environment of the CuO nanomaterials. When the nanomaterials' size is too small compared to the incident wavelength, which confirms the nano-size of the synthesized material, similarly observation found here. (Das et al., 2013) As this peak is sensitive to surrounding environments, this can be used as a sensing parameter. According to the PVP and CTAB (capping agent), there is a slight variation in this peak position with capping agents; as shown in Figure 2, results indicate that CuO nanostructures capped with respective capping agents.

Figure 3 shows the FE-SEM images of UC-CuO (image a), CTAB-CuO (image b), and PVP-CuO (image c) nanostructures. In UC-CuO, the particular shaped structures are not visible apart from the few rod-like structures that appeared. While in PVP-CuO and CTAB-CuO, rod-like structures are visible. These structures show the presence of high surface energy on the nanostructures leading to non-defined structures in UC-CuO. (Wang et al., 2001) While in capped nanostructures, the surface energy was minimized, but still, some agglomerations are visible, which is due to the nature of the PVP and CTAB capping present in these samples. The inset of each image shows the corresponding contact angle. For UC-CuOnrs and PVP-CuOnrs, the contact angles were 51° and 57°, respectively, showing the hydrophilic nature due to the presence of the hydroxyl groups. However, CTAB-CuOnrs exhibited it increased to 97°, making it hydrophobic. This is due to the long chain of the carbon groups present in the CTAB molecular structure.

TEM study was carried out to observe the structure and the crystallinity of the samples. Figures 4 (a, b, and c) show the TEM images of the UC-CuOnrs, CTAB-CuOnrs, and PVP-CuOnrs. In each of the images, parts (i) and (ii) show the TEM micrographs at 100 nm and 20 nm scale, part (iii) shows the SAED pattern, and part (iv) shows the HR-TEM image of the respective samples. It can be seen that rod-like structures appeared in all UC-CuO, CTAB-CuO, and PVP-CuO nanostructures. (Batchelor et al., 2008, Wang et al., 2003) In each of the samples, the diameter of the rods is in the range of 10-15 nm, which is correlated with the particle size calculated from the XRD. In each Selected area electron diffraction (SAED) pattern, well-defined rings have been obtained. The d-spacing of these rings was calculated using the following formulae: (Kujur et al., 2020, Sarkar et al., 2020)

$$D = \frac{L\lambda}{2R} \quad (ii)$$

Where D is the d spacing, L is the camera length (0.2 m), $\lambda$ is the wavelength of the electron beam, R is the radius of the ring in the SAED pattern. The d-spacing and corresponding planes were matched using XRD data. Using the above formulae, the rings were indexed as (110), (-111), (111), (-202), (020), (202), and (-113) corresponding to the monoclinic structure of CuO.

Transmission electron microscopy analysis

These well-defined rings indicate the nanocrystalline nature of the material. In the HR-TEM image of each sample, d-spacing was calculated and found to be 2.7 Å, corresponding to the (110) plane. (Cheng et al., 2011) The lattice fringes obtained from the image are very well defined and have a long-range crystalline order. This is further confirming the nanocrystalline nature of all the samples. Thus, TEM analysis confirmed the material’s shape, morphology, and nanocrystalline nature with almost rod-shaped nanostructures.

UV-Visible absorption-based interaction study
Interaction studies of UC-CuO, CTAB-CuO, and PVP-CuO were conducted with A.D. and C.P. using the UV-Visible absorption technique. The readings were recorded in the range of 300-450 nm using a UV-vis spectrophotometer. The concentration for Aldicarb & Chlorpyrifos was in the range of 50 pM to 5 nM and 0.1 nM to 100 nM, respectively. For each of the UV-Vis studies, 3 ml of CuO solution was taken mixed with 500 μl of pesticide.

(i) Interaction study of UC-CuO with A.D. and C.P.

Figure 5 (a) and (b) shows the interaction response study of A.D. and C.P. with UC-CuO, respectively. The absorption peak position is the same in each case, but the surface plasmon absorption peak intensity is changed. The intensity of the peak positions was plotted with increasing concentrations of A.D. (0, 50 pm, 100 pm, 250 pm, 500 pm, 1 nM, 2 nM and 5 nM) and C.P. (0, 1, 2, 5, 10, 25, 50, 100 nM). The change in the absorption spectra is shown in the inset. It was observed that the absorption peak intensity systematically decreases with increasing order of A.D. concentrations varies from 0-5 nM [inset, Fig. 5(a)], indicating the systematic interaction of A.D. with UC-CuO. However, during the interaction of UC-CuO with C.P., the absorption peak not steady decreases but abrupt changes with increase concentration of C.P. [inset, Figure 5(b)]. These results indicate that C.P. does not interact with UC-CuO.

The possible mechanism for the interaction of A.D. and UC-CuO has been explained in Figure 5 (c). The binding of A.D. with the UC-CuO molecule is the possible reason for the linear response with increasing A.D. concentrations. UC-CuO showed a highly reactive nature (less stable) than CTAB-CuO and PVP-CuO. It has no surfactant agent to stabilize the highly active surface area of UC-CuO, which was also observed from SEM images. This is because, in UC-CuO, Cu^{2+} leads to the baseline region (according to Pearson “HSAB concept”). Therefore it can behave as Hard acid or Soft acid to react with either a Hard base such as “O” (oxygen) or a Soft base as “S” (Sulphur). (Pearson, 1963) In FTIR spectra, Cu-O vibration bonds were observed at two frequencies, 494 and 556 cm^{-1}. This proves that carbonyl oxygen of A.D. tends to interact with UC-CuO to form Hard–Hard acid-base like a bond (ionic bond). As a result, the decrease in UV-visible absorbance took place in UC-CuO (Figure 5). C.P. does not have the carbonyl O and did not interact with sulphur as there was no other peak found in the FTIR spectrum with UC-CuO.

(ii) Interaction study of CTAB-CuO with C.P. and A.D.

Further, similar experiments were conducted to monitor interaction study between the CTAB-CuO with C.P. and A.D. at similar experimental conditions. Figure 6 (a) and (b) show the interaction study of A.D. and C.P. with CTAB-CuO. Here, the interaction behaviour of CTAB-CuO is opposite to the UC-CuO with A.D. and C.P. CTAB-CuO showing non-systematic interaction with A.D., i.e., absorption peak intensity is abruptly decreased with increased concentration of A.D. However, absorption peak intensity is uniformly or systematically decreases with the increasing concentration of C.P. There are two possibilities for the decrease in absorbance of CTAB-CuO after the addition of C.P. The possible mechanism for the systematic response of C.P. with CTAB-CuO has been explained in Figure 6 (c).

The first possibility was the de-functionalization of CTAB (surfactant) from the surface of CuO and the surrounding surface of C.P. with hydrophobic- hydrophobic or Vander –Waal or supra-molecular interactions (1). (Gebremariam et al., 2012) The second possibility is that without de-functionalization, the whole CTAB-CuO surround the C.P. to form a micellar kind of structure around C.P. (Figure 6) and thereby decreasing the absorbance (ii). There is a slight decrease in absorption with the addition of A.D. also, but not very prominent between A.D. and CTAB-CuO as A.D. is hydrophilic and unable to remove CTAB from the surface of CuO as efficient as C.P.

Figure 7 (a) and (b) show the interaction studies of A.D. and C.P. with PVP-CuO, respectively. The response of both A.D. and C.P. showed a non-systematic response with PVP-CuO. The possible reason for this is explained in Figure 7 (c). As shown in Figure 7 (c), PVP has a high binding affinity to CuO, increasing its stability. Therefore, the addition of A.D. and C.P. could not interact with CuO as the capping agent PVP protected it from interaction leading to a non-systematic response with the addition of A.D. and C.P. These possible mechanisms were further studied using FTIR spectra.
FTIR study

Figure 8 shows the FTIR spectra of UC-CuOnrs, UC-CuOnrs with A.D., and C.P. (a); PVP-CuOnrs, PVP-CuOnrs with A.D. and C.P. (b), CTAB-CuOnrs, CTAB-CuOnrs with A.D. and C.P. (c). In the FTIR spectra of UC-CuOnrs, the peak observed at 426, 460, 496, and 586 cm\(^{-1}\) are related to CuO due to the stretching band. While the peak around 1638 cm\(^{-1}\) corresponds to the bending mode of water. (Prakash and Diwan, 2015) The FTIR spectrum of PVP-CuOnrs (b) shows a peak around 1028 cm\(^{-1}\), which was attributed to the rocking vibration of CH\(_2\). The FTIR spectra of C.P. show the peak at 1644 cm\(^{-1}\), which is due to the stretching vibration of carbonyl peak, which showed an intensity change in UC-CuOnrs-CP [curve top (a)] and appeared in PVP-CuOnrs-CP spectra [curve top (b)]. (Affam et al., 2016) The presence of this peak in both UC-CuOnrs-CP; PVP-CuOnrs-CP indicated the reduced interaction of C.P. with these two nanomaterials, whereas there is no sign of this peak in CTAB-CuOnrs-CP [curve top (c)]. This is due to the interaction between CTAB-CuOnrs and C.P., leading to the systematic detection of C.P., which was also observed in UV-Vis detection.

In the FTIR spectrum of UC-CuOnrs-AD [curve middle (a)], the broad peak around 1640 cm\(^{-1}\) attributed to the stretching vibration of carbonyl peak mixed with –OH bending vibration peak was observed. Also, there was an intensity change in the Cu-O peaks that occurred around 505 cm\(^{-1}\) and 556 cm\(^{-1}\) observed, indicating the interaction of A.D. with UC-CuOnrs. In the other two cases of CTAB-CuOnrs-AD [curve top (b)] and PVP-CuOnrs-AD [curve top (c)], there was no significant change in Cu-O peaks were observed, indicating the reduced interaction of these two materials with A.D. The capping of CuO with PVP showed by several small peaks in the spectra. The peaks do not show much difference after C.P. and A.D., indicating the non-systematic interaction between them.

The FTIR study has confirmed the specific interaction of A.D. with uncapped CuOnrs and C.P. interaction with CTAB-CuOnrs. The above studies show that by changing the capping agent on the surface of CuO, we change their interaction with the pesticides. Such a type of study can be used to fabricate a pesticide sensor for the early detection of pesticides in various food products.

Conclusions

Uncapped-CuOnrs, PVP-CuOnrs & CTAB-CuOnrs have been successfully synthesized using the co-precipitation method. The average crystallite size was calculated using XRD and was found to be between 10-12 nm. UV-Vis absorbance study showed a broad absorbance centered around 380 nm for all three samples indicating the surface plasmon absorption of metal oxide nanostructures. FE-SEM study showed small nanostructures with high agglomeration. The contact angle value was obtained for UC-CuOnrs as 51°, 57° for PVP-CuOnrs, and 97° for CTAB-CuOnrs. TEM study showed a rod-like structure for UC-CuOnrs, PVP-CuOnrs, and CTAB-CuOnrs. The interaction response studies of A.D. and C.P. were performed using UV-Vis absorbance for UC-CuOnrs, PVP-CuOnrs, and CTAB-CuOnrs. A.D. showed systematic interaction with UC-CuOnrs in the concentration range of 50 pM to 5 nM. C.P. interacted systematically with CTAB-CuOnrs in the concentration range of 0.1 to 100 nM. While PVP-CuOnrs did not show the systematic response, either A.D. or C.P. FT-IR study further confirmed the specific interaction of A.D. with UC-CuOnrs and C.P. with CTAB-CuOnrs. These studies confirm the selective response of the pesticides depending upon the capping of the CuO.

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Competing Interests

The authors declare no competing interest.

ORCIDs

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References


**Figures and figure captions**
Figure 1. X-ray diffraction (XRD) plot of UC-CuO, CTAB-CuO, and PVP-CuO nanostructures.
Figure 2. UV-Vis absorption spectra of UC-CuO, CTAB-CuO, and PVP-CuO nanostructures

Shape, morphology, and wettability study

Figure 3. FESEM images of a) UC-CuO, b) PVP-CuO, and c) CTAB-CuO. Figure 3 d), e) and f) shows the corresponding contact angle snapshots for UC-CuO, PVP-CuO, and CTAB-CuO, respectively.
Figure 4. The TEM image of a) UC-CuOnrs, b) CTAB-CuOnrs, and c) PVP-CuOnrs. In each image i) and ii) shows the TEM images at two magnifications, iii) SAED pattern, and iv) HR-TEM images.

Figure 5. (a) and (b) Response plot and corresponding UV-vis absorption plot (Inset) for the interaction of A.D. and C.P. using UC-CuOnrs, c) possible mechanism for the interaction of A.D. with UC-CuOnrs.
Figure 6. Response plot and corresponding UV-vis absorption plot (Inset) for the interaction of a) aldicarb (A.D.) and b) chlorpyrifos (C.P.) using CTAB-CuO-nrs, and c) shows the possible mechanism for the interaction of C.P. with CTAB-CuO-nrs.
Figure 7. Response plot and corresponding UV-vis absorption plot (Inset) for the interaction of a) aldicarb (A.D.) and b) chlorpyrifos (C.P.) using PVP-CuO, and (c) possible mechanism for no interaction.

Figure 8. FTIR plot for a) UC-CuO@rs, UC-CuO@rs with A.D., & UC-CuO@rs with C.P., b) PVP-CuO@rs, PVP-CuO@rs with A.D., & PVP-CuO@rs-CP, & c) CTAB-CuO@rs, CTAB-CuO@rs with A.D. and CTAB-CuO@rs with C.P.