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Surface modification of TiO_2 nanoparticles with CuO for visible-light antibacterial applications and photocatalytic degradation of antibiotics

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ABSTRACT

This paper investigates the synthesis and characterization of photoactive TiO_2/CuO nanocomposites for the simultaneous antibacterial applications and photocatalytic removal of Amoxicilline from wastewaters. Effective removal of biological and organic contaminants from water resources has become a global challenge due to contaminants' complexity and extensive use. TiO_2/CuO heterojunctions with different CuO loadings were synthesized using a straightforward precipitation method. Electron microscopy, energy-dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), Fourier transformed infrared (FTIR), ultraviolet–visible (UV-VIS) analyses were used to characterize synthesized samples. Antibacterial activities of samples were investigated against *Staphylococcus aureus*. Also, the applicability of synthesized powders in the photocatalytic removal of Amoxicilline from wastewater was methodically investigated. Results showed that the photocatalytic activity of synthesized TiO_2/CuO nanocomposites is highly dependent on the CuO loadings of samples. CuO loading can also increase the light absorption within the visible light region, making TiO_2/CuO samples applicable in the visible light region. Results also showed that CuO loading greatly enhances the antibacterial characteristics of samples.

1. Introduction

Effective removal of bacterial and organic contaminations in industries like food processing, drinking water treatment, medical equipment manufacturing, textile industry, or other high-risk environments like hospitals has always been a challenging issue because of the high adaptability of bacteria and other microorganisms [1–3]. Antibacterial agents, mainly comprised of antibiotic compounds such as penicillin, cefalexin, and Amoxicillin, are essential to fight infectious diseases and bacterial contaminations in hospitals and other industrial sectors. However, because of the massive and sometimes unnecessary use of antibiotics, the world is now facing the challenge of emerging resistant bacteria more than any time before [3]. Bacterial microorganisms can mutate to cope with antibiotics and form some degrees of resistance against antibiotics. Multiple mechanisms cause this resistance. The primary mechanism is the production of some enzymes in bacteria that can inactivate the antibiotic [4]. A case in point is the ability of bacteria to produce the β-lactamase enzyme, which cleaves the β-lactam ring, which in turn neutralizes penicillin-based compounds [5]. With that said, finding new biological/chemical approaches and methodologies to fight against bacterial infections and other harmful microorganisms appears to be extremely important. With the development of nanotechnology, it has become possible to employ promising nanomaterials as anti-microbial/anti-bacterial agents. The interest in metal oxide nanoparticles such as titanium, zinc, and copper oxides as antimicrobial agents has been growing due to their low costs, chemical instabilities, non-toxicity, tunable properties, multi-functionality, and fast effects [6]. Such nanoparticles have already been used for anti-bacterial purposes. They are now being studied in advanced bioapplications, such as treating localized bacterial infections when tissue integration is a concern [7,8]. Moreover, nanoparticles have also proven to be effective in antimicrobial photodynamic therapeutic procedures [9], photocatalytic disinfection [10], light-induced acidification [11], and photothermal bacterial lysis [12].

The photocatalytic/antimicrobial properties of metal oxide nanoparticles depend on their composition, morphology, and size [13–15]. It

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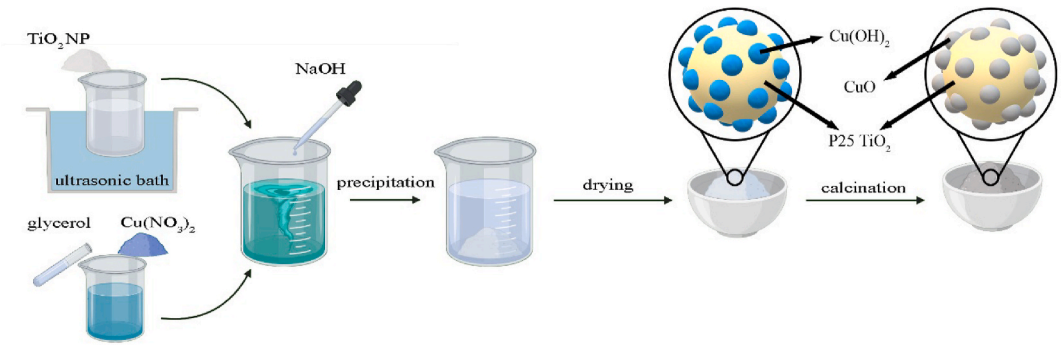

Fig. 1. Schematic diagram of the synthesis process of CuO surface modified TiO_2 nanoparticles.

Fig. 2. Images of bare TiO_2 nanoparticles and CuO-modified TiO_2 photocatalyst samples.

is postulated that in metal oxide nanomaterials, the antimicrobial behavior is due to a combination of photocatalytic and ionic antimicrobial mechanisms. The former mechanism involves the generation of reactive oxygen species (ROS) via photodegradation reactions. In contrast, the ionic mechanism has to do with electrostatic interaction and disruption of the integrity of the bacterial cell membrane [3,4], which in turn would result in the demise of the species (bacteria). An intriguing upside of using photoactive metal oxide nanoparticles as antibacterial agents is the fact that such photoactive agents can have a dual functionality; degradation of remaining antibiotics and combating the emergence of more resistant bacterial strains. The fact that photocatalytic antibacterial mechanisms of these nanomaterials can also be used for the degradation of antibiotic compounds adds extra functionality to these nanoparticles [16–18]. Photocatalytic and antimicrobial properties of TiO_2 nanoparticles have long been used in different applications since 1984 [19]. Recent studies have been conducted on photoactivated antimicrobial applications of TiO_2 with different crystalline structures on various bacterial strains, often under UV irradiation [20–23]. However, it is known that TiO_2 by itself is not really an antimicrobial/photocatalyst agent under visible light irradiation. This has to do with the inherently large bandgap energy of TiO_2 as well as its relatively fast recombination of electron-hole pairs [24–27]. This clearly is a significant drawback when it comes to the photocatalytic applications of TiO_2 under visible light irradiations. Various methodologies have been examined to enhance the visible-light driven photocatalytic antimicrobial efficacy of TiO_2 nanoparticles, including doping of TiO_2 with Co, Mn or Ni [28], silver halide (AgX, X = Cl, Br, I) deposition [28,29], or semiconductor combination [30]. These methods are primarily intended to lower the bandgap energy, enhance the photo-response of TiO_2 under visible light, and delay the electron-hole recombination time, and therefore, produce more stable ROS. Among the aforementioned methods, the deposition of metal oxides on TiO_2 nanoparticles appears to be a promising line to decrease bandgap energy and extend the lifetime of photogenerated charge carriers. This can reportedly improve the photocatalytic response and the application range of TiO_2 nanoparticles down to the visible light region [31,32]. The deposition of metal oxides on TiO_2 nanoparticles is reportedly associated with the formation of heterojunctions over the surface of TiO_2 nanoparticles. A heterojunction is a place where two different semiconductor materials (p- and n-type semiconductors) with different bandgaps form an interface [33]. Copper (II) oxide (CuO), being one of the most easily accessible and cheapest transition metal oxide, has excellent potential to pair up with TiO_2 to form heterojunction areas. CuO has been widely used in various applications such as photocatalytic removal of organic pollutants, as an effective antimicrobial agent, or as a catalytic material due to its narrow gap. More importantly, the non-toxicity of this oxide is also an important aspect [34]. With that said, the TiO_2–CuO oxide system is expected to have promising optical and photocatalytic properties, as compared with TiO_2 or CuO alone. Surface modification of TiO_2 nanoparticles with CuO nanoparticles is expected to end in photoactive particles with superior properties. The co-existence of TiO_2 and CuO nanoparticles can activate two bactericidal mechanisms, i.e., photocatalytic and ionic mechanisms, which expectedly lead to a better antimicrobial behavior under visible light irradiation. This study investigates a facile method for the surface modification of TiO_2 nanoparticles with CuO nanostructures and its application as an antibacterial agent as well as a photocatalyst for the degradation of antibiotics using visible light. Concurrent photocatalytic and antimicrobial properties of TiO_2/CuO nanoparticles make these nanoparticles an excellent disinfection option in applications in the healthcare sector, especially when it comes to the elimination of bacterial contaminations as well as reduction of antibiotic pollution from wastewater and other biological wastes.

2. Materials and methods

2.1. Materials

P25 TiO_2 nanopowders (<25 nm, ≥99.5%), copper (II) nitrate hemi (pentahydrate) (98%), and sodium hydroxide (98%) were all purchased from Sigma-Aldrich and were used as received. Glycerol (>99%) was obtained from Tetachem. All solutions were prepared using double-distilled water.

2.2. Surface modification of TiO_2 nanoparticles

Surface modification of TiO_2 with CuO nanostructures was done using a precipitation method. Glycerol and copper nitrate pentahydrate ($Cu(NO_3)_2.2.5\ H_2O$) with molar ratios of 2:1 were first added to 50 ml of double-distilled water and stirred on a magnetic stirrer for 15 min to form an aqueous copper (II)–glycerol complex. Masses of the used glycerol and copper nitrate pentahydrate were by nominal loadings of 0.5, 5, 7.5, and 10% CuO on TiO_2. Then, 1 g of TiO_2 was added to 50 ml of double-distilled water while being sonicated in an ultra-sonic bath to ensure good dispersion of nanoparticles. The copper (II)–glycerol

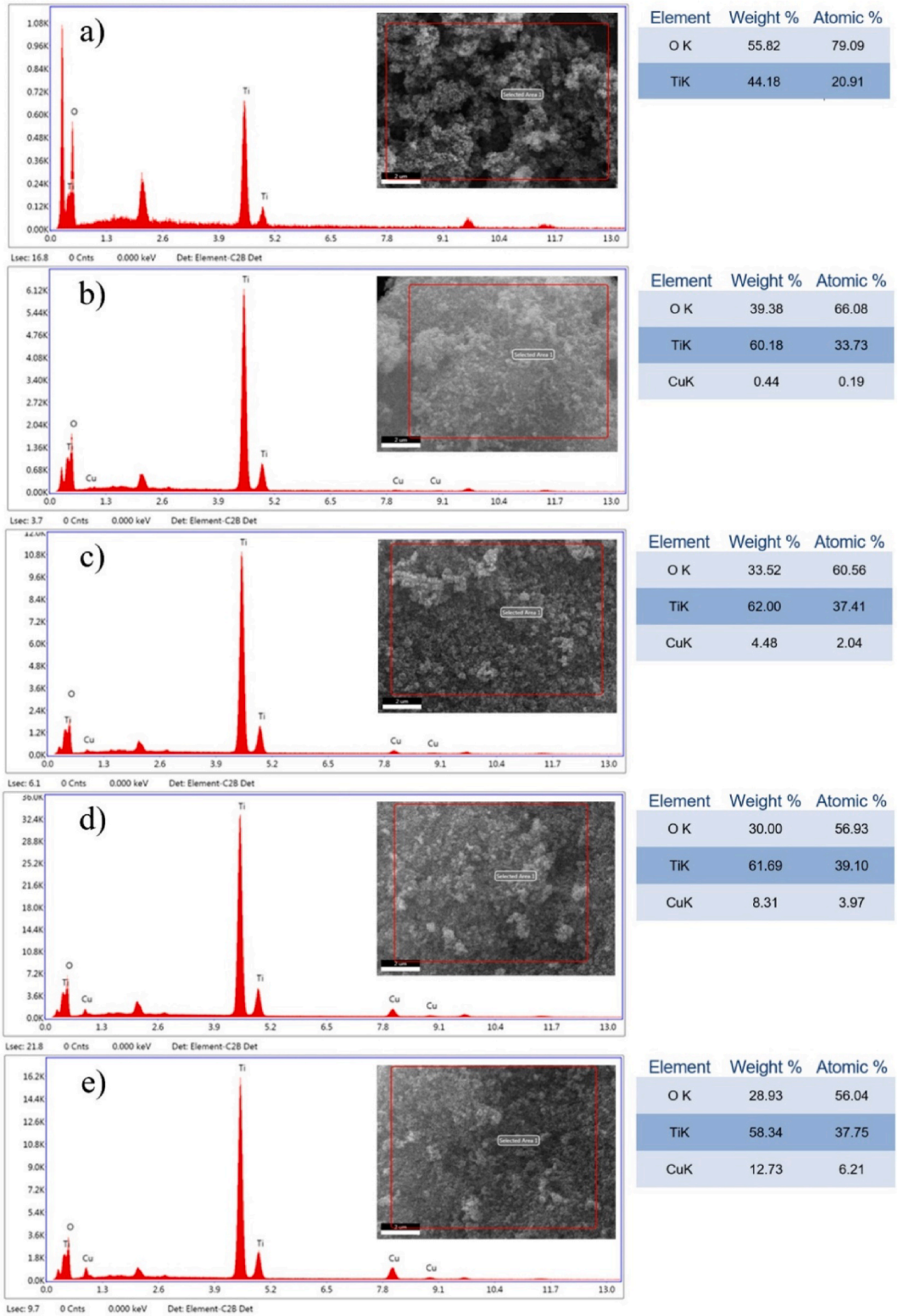

Fig. 3. SEM images and EDS chemical analysis of a) TiO_2, b) TC1, c) TC2, d) TC3, and e) TC4 photocatalyst samples.

complex solution was then added to TiO_2 nanoparticles and stirred on a magnetic stirrer for 15 min. Cu(OH)2 was then precipitated on TiO_2 nanoparticles by dropwise addition of 0.1 M NaOH into the copper (II)–glycerol complex under stirring until it reached a pH of 11. The resulting light blue powders ($Cu(OH)2/TiO_2$) were collected using centrifugal separation and washed with double-distilled water and then dried in an oven overnight at 75 °C. The $Cu(OH)_2/TiO_2$ powder was then calcined at 300 °C for 2 h in a muffle furnace to obtain CuO-modified TiO_2. Synthesized photocatalyst nanocomposite TiO_2/CuO particles with the nominal CuO loadings of 0.5, 5, 7.5, and 10% were named TC1, TC2, TC3, and TC4, respectively. Fig. 1 shows a schematic diagram depicting the whole synthesis process of CuO surface modified TiO_2 nanoparticles.

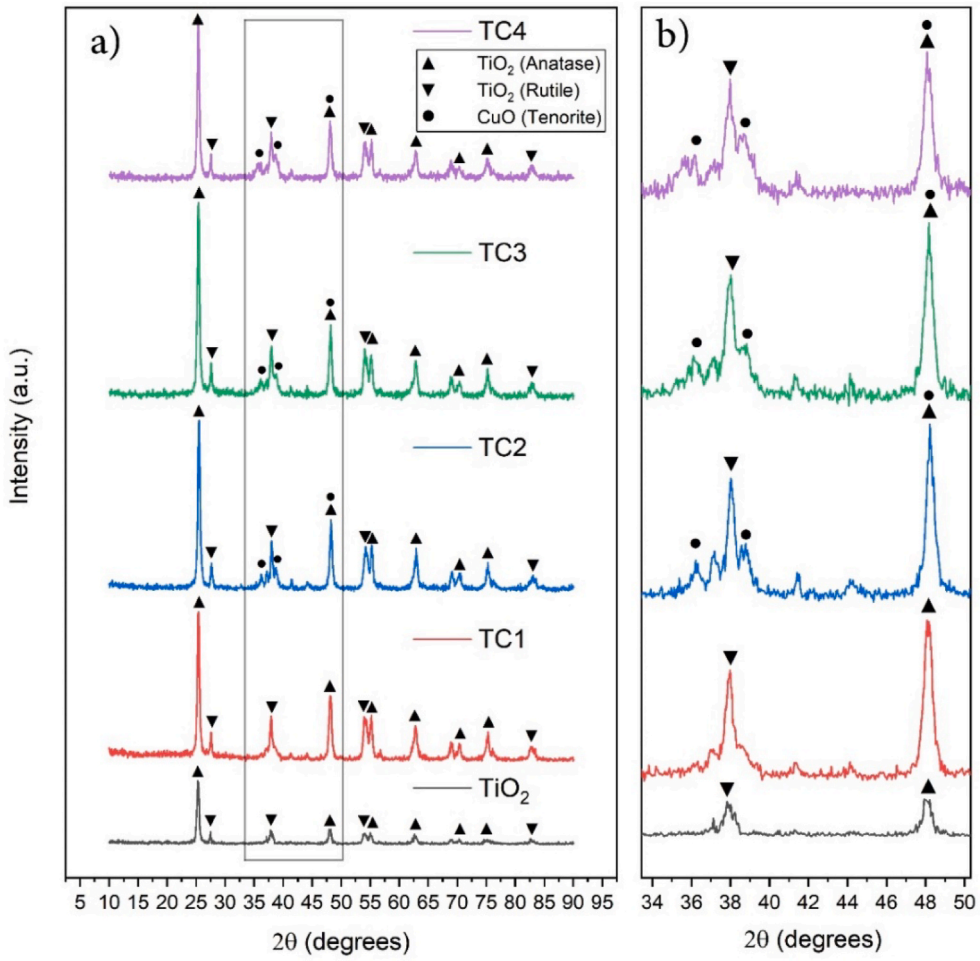

Fig. 4. XRD patterns of a) CuO-surface modified and bare TiO_2 photocatalyst samples and b) peaks correlated to CuO nanostructures.

Table 1
Average crystallite sizes of different phases, calculated using the Scherrer equation.

Photocatalyst Sample	Crystallite size (nm)		
	anatase	rutile	tenorite
TiO_2	23.7	44.5	–
TC1	23.8	42.9	
TC2	24.2	43.2	13.5
TC3	23.8	42.8	14.3
TC4	23.6	43.3	14.8

2.3. Characterization

Scanning electron microscopy (SEM) of CuO surface modified TiO_2 samples was done using Philips XI30 equipment. Chemical analysis of the synthesized nanocomposite particles was carried out by energy-dispersive X-ray spectroscopy using Seron AIS 2300 equipment. CuO surface modified photocatalyst particles were also characterized using a transmission electron microscope (TEM, JEOL JSM-6710F). X-ray Diffraction (XRD, Philips) with CuKα radiation (λ = 1.54 Å) was also conducted. The UV–Vis diffuse reflection spectra measurements by a Univkon-XL UV–VIS–NIR scanning spectrophotometer were carried out within the 190–900 nm range. Fourier transformed infrared (FTIR) analysis was conducted using a Perkin–Elmer Spectrum 100 series for 200 scans at a resolution of 4 cm^{-1}.

2.4. Photocatalytic antibacterial activity under visible light irradiation

The bactericidal effects of four different samples were conducted on a gram-positive bacterium, *Staphylococcus aureus*, which was grown on nutrient agar (NA) at 35° overnight. 0.2 mg/ml of synthesized samples were dispersed in a fresh nutrient broth (NB) medium and then sterilized during autoclaving. The bacterial suspension in a saline solution containing 10^8 CFU/ml was inoculated in the latter medium and placed in a shaker/incubator with white light irradiation. After every 15 min of light irradiation, the aliquots of 0.1 ml of the bacterial suspension from the test suspension samples were spread on NA media and incubated at 35° for 24 h. To demonstrate the bactericidal efficacy, the colony-forming units were calculated by the standard plate count method. The same experiment was conducted in dark conditions (without any light irradiations). All experiments were repeated three times and were conducted under sterile conditions.

2.5. Photocatalytic amoxicillin degradation under visible light irradiation

The photocatalytic activity of the bare and CuO surface modified photocatalyst samples was evaluated by the decomposition of Amoxicillin, as a model antibiotic pollutant, under visible light. For this purpose, the degradation experiments were conducted by adding 0.005 g of each of the photocatalyst powders to 25 ml of 1 g/l solution of Amoxicillin in double-distilled water. For homogenization, amoxicillin-containing solutions were stirred in an ultrasonic bath for 20 min. Then, photocatalyst powders were subjected to visible light by a solar light simulator while being stirred using a magnetic stirrer.

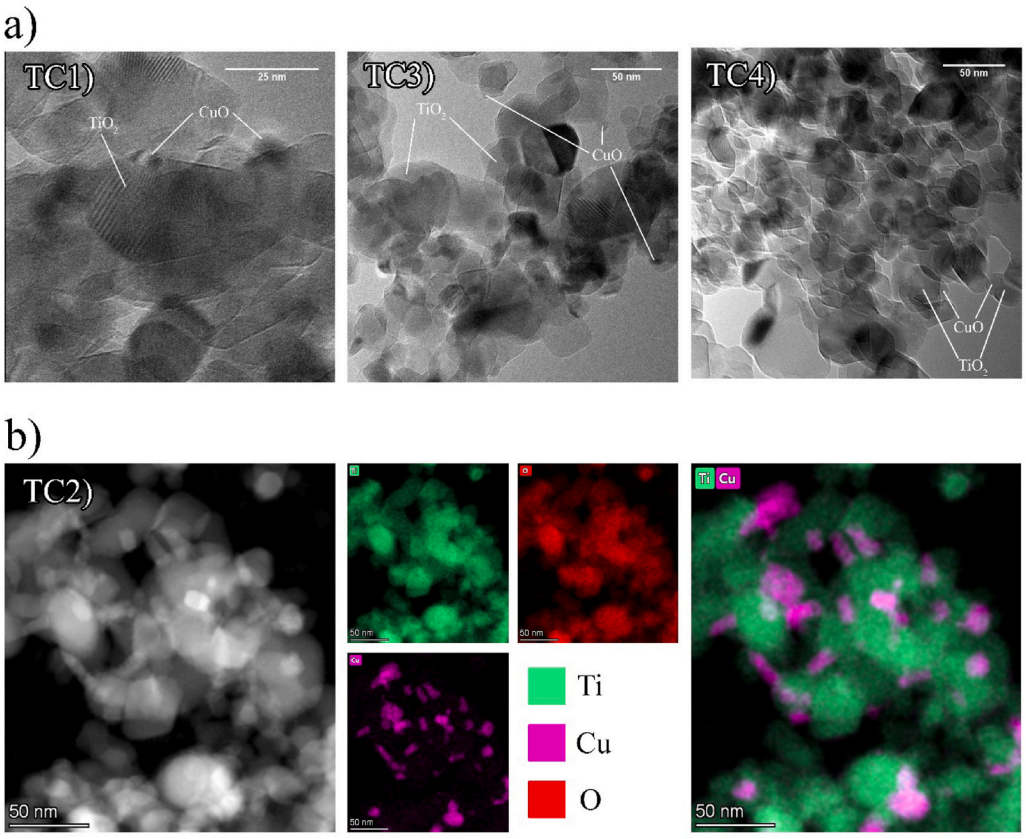

Fig. 5. TEM micrographs of a) TC1, TC3, and TC4 samples and b) HRTEM micrograph and elemental mappings of TC2 sample.

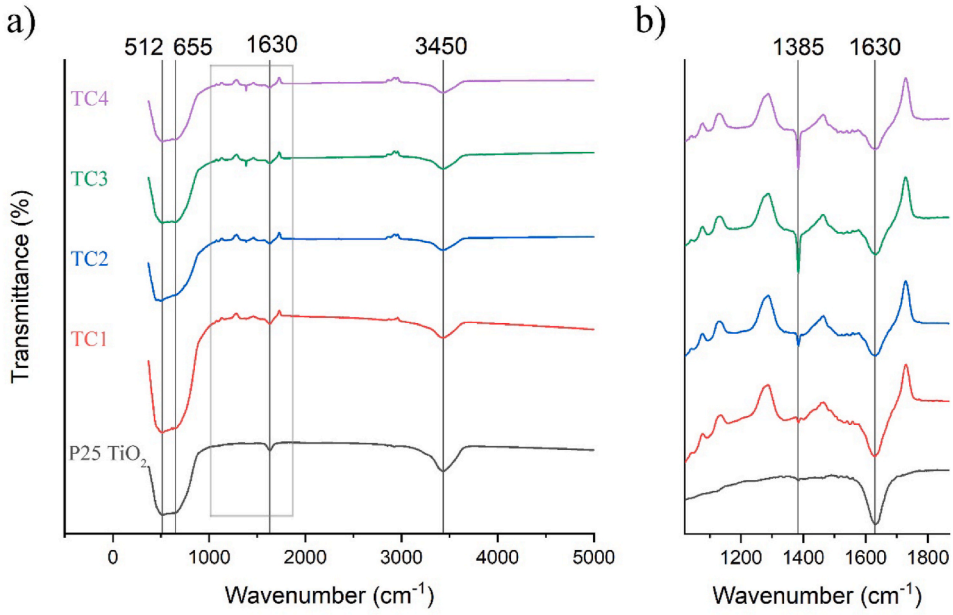

Fig. 6. FTIR spectra of a) CuO surface modified and bare TiO_2 photocatalyst samples and b) peaks correlating to CuO nanostructures.

3. Results and discussion

Fig. 2 shows the appearance of as-received TiO_2 nanoparticles and CuO-modified TiO_2 nanoparticles, calcined at 300 °C for 2 h. At low CuO loading (TC1 photocatalyst sample), the calcined powder has a light green color. An increase in CuO loading turns the color of synthesized powders into light grayish (for TC2 photocatalyst) and black. The higher the CuO loading, the darker the color of synthesized samples, which indicates the successful deposition of (black) CuO structures on the surface of TiO_2 nanoparticles.

SEM-EDS analyses were utilized to assess the CuO content of modified TiO_2 nanoparticles. As shown in Fig. 3, all modified photocatalyst samples contain Ti, O, and Cu atoms. Also, it is clear that the Cu content of photocatalyst samples proportionally increases with increasing the Cu

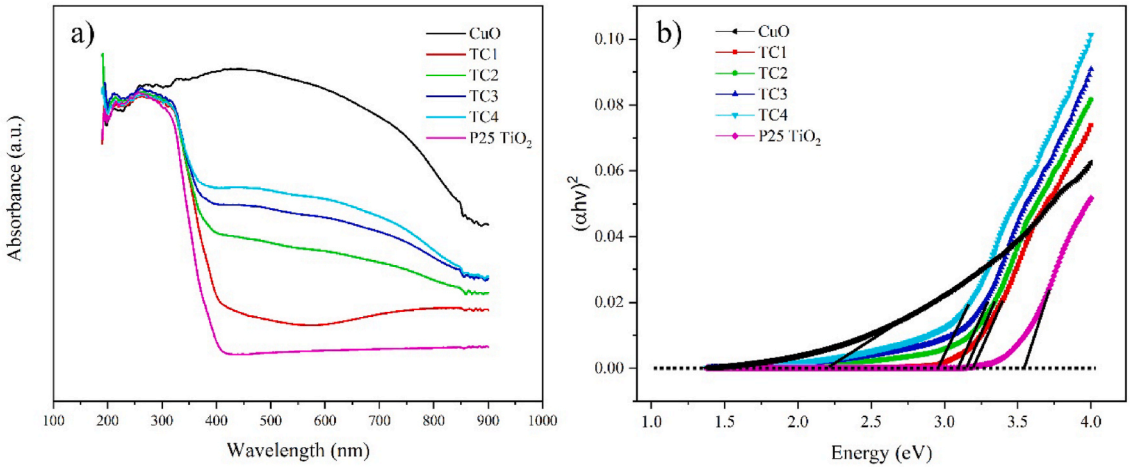

Fig. 7. a) UV–Vis diffuse reflection spectra, and b) Tauc plot of P25 TiO_2, CuO nanoparticles, and CuO-surface modified TiO_2 nanoparticles.

loading in the precursor, i.e., the Cu content has increased from roughly 0.5 wt% in sample TC1 to 13 wt% in sample TC4.

XRD was used to study the crystalline structures of synthesized materials. The XRD patterns of different photocatalyst samples are presented in Fig. 4. As can be seen from Fig. 4a, anatase and rutile phases are present in as-received P25 TiO_2 nanoparticles, with correlating peaks being in good agreement with the standard JCPDS (Card No: 96-720-6076 for anatase and Card No: 96-900-4143 for rutile phases). XRD peaks, associated with the CuO structure, are also according to the standard JCPDS (Card No: 96-900-8962) and show that the synthesized CuO nanostructures are tenorite phase [31,35]. According to Fig. 4, the TC1 photocatalyst sample shows no peaks belonging to CuO, which has to do with the relatively low content of CuO in this sample. CuO-related peaks are more visible in TC2, TC3, and TC4 samples, though these peaks have relatively weak intensities compared to anatase or rutile phases.

The average crystallite sizes of anatase, rutile, and tenorite phases, calculated using Scherrer's equation, are listed in Table 1. Average crystallite sizes of anatase and rutile phases in all samples are similar. This indicates that the CuO deposition process does not influence the crystallite size, which is expected as the calcination temperature is not high enough to induce crystal growth in TiO_2 nanoparticles [36].

TEM and HRTEM were used to study the morphology, distribution, and size of TiO_2 and CuO nanoparticles in different samples. TEM micrographs of CuO-modified P25 TiO_2 photocatalyst samples are shown in Fig. 5. As indicated in Fig. 5a, crystalline TiO_2 nanoparticles have sizes ranging from 5 nm to 40 nm. The average particle size in this sample is 25 nm. As shown in Fig. 5b, EDS analysis of the TC2 sample indicates a homogenous distribution of CuO nanostructures on the surface of P25 nanoparticles. The synthesized CuO nanostructures have an average diameter of 14 nm, agreeing with the calculated crystallite sizes shown in Table 1.

The bonding characteristics of bare and surface modified TiO_2 Nanoparticles were studied using FTIR analysis. Results are shown in Fig. 6. The peaks observed at 1630 and 3450 cm^{-1} are related to bending modes of Ti–OH and stretching vibrations of OH groups, resulting from adsorbed H_2O molecules on the surface of the TiO_2 nanoparticles [37]. The peaks shown within the 512 to 655 cm^{-1} range are due to metal-oxygen bonds. These peaks correlate to the vibrational stretching mode of O–Ti–O and also the bending vibrations of Ti–*O*–Ti groups [38,39]. The presence of CuO structures on the surface of TiO_2 nanoparticles is confirmed by the 1385 cm^{-1} peak, which is known to represent the stretching vibrations of Cu–*O*–Ti groups [40]. This confirms the formation of the chemical bond at the interface of CuO and TiO_2 structures. It can be seen that as the amount of Cu loading in the precursor increases, the 1385 cm^{-1} peak intensity increases accordingly.

The UV–Vis diffuse reflection spectra measurements were done to evaluate the light absorption of the synthesized photocatalysts. As shown in Fig. 7a, a comparison between TiO_2 nanoparticles and the CuO-modified TiO_2 photocatalyst sample shows a significant increase in the light absorption in the visible-light region above 380 nm. It is noticeable that the increase in CuO loading has significantly enhanced the absorption in the visible-light region. There is no apparent change in the absorption edges of CuO-modified photocatalyst samples compared with the reference TiO_2 nanoparticles. This indicates that the intermingling of CuO nanoparticles with TiO_2 nanoparticles can dramatically change the light/TiO_2 interaction within the visible-light region. This is due to the charge imbalance between Ti^{4+} and Cu^{2+} that prevents the substitution of a lattice ion with a new element with a different valence as it results in a lack or excess of charges [35,41].

As shown in Fig. 7b, to determine the bandgap energies of the CuO-modified photocatalyst samples, the Tauc plot of the modified Kubelka–Munk (KM) function was drawn, and a linear extrapolation of the graph was used [42]. TiO_2 nanoparticles showed a bandgap value of 3.51 eV. The deposition of CuO structures onto the surface of P25 TiO_2 nanoparticles is shown to decrease the bandgap energies to 3.21 eV, 3.14 eV, 3.08 eV, and 2.92 eV for TC1 TC2, TC3, and TC4 photocatalyst samples, respectively, and CuO nanoparticles have a bandgap of 2.19 eV. This indicates that CuO-modified photocatalyst samples are expected to show better photocatalytic, and consequently, antimicrobial properties under UV and visible light compared to bare TiO_2 nanoparticles [43].

3.1. Photocatalytic activity

Photocatalytic degradation of Amoxicillin on CuO surface modified P25 TiO_2 nanoparticles was evaluated under visible light. Amoxicillin is a common semi-synthetic β-lactam antibiotic that is used to treat several diseases. It is chemically stable with low rates of degradation and relatively high toxicity. Amoxicillin traces are often found in hospital and pharmaceutical wastewater samples. Amoxicillin is also sometimes traceable in natural water sources due to its extensive medical applications [44]. Fig. 8a shows the changes in the relative concentrations (C/C_0) of Amoxicillin during the photodegradation experiments. As expected, TiO_2 hardly shows any visible light photocatalytic activity and does not affect the amoxicillin concentration. As shown in Fig. 8a, the photocatalytic efficiency of CuO surface-modified TiO_2 nanoparticles significantly correlates with the amount of CuO loading as the CuO-containing photocatalyst samples show a comparatively higher photocatalytic efficiency in comparison to the bare TiO_2 photocatalyst sample. It is evident that the photocatalytic activity generally increases with the increase of CuO loadings as the TC2 and TC3 photocatalyst

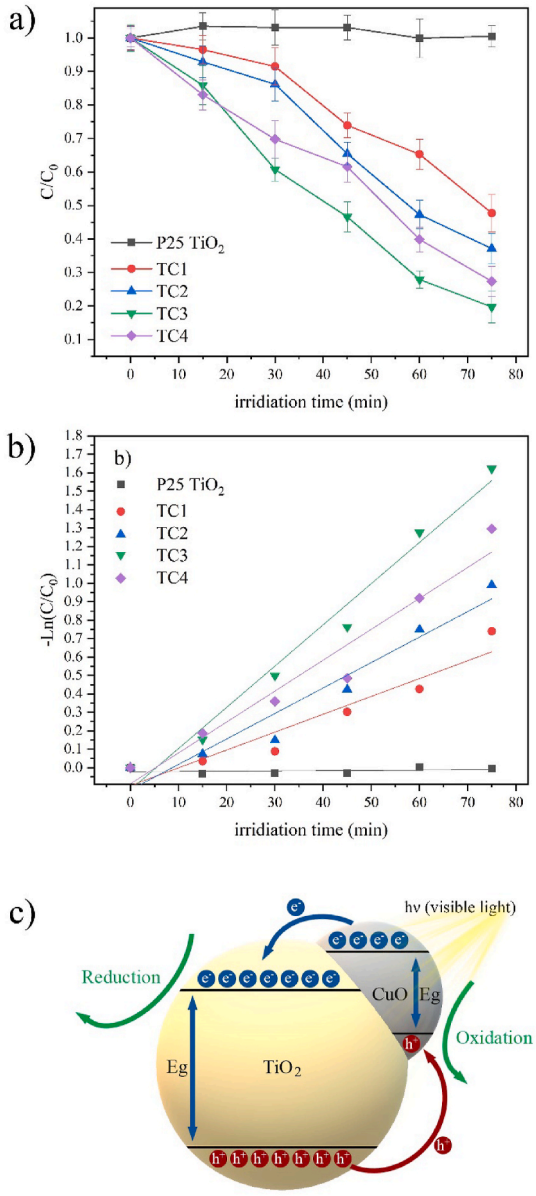

Fig. 8. a) Relative concentration changes of Amoxicillin under visible light on P25 TiO_2 and CuO-surface modified TiO_2 photocatalysts, b) First-order kinetic curves of visible light degradation of Amoxicillin under visible light on P25 TiO_2 and CuO surface modified TiO_2 photocatalysts, and c) schematic diagram of charge transfer on the CuO surface modified TiO_2 nanoparticles.

samples demonstrate higher photocatalytic activity in visible light compared to the TC1 sample. TC4 photocatalyst sample shows a reduction of visible light photocatalytic activity in comparison to the TC3 sample. This could be explained by the partial blockage of the active sites in the TiO_2 nanoparticles, which act as a substrate for the deposited CuO nanostructures due to the excessive amounts of CuO loadings or by the decline of the visible light photocatalytic behavior of CuO nanostructures as a result of their particles size enlargement [45].

Visible light photocatalytic degradation of compounds such as Amoxicillin through heterogeneous reactions could be described by a Langmuir - Hinshelwood (L-H) kinetic model, i.e.:

$$r_0 = k_r \frac{KC_{eq}}{1+KC_{eq}} \Leftrightarrow \frac{1}{r_0} = \frac{1}{k_r K}\frac{1}{C_{eq}} + \frac{1}{k_r} \quad (1)$$

where r_0 is the initial rate of the reaction, C_{eq} is the equilibrium concentration, K is the adsorption constant onto the catalyst's surface, and k_r is the intrinsic reaction rate constant. When the extent of adsorption and/or substrate concentration is small, i.e., $KC_{eq} \ll 1$, as is the case for the visible light photocatalytic degradation of Amoxicillin on the CuO surface-modified P25 nanoparticles, equation (1) is reduced to a first-order kinetic expression as:

$$-\frac{dC}{dt} = k_{app}C \Leftrightarrow \ln\frac{C_0}{C} = k_{app}t \quad (2)$$

where k_{app} is the rate constant. Fig. 8b shows the -ln (C/C_0) plotted against reaction time. To obtain the rate constant, a linear fitting was performed. As expected, the constant rate for the TiO_2 photocatalysts was calculated to be 1.519×10^{-4}, indicating no noticeable photocatalytic activity under visible light. The constant rate of TC1, TC2, TC3 and, TC4 are calculated to be 0.00968, 0.01382, 0.02237, and 0.01677, respectively, indicating that the kinetic of amoxicillin degradation is significantly influenced by CuO loading on TiO_2 nanoparticles. The enhancement of photocatalytic behavior of wide bandgap semiconductors, such as TiO_2, through heterojunction formation with narrow bandgap semiconductors, such as CuO, has been studied extensively [45–48]. The formation of CuO nanostructures on the surface of TiO_2 nanoparticles extends the photoresponse of TiO_2 into the visible region. Since the conduction band of TiO_2 is more positive than that of CuO, the photogenerated electron injection is expected to be from the bandgap of the CuO nanostructures into the TiO_2 conduction band, whereas holes can accumulate in the valence band of deposited CuO nanostructure to form hole centers [49,50]. These holes can participate in the oxidation process and be consumed (see the schematic in Fig. 8c). The produced photo-excited electrons and photo-excited holes could convert the water molecules adsorbed on the surface of CuO surface-modified TiO_2 nanoparticles catalyst into H^+ and OH^- [51]. The adsorbed OH^-onions can be oxidized by reacting with accumulated holes in the valence band of the CuO structures to form hydroxyl radicals ($OH^\bullet$), Concentrated electrons in the conduction band of TiO_2 nanoparticles can transfer to adsorbed oxygen atoms on the surface of TiO_2 to form superoxide radical anion ($O_2^{\bullet -}$). The adsorbed oxygen atoms can also react with H^+ cations to form adsorbed hydroperoxyl radical (HO_2), which combines with H^+ and e^- to form Hydrogen peroxide (H_2O_2). H_2O_2 can react with a superoxide radical anion, reducing to hydroxyl radicals. Predominantly, the degradation kinetics of a particular concentration of an organic compound, such as Amoxicillin, is controlled by the concentration of OH radicals [52]. The photocatalytic reactions resulting in the formation of free radicals are given as follows:

$$\frac{CuO}{TiO_2} \xrightarrow{h\nu} \frac{CuO}{TiO_2}(h^+ + e^-) \quad (3)$$

$$H_2O \leftrightarrow H^+ + OH^- \quad (4)$$

$$OH^-_{ad} + h^+ \rightarrow OH^\bullet_{ad} \quad (5)$$

$$O_{2ad} + e^- \rightarrow O_2^{\bullet -} \quad (6)$$

$$O_{2ad} + H^+ \rightarrow HO^\bullet_{2ad} \quad (7)$$

$$H_2O_{ad} + h^+ \rightarrow OH^\bullet_{ad} + H^+ \quad (8)$$

$$HO^\bullet_{2ad} + e^- + H^+ \rightarrow H_2O_{2ad} \quad (9)$$

$$H_2O_{2ad} + O_2^{\bullet -} \rightarrow 2\cdot OH_{ad} \quad (10)$$

The mechanism of amoxicillin degradation by OH radicals has been previously studied [52–55]. In short, it is postulated that the photodegradation of Amoxicillin is comprised of fragmentation at the peptide bond of the Amoxicillin to form a phenol and a bicyclical lactamic product and also other smaller molecules including CO_2, NH_4^+, and H_2O [54]. The phenol can be further degraded into oxalic acid, and the other big molecule can also degrade into oxalic and oxamic acids. The final

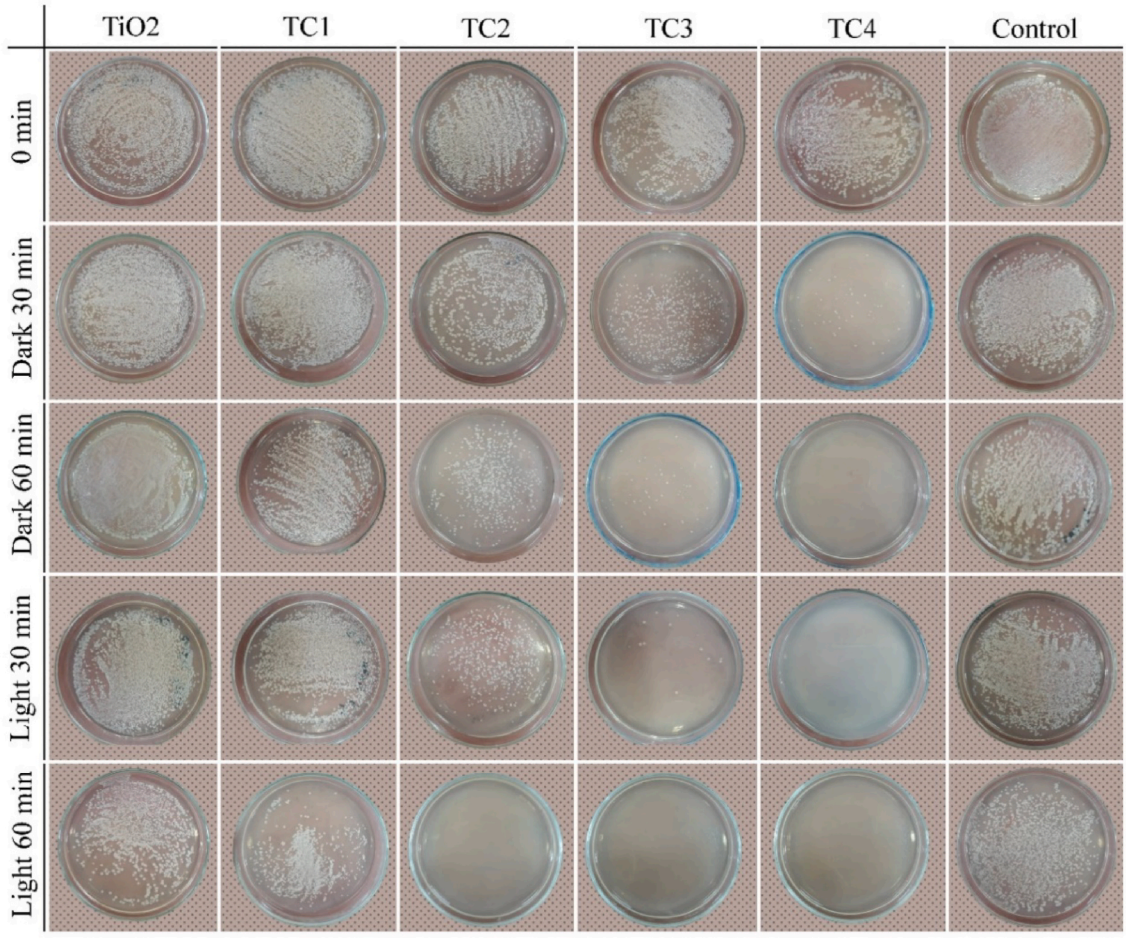

Fig. 9. Survived colony growth of *S. aureus* treated by TiO_2 and CuO-surface modified TiO_2 photocatalyst samples at 0, 30, and 60 min under dark and visible light illumination.

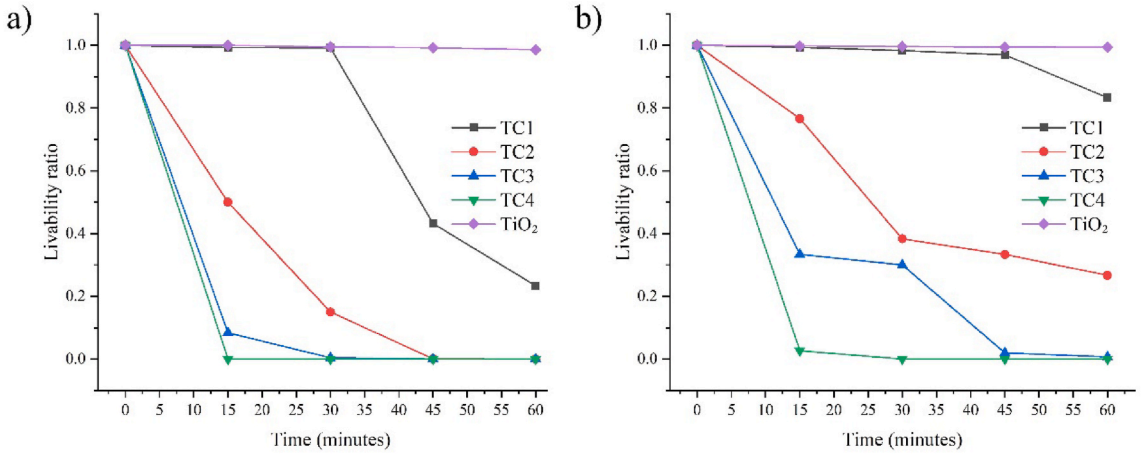

Fig. 10. Liveability ratio of *S. aureus* bacteria treated with bare and CuO-surface modified TiO_2 nanoparticles as a function of time, under a) visible light and b) dark conditions.

products from the degradation are smaller molecules of CO_2, H_2O, HNO_3 [53,56].

3.2. Antibacterial assay

The bactericidal activity of bare and CuO-surface modified TiO_2 nanoparticles was evaluated under visible light and also in a dark environment. Fig. 9 shows the formed *S. aureus* colonies from the bacterial solution in different time periods in both dark and under visible light environments, and Fig. 10 represents the cell viability of *S. auroes* bacteria against different photocatalyst samples. It is evident that bare TiO_2 nanoparticles show no apparent antibacterial activity against the gram-positive *S. aureus* bacteria under visible light or dark environments. No sensible reduction in the cell viability of the bacteria can be

detected. It is noteworthy, considering that TiO_2 nanoparticles are being used as antimicrobial agents in various commercial applications [6]. CuO-surface modified photocatalysts show antimicrobial properties in both dark and light environments, indicating two mechanisms, i.e., the ionic antibacterial activity and the photocatalytic mechanisms, are simultaneously active. According to Fig. 10, the TC1 photocatalyst sample reduces the bacterial liveability to about 86% of the initial amount in the dark environment. Whereas under visible light, the liveability of the bacteria is reduced to 23%. As for the photocatalyst TC2, after 60 min in dark conditions, the bacterial liveability is reduced to 26% percent. But, when visible light irradiation is present, all bacteria are dead within 45 min of incubation. At higher concentrations of Cu ions in the synthesized CuO nanostructures on the surface of TiO_2 nanoparticles, namely the TC3 and TC4 photocatalysts, show the almost complete inhibition of *S. aureus* colony formation after 60 min of incubation, even in dark conditions. This is due to the ion release from CuO nanostructures. In this process, copper oxide nanostructures release Cu ions in the presence of oxygen and H_2O molecules [57]. Cu ions, released by the CuO nanostructures, could adhere to the negatively charged bacterial cell wall and cause the rupture of the cell wall; this would lead to protein denaturation and result in the death of the bacteria [58,59]. Within the bacteria, Cu ions can bind to DNA molecules and get involved in cross-linking within and between the nucleic acid strands, resulting in disorganization of the helical structure of the DNA. Also, Cu ions have been found to interrupt critical biochemical processes necessary for the liveability of the bacteria [15]. For these reasons, any material capable of Cu ion release is expected to show bactericidal activity to different extents. Under visible light irradiation, photocatalysts TC3 and TC4 reduced the bacterial liveability to 0 after 30 min and 15 min of incubation, respectively. This high antibacterial activity can be ascribed to the synergic effects of Cu ion release and the photocatalytic antibacterial mechanisms of CuO surface modified TiO_2 photocatalyst. Under light irradiation, the photocatalytic behavior of photoactive nanomaterials has been attributed to the formation of ROS. The free radicals generated through photocatalytic reactions under visible light irradiation (as previously seen in reactions 1–8) on the surface of CuO surface-modified TiO_2 nanoparticles can interact with the bacterial membrane surface or the intercellular cytoplasm and result in the ROS-mediated alteration of the membrane protein activity which in turn can result in bactericidal activity of the photoactive nanomaterials [60]. Formation and effectivity of these photogenerated species against various pathogens have been widely studied [15,61–64]. It is considered that photocatalytic production of hydroxyl radicals, superoxide radicals, singlet oxygen, and electrons under visible light irradiation on the surface of the CuO surface-modified TiO_2 nanoparticles can cause damage to the bacteria by creating oxidative stress on it and result in its inactivation [6]. These active species are the most prominent when considering photocatalytic inactivation of pathogens. Most importantly, the photogenerated $OH^{\bullet}$ can be responsible for the peroxidation of lipids in the bacteria's outer cell wall and the damage of cell organelles and DNA structure [65].

An increase in the concentration of photogenerated ROS (such as hydroxyl radicals and superoxide radicals) directly affects the photocatalytic antibacterial efficiency of photoactive nanomaterials. It has been concluded via photocatalytic degradation measurements that CuO surface modification of TiO_2 nanoparticles results in higher visible light photocatalytic activity through the transfer of the photoexcited electrons from the CuO nanostructures to the conduction band of TiO_2 nanoparticles, which can significantly enhance the photocatalytic ability. Synergic effects of the ion release mechanism and visible light photocatalytic activity of CuO surface-modified TiO_2 nanoparticles have made these structures good candidates for the antibacterial treatment of hospital wastewater under visible light (considering the proven photocatalytic behavior for degradation of antibiotics such as Amoxicillin) or as antimicrobial agents for applications in coatings and textiles.

4. Conclusions

This paper investigates the synthesis and characterization of photoactive TiO_2/CuO nanocomposites to be applied for the photocatalytic removal of Amoxicilline from wastewaters and antibacterial applications. The development of multi-functional strategies to treat biological/organic contaminants from wastewater has recently gained lots of attention because the complexity and contents of biological/organic contaminants have tremendously increased in the last decade. In this investigation, CuO surface modification of TiO_2 nanoparticles with different CuO loadings was carried out using a straightforward precipitation method. Antibacterial activities of samples were investigated against gram-positive *S. aureus* bacteria. Also, the applicability of synthesized powders in the photocatalytic removal of Amoxicilline from wastewater was methodically investigated. Following results were obtained from this investigation:

- The proposed synthesis method resulted in a homogeneous distribution of copper in the final powder product. There is no indication of a local copper enrichment or excessive agglomerations. XRD results also confirm the existence of CuO in synthesized samples. CuO nanoparticles are spherical with an average size of 30 nm.
- The presence of CuO structures on the surface of TiO_2 nanoparticles was also confirmed by FTIR results. FTIR results confirmed the formation of a chemical bond at the interface of CuO and TiO_2 structures.
- CuO loading vastly increases the light absorption in the visible-light region above 380 nm. This infers that CuO-loaded samples can be used under visible light radiation. It was shown that CuO loading could significantly decrease TiO_2 bandgap to values as low as 2.92 eV.
- CuO-loaded TiO_2 specimens showed great functionality in removing Amoxicillin from wastewater. Also, the CuO-loaded TiO_2 nanoparticle showed an impressive antibacterial response. This high antibacterial activity was ascribed to the synergic effects of Cu ion release and the photocatalytic antibacterial mechanisms of CuO-surface modified TiO_2 photocatalyst.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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