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Copper oxide nanoparticles for photocatalytic and antibacterial applications: a review

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Abstract. Copper oxide (CuO) is a well-known semiconductor material, which has been widely used in many different fields such as energy, environment, and medicine. The need for effective and feasible synthesis of a nanostructured CuO for various applications is an urge. Therefore, the method for synthesizing CuO, ranging from the oldest to the more advanced with different approaches, is summarized in this review to shed light on the viable options for synthesizing this promising material for specific needs. Moreover, the trade-off of each synthesis route is heavily emphasized in this review to highlight the actual advantages and disadvantages of various methods. In addition, applications of CuO in various fields, including photocatalysis and antibacterial, is discussed, in turn, the main application of CuO in the photodegradation of organic pollutants and antibacterial properties is presented in detail along with misconception and revalidation of various mechanism. Future perspectives are also given to mention and tackle the current and future challenges for the synthesis as well as the application of the material.

Keywords: copper oxide, photocatalytic, antibacterial, phyto-synthesis

Classification numbers: 3.2.1, 3.4.5

1. INTRODUCTION

Nanostructured metal oxide has caught the attention of worldwide scientists with its fascinating properties, specifically high surface area and volume ratio and great surface energy. One of the top highlights of nanostructured metal oxide is the photocatalytic degradation of organic dye to resolve water pollution. Apart from this, another significant source of water contamination is derived from microorganisms which may have developed resistance toward various antimicrobial agents, in addition, these microorganisms also afflict various health issues. Amongst these metal oxide, copper (II) oxide nanoparticles (CuONPs) are in great consideration

as they can pose as a great substitution for more expensive noble metal oxide [1 - 2], and as a promising catalytic property under visible light thanks to the low bandgap (1.35 eV) [3 - 4]. Besides, CuONPs have been also reported for the application of antimicrobial activity due to their potent biocidal properties [5 - 7].

On the other hand, there are three primary approaches for fabricating nanoparticles such as physical, chemical, and biological methods. Herein, the chemical methods require the usage of various toxic chemicals, thus, giving adverse effects on the material such as fine-tuning of the size of the particles. It should be taken into consideration that the agents that are used for this route can be quite detrimental to the environment. Meanwhile, physical methods offer ease of operation and applicability. However, these methods might be deemed unsuitable for tailoring the nanostructure of CuONPs. Thus, bio-synthesis approaches, possessing the alleviation of potential drawbacks of chemical and physical methods, are performed [8 - 9]. Currently, the preparation of metal oxide nanoparticles is focused on the utilization of microorganisms and natural compounds such as flavonoids, steroids, and phenolics from plants as a reductant with highly bio-compatible and the ability to upscale to industrial size. Indeed, plant extracts work as potential agents for the synthesis, as it possesses rapid growth with low consumption, dispersion of natural compounds, cost-effectiveness, high stability, and safe measurement. The mentioned components in plants can pose as the reductants and also the desired stabilizers for the process. Simultaneously, the biomolecules presented in the extract also increase the electron donor process in photocatalytic reactions, enhancing the role of nanoparticles as catalysts [10 - 11]. Therefore, green synthesis from plants is a potential method for metal and metal oxide nanoparticles since the available organic compounds in the extracts are considered non-toxic stabilizing and reducing agents.

It should be taken into consideration that every synthesis route has its own trade-off, scalability and viability [12]. To the best of our knowledge, there has been no report on these factors when it come to the synthesis of CuONPs. Therefore, in this review, light is shed onto these trade-off to value the synthesis methods for its scalability and sustainablity. In addition to the synthesis of CuONPs, in-depth mechanism and common misconception for photodegradation of organic molecules and the gap in the finding for the antibacterial application using CuONPs is mentioned and heavily emphasized. In addition to the heavily focused photocatalytic degradation of dye and antibacterial utilization of CuONPs, energy-based applications are also mentioned to further expand the application of CuONPs.

2. FUNDAMENTAL ASPECTS OF COPPER (II) OXIDE (CuO)

2.1. Structure

CuO is considered one of the three binary phases of p-type semiconductor copper (II) oxide, known as tenorite mineral. Its lattice is composed of Cu^{2+} ions and O^{2-} ions coupled by an ionic connection with an empirical formula of CuO [1]. In addition to chemical bonding, four copper atoms located in the corners of a warped tetrahedron coordinate with each oxygen atom as shown in Figure . The tetragonal PdO structure is distorted monoclinically in this configuration [3 - 4]. Although most transition metal oxides are typically classified as having a greater proportion of ionic than covalent bonds, the bonding in CuO can be considered to be predominantly covalent due to the difference in Pauling electronegativity between oxygen and copper of 1.8 [13 - 14].

Like many important prototypical materials, CuO has obtained outstanding physical and chemical properties with a highlight on crystal, electronic, and bandgap structures. In order words, CuO has a narrow direct energy band gap (E_g) of 1.0-2.08 eV at low temperatures via some investigations using the local-density approximation (LDA+U) and hybrid functionals and is known to be an antiferromagnetic semiconductor [16 - 17]. With large surface area and probable size of CuONPs is considered a potential material for rechargeable lithium-ion batteries and the manufacture of solar cells [10 - 11]. It also possesses a wide range of intriguing qualities, including high thermal conductivity [18], photovoltaic capabilities [19], high stability, and antibacterial activity [20], which can be employed in a variety of promising technological domains such as active catalyst, gas sensor, high-efficiency thermal conducting material, magnetic recording medium, very good selectivity, and solar cell applications. Furthermore, the participation of CuO nanoparticle as a catalyst can be effectively applied in some organic bond formations like the C–N coupling and C–S cross-coupling of aromatic and aliphatic thiols with iodobenzene reactions due to their recyclability [21]. An unspeakable ability of CuO is hydrophobicity, which is employed as a potential choice for reused catalysts in aqueous medium as well as surface protection agents based on the Lotus effect [22]. Besides, various shapes and dimensions of copper (II) oxide CuO could be indicated zero-dimensional (0D) nanoparticles, one-dimensional (1D) nanotubes, 1D nanowires/rods, two-dimensional (2D) nanoplates, 2D nanolayers, and several complex three-dimensional (3D) nanoflowers, spherical-like, and urchin-like nanostructures, which is obtained via different technological methodologies. The considerable effects of synthetic approaches on the physicochemical properties of nanostructure CuO were inspected and introduced to fabricate numerous CuO morphologies [23 - 24].

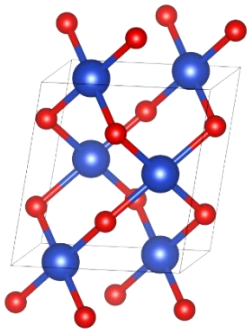

Figure 1. Structure of CuO [15]. The image was adapted from the work of Aroussi et al. under the permission from the terms and conditions of the Creative Commons Attribution 3.0 license.

2.2. Synthesis method

The insights in synthetic methods have significantly caught tremendous attention as functional components for the development of nanostructure material. Fabrication strategies are extremely important to obtain manageable dimensions and sizes with various unique properties for diverse industrial applications. According to previous literature, various synthetic methodologies in preparation of CuO could be classified into three main categories, including physical (e.g. electro-spraying, laser pyrolysis, laser ablation, and evaporation-condensation), chemical (e.g. sol-gel, solve/hydrothermal, co-precipitation, and combustion), and biological (e.g. the uses of different organism and extract from plants) [25]. In addition, the synthesis of CuONPs can also be categorized into bottom-up or top-down approaches.

2.2.1. Physical approach

In physical methods, the electric current plays a crucial role as a source of electrons in the formation of necessary electrons during the operation. Firstly, a single-step, top-down method for nanoparticle synthesis in a colloid is pulse laser ablation [26]. A dense plasma plume that is

contained by water molecules forms at the target-water interface when a pulsed power laser hits the target, first ablating it and then forming the dense plasma plume. The target vaporizes as a result of the remaining light being absorbed by the target's surface and liquid. Metal hydroxide nanoparticles are formed when copper species interact chemically with ionized water molecules in the interfacial region between plasma and water, and these particles eventually break down into metal oxide nanoparticles. By adjusting the laser source's wavelength, temperature, pulse width, ablation time, laser fluence, and repetition rate, it is simple to adjust the form, size, and concentration of nanoparticles [27]. The synthesis of controllable-sized NPs with regulated characteristics without any contaminations is one of the many benefits of laser ablation of material in a liquid medium/vacuum [28]. The synthesis of the metal oxide via laser ablation is summarized in Figure 2.

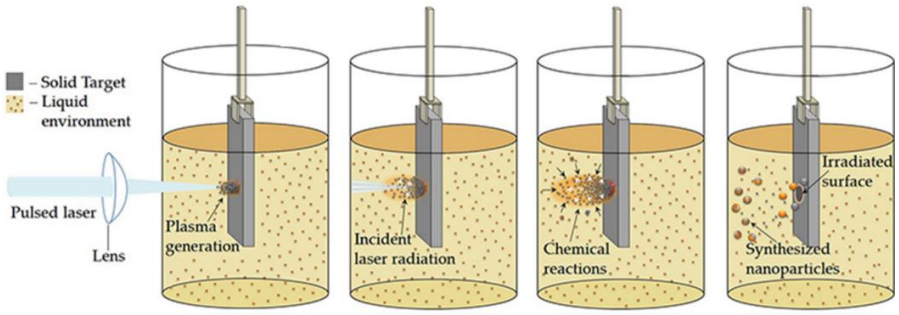

Figure 2. Mechanism for the pulsed laser ablation in liquids for the synthesis of metal oxide anoparticles [29]. Images were adapted from the work of Svetlichnyi under permission from the terms and conditions of the Creative Commons Attribution 3.0 license

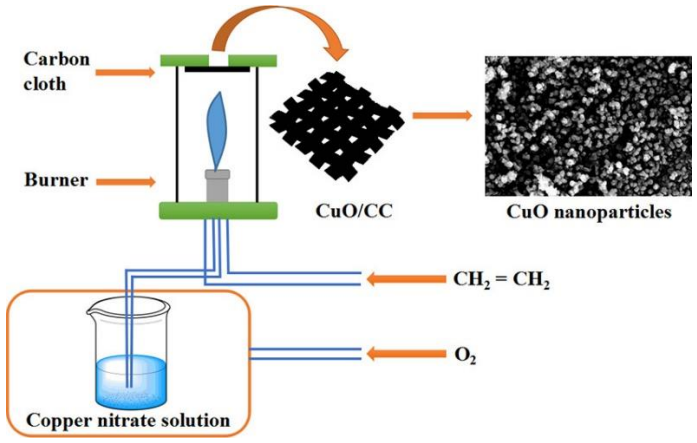

Figure 3. Schematic pulsed wire explosion system [30].
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In recent years, flame aerosol synthesis of various metal oxide nanostructures has caught the attention of researchers around the world, especially CuO. Briefly, copper precursor solution such as copper (II) nitrate is atomized into an aerosol system under the presence of a flame source. The obtained CuO nanostructure is captured on a substrate such as carbon cloth, or other semiconductors as shown in Figure 3 [31 - 32]. Such a method has been proven to be effective in the synthesis of CuO nanostructure owing to its feasibility and economics. The scheme for such a synthesis route is demonstrated in According to the work of Xe et al., the occurrence of thermal compression during the synthesis of CuO nanostructure can force the crystal to grow vertically along the grain of the crystal, resulting in the formation of a 2D

nanowire CuO structure [33]. Moreover, As revealed by Yang et al., CuO is synthesized by controlling the flow rate of the precursor solution into the atomizer, Yuan et al. reported the synthesis of quantum dot CuO [31]. These results reveal the ability to tailor the structure of CuO of this approach for specific needs.

Another physical method that could be mentioned is electrospinning for the fabrication of CuO nanofiber. The procedure offers a straightforward, cost-effective, and easy-to-use method to form highly reproducible nanofibers with ultra-thin diameters (<100 nm) [34 - 35]. As shown in Figure 4, the major components for conducting such a method include a high-voltage power supply, a syringe pump, a spinneret or a nozzle, and a conductive collector. Once the precursor is ejected out of the nozzle, the surface tension of the liquid induces the formation of a pendant droplet. Once the electrification of the droplet is carried out, the deformation of the droplet into a Taylor cone occurs due to the electrostatic repulsion. Subsequently, a charged jet originating from the Taylor cone is obtained and further extends in a straight line. As time goes by, the motion of the charged jet changes from straight to whipping due to the occurrence of bending instabilities. Following the change in motion, the charged jet further extends and solidifies, resulting in the formation of a thin solid fiber on the grounded collector [36]. The precursor solution that is used for such a synthesis method is composed of a copper (II) precursor salt and other additives such as surfactants or polymers to enhance the overall viscosity of the solution to achieve the Taylor cone shape during the electrification [37]. The electrospinning with copper (II) nitrate as an oxide precursor was effectively supported by poly(vinylbutyral) for the generation of nanofibers [38]. The potential for obtaining desired nanograin sizes for CuO nanofiber applications in gas sensing by controlling the temperature and calcination duration [39]. Rahman et al. reported the successful synthesis of a CuO line with a width of 54 μm and a thickness exceeding 1.4 μm. Such results demonstrate the feasibility of this approach for creating the 2D elongated structure of CuO [40].

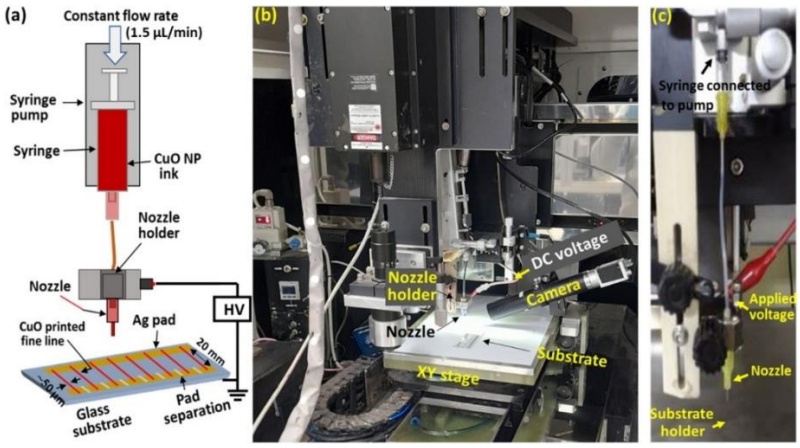

Figure 4. (a) Schematic electrospinning system. (b) photo of the actual system,
and (c) nozzle components [40]. Image was adapted from the work of Rahman et al. with permission under the terms and conditions of Creative Commons Attribution 4.0 International License.

Furthermore, the pulsed wire explosion approach was also taken into account as a novel method in the preparation of CuO nano-rod [41]. In the system, as shown in Figure 5, the system's top was equipped with a Cu coil wire, which was fed between two electrodes connected to a high-voltage power source and touching two high-voltage extension bars. The copper wire was blown up during the procedure to create CuONPs. Different variations in deionized water temperature could produce a variety of sizes and shapes of nanoparticles [42]. The principle mechanism of CuO nano-rod was an oriented attachment mechanism based on the

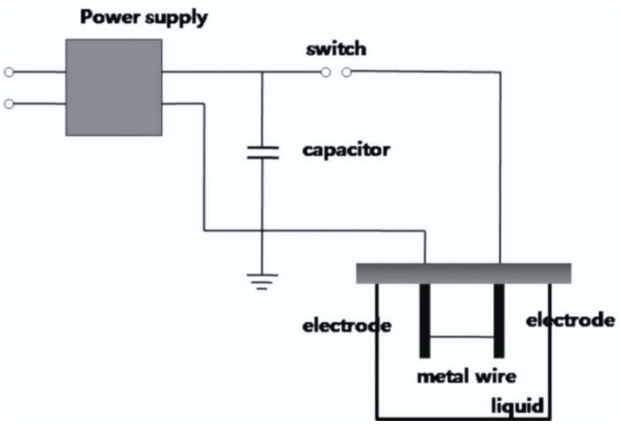

Figure 5. Schematic pulsed wire explosion system [43].
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directional aggregation with the massive influence of Ostwald ripening and aggregation supported by Brownian coagulation at high temperatures [8]. This method is suitable for the synthetic method of low-dimensional metal oxides without the usage of any surfactants to guide the directional growth of the crystal. The physical approaches have the benefit of producing CuONPs that are consistent, controllable in size, and high purity. Despite these obvious benefits, the cost of infectivity, operating skills, high power, and energy requirements present a significant disadvantage.

2.2.2. Chemical approach

The traditional chemical methods were mainly conducted with the utilization of some chemical agents for the reducing process of copper ions in copper salts and for the complexation of the copper ions. Some chemical methods can be employed, including solution-based methods, solid-state thermal conversion of precursor, electrochemical, and thermal oxidation methods [44].

Among various solution-based methods, hydrothermal synthesis has been typically technique using water as a solvent at high pressure and elevated temperatures during the reaction as shown in Figure 6. The technique involves the mixing of a copper (II) precursor salt and alkaline solution before the sealing of the obtained solution into a Teflon-lined autoclave. The formation of CuO nanostructure can be achieved through the thermal decomposition and oxidation of $Cu(OH)_2$ under elevated temperature and pressure. The synthesis of CuO nanostructure can be achieved at relatively low temperatures which is in the range of 90 – 180 ^oC, unlike other methods that require the calcination of $Cu(OH)_2$ at elevated temperatures as high as 900 ^oC [46]. Due to the requirement of a much lower temperature for the formation of

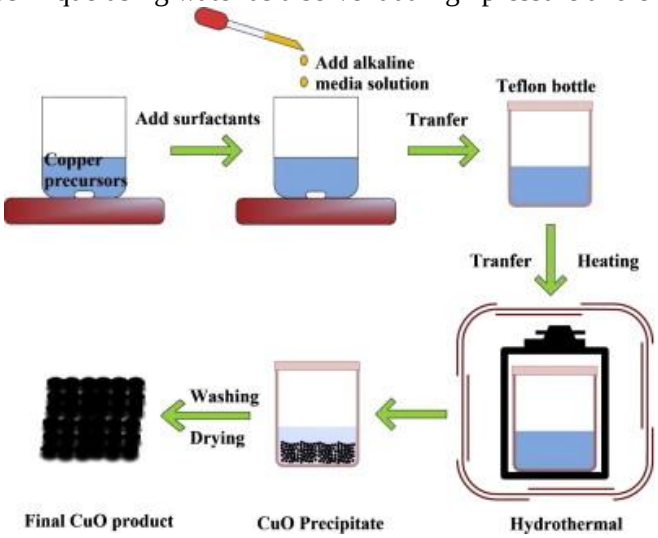

Figure 6. Hydrothermal synthesis of CuONPs [45].
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CuO nanostructure, scalability, controllability, and practicality, this method is still highly favored over other methods. According to a previous study, Sonia *et al*. prepared a highly stable CuO nanostructure with a leave-liked shape using copper (II) acetate dehydrate and tri-sodium citrate as oxide precursor and structure directing agent, respectively. Their approach confirmed the crystalline formation of CuO nanoleaves ranging from 13 - 17 nm [47]. The nano leaves CuO exhibited the high performance of the photocatalytic activity of methylene blue degradation in the UV region. In addition to nanoparticles, the CuO nanostructure can be synthesized with various sizes and morphologies such as 1D nanostructures (e.g. nanorods, nanotubes, and nanoneddles) [48 - 49], or 2D/3D nanostructure [50].

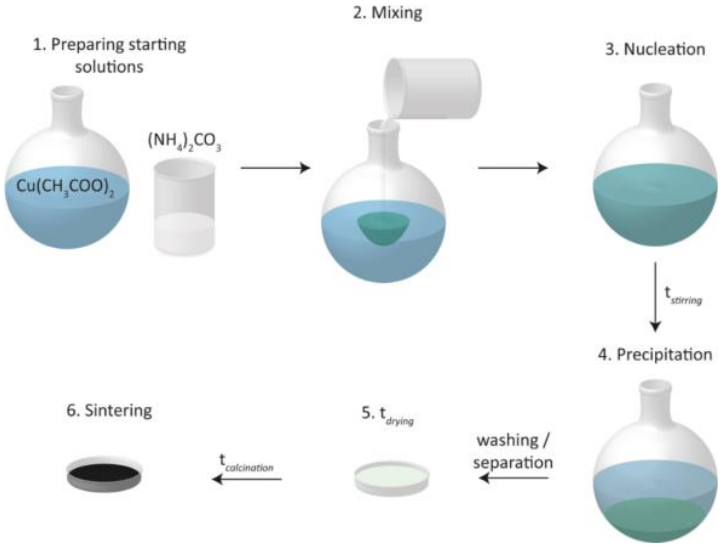

Figure 7. Synthesis of CuONPs using precipitation method [51]. The image was adapted from the work of Dörner et al. under the terms and conditions of the Creative Commons Attribution 4.0 license.

Another common solution-based method employed popularly is the chemical precipitation method based on the principle of homogeneous precipitation reaction associating with two stages (i.e. nucleation and nuclei growth). The reaction process is greatly influenced by the essential solute concentration that starts the process, with growth being brought by solute diffusion on the surface [52]. Besides, the utilization of different precursors (e.g. $Cu(NO_3)_2$, $CuSO_4$, or $CuCl_2$) is required for the development of CuO nanostructure [53]. The substance responsible for forming a precipitate, precipitating agent, is commonly sodium hydroxide or ammonia solution, followed by calcination to obtain CuONPs [51 - 54]. Due to the formation of CuO nanostructure is mainly derived from the thermal decomposition of Cu-based precipitation, such a method requires high energy demand. At elevated temperatures, thermal sintering, and particle agglomeration occur which can negatively impact the activity of the CuO nanostructure. In addition, recrystallization and defect formation also take place at elevated temperatures, which can greatly enhance the specific activity of the nanostructure. Therefore, a trade-off between the particle size, crystallinity, and availability of defect has to be made to obtain a nanostructure with desirable activity. The synthesis of CuONPs via precipitation is summarized in Figure 7. The flexible and adaptable optical characteristics of CuO nanoparticles are also dependent on the reaction temperature, which is demonstrated by the work of Rahnama and Gharagozlou with the investigation of effects of temperature ranging from 10 to 115 ^{o}C and ultrasonic irradiation conditions on the formation of CuONPs [55]. As revealed in the work of Ali et al., an increase in the particle size of CuO nanoparticles was observed when the precipitate was calcinated beyond 600 ^{o}C, resulting in the formation of irregular flake-like shapes made up of small and large particles with uneven distribution. In addition, a complete agglomeration of the particle was achieved through the observation of scanning electron images with purely large particles for the sample calcinated at 650 ^{o}C [56]. These results clearly demonstrate the influence of Lucrative

sources as reducing agents for the biological approach that have been investigated are the utilization of microorganisms and plants. Nanoscale structures of materials could be referred to as the mechanisms of biological reactions using biomolecules in the nanoscale. These mechanisms have existed in the nature of prokaryotic (e.g. bacteria) and eukaryotic (e.g. fungi and plant) organisms via extra or intra-cellular reactions for the generation of nanomaterials [57]. The biological approach is major divided into two types based on the uses of different organisms. Whereas the use of microorganisms (e.g. bacterial, fungi, and algae) in nanomaterial synthesis is also known as microbial synthesis, plant-mediated synthesis is the employment of different parts of a plant as either reducing or stabilizing agents of metal ions.

In recent years, bacteria have been one the most plenteous microorganisms with the identification of prokaryotic cells. They are potential candidates for metal oxide fabrication due to the ability to reduce metal ions attributed from proteins, enzymes, and the biochemical and interactive routes [58]. The main principle of this approach can be classified as two possible mechanisms including biologically controlled and biologically induced methods. Although biologically controlled synthesis naturally occurs to adjust several characteristics like size, composition, and surface area of particles, it still has limitations such as the number of used strains or the number of prepared particles. In contrast, biologically induced synthesis has been widely employed to generate metal oxides from simple precursors, which results from the bioremediation of metal ions toxicity. For instance, Nasrin *et al*. presented the biosynthesized CuONPs by using *Morganella morganii* bacteria with a particle size of less than 10 nm [59]. In another study, the CuONPs prepared via a biological route with the presence of *Phormidium cyanobacterium* biomass explained the formation from the extracellular hydrolysis process of copper (II) cation precursor [60]. Abdul et al. confirmed that proteins not only play an essential role in the reduction of copper ions but also serve as stabilizing agents during the formation of copper (II) oxide nanoparticles. Besides, an intracellularly environmental reaction by the death of cell membranes in bacterial-mediated synthesis with the presence of *Serratia* was reported by Han *et al*. [61]. The as-prepared CuONPs also show crystallinity with nanostructure ranging from 10-30 nm in diameter. So, there are some remarkable benefits like less use of hazardous and expensive substances and the capacity for large-scale production [62].

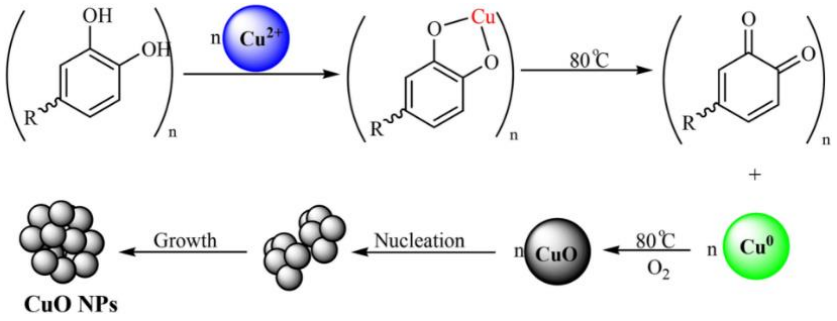

Figure 10. Green synthesis of CuONPs using phytocompounds found in plant based-extract [63]. Images were adapted from the work of Veisi et al. under the terms and conditions of the Creative Commons Attribution 4.0 International License.

Despite possessing eco-friendly benefits, the microbial synthesis for nanoparticles from microorganisms has drawbacks including time consumption, difficulty of isolation, and lengthy incubation process as well as difficulty in controlling size, shape, and crystallinity. A possible alternative that can be applied is the use of plant extracts as surfactant, capping, and stabilizing

agents in the synthesis of nanoparticles. With the hyperaccumulation effect, plants absorb available metal ions in the soil where t

The *in vitro* biogenic synthesis of metal oxides has been conducted using biomass or extracts from different parts of plants (e.g. roots, leaves, peels, and flowers), which contain phytochemicals as a role of stabilizing and reducing agents. If the alkaline pH facilitates the formation of metal oxide particles, the effects of temperature, reaction time, and precursor contents can reflect the growth orientation of nanoparticles. In order to confirm the convenience of the green chemistry-based method, Obakeng *et al*. carried out the synthesis of CuONPs using the sol-gel method as a conventional chemical method and green synthesis with the presence of *Terminalia phanerophlebia* leaf with different solvents [64]. Due to the relatively high negative surface charge from the Zeta potential analysis, the green synthesized CuO is more stable than the chemical synthesized CuO, which leads to the fact that the agglomeration of CuO nanoparticles can be prevented through the application of aqueous extract of the plant. The green synthesis of CuONPs was also conducted with another part of the plant, especially *Cordia sebestena* flower [65]. The as-prepared CuO also shows crystallinity with a spherical shape and high negative charge surface, which can be utilized as an efficient catalyst for organic reactions. Due to the plant biodiversity, the plant-based synthesis method, supplied with various sources for the biological preparation of CuONPs, can produce diverse morphologies and size distribution. For example, Velsankar *et al*. presented the spherical and reactangular-rod shaped CuO nanoparticles prepared using the aqueous extract of *Capsicum frutescens* leaf combined with the calcination process at 400 ^{o}C in the atmospheric condition[66]. From the analytical result of TEM images, the rectangular-rod-shaped CuO nanoparticles possess a width ranging from 20 - 40 nm. Similarly to the nanorod structure, Vidhya *et al*. also applied the plant-mediated route supported by the *Muntingia calabura* leaf extract with copper (II) nitrate trihydrate as an oxide precursor[67]. The scanning electron microscopy and transmission electron microscopy images show the formation of CuONPs with uniform-sized distribution, especially with thickness and length of approximately 23 and 79 nm, respectively, in nanorod-shaped structures.

In conjunction with the ideology of greener production, the reuse of waste can also be considered a green synthesis method as such a method can effectively reduce waste, especially animal-based waste. Aside from plant-based biomass, some animal parts have been recorded to be able to be utilized for the synthesis of CuO nanostructure. According to the work of Mobarak et al., scales from *Labeo rohita* can effectively be used for the green coprecipitation synthesis of CuO nanostructure. It is revealed that type I collagen presenting in the scale is denatured to gelatin when being heated. This denatured organic compound can serve as a capping agent to effectively stabilize the growth of the $Cu(OH)_2$ crystals, followed by calcination at vacuum to obtain CuO nanostructure. As revealed by their results, the obtained CuO nanostructures take various shapes namely, rod, plate-like, and sphere [68]. Nandisha and Sowbhagya reported that the urea and uric acid in Gomutra (cow urine) could also be utilized for the synthesis of CuO nanostructure. They revealed that the formation of CuO nano bundles with an overall length of 78.8 nm in which each bacillus-like structure has a length of 52.8 nm, was observed [69]. In recent years, the *in vitro* biogenic synthesis of CuO has expanded to the usage of human urine as a reducing agent as revealed from the work of Dabhane et al [70]. The formation of CuONPs from such a route can be attributed to the complexation of Cu^{2+} ions and urea, followed by the precipitation of the complexation by the addition of OH^- ions and calcination. They reported that the obtained human urine-derived CuONPs have a grain size of 6.78 nm with high crystallinity, a strong photocatalytic activity toward phenol along potent antibacterial properties toward various strains.

3. APPLICATIONS

3.1. Photodegradation of organic pollutants

Nowadays, there are various methods utilized to degrade organic matter in water sources. Photocatalytic degradation has been taken into account in the environmental treatment for some advantages including high processing efficiency, short operating time, and reusability of materials. In the photodegradation process, the material is an important factor in determining the treatment efficiency. Photodegradation could thoroughly treat organic pollutants without generating secondary pollution in water. In particular, high-performance degradable optical materials have the following characteristics: low band gap energy, simple synthesis process, environmental friendliness, stability, and reusability.

The photocatalytic mechanism is illustrated, as shown in Figure 11. The absorption of a photon leads to the generation of e^- and h^+, which is one of the compulsory factors for the photocatalytic process. When being illuminated with a photon with energy ($E = h\nu$) that is higher or equal to the bandgap of material, electrons (e^-) and holes (h^+) are generated, then e^- moves to the conduction band (CB) meanwhile h^+ remains at the valence band (VB) as shown in Equation (1). The difference in the energy value for CB and VB is deemed as bandgap.

$$h\nu + \text{photocatalyst} \rightarrow e^- + h^+ \quad (1)$$

The photocatalytic process occurs in two cases: Direct and indirect. In a direct situation, h^+ carries out the oxidation process of pollutants as Equation (2). In the other case, e^- combines with O_2, and h^+ combines with H_2O, creating $\bullet O_2^-$ and •OH, respectively, as shown in Equations (3) and (4). After that, generated •OH and $\bullet O_2^-$ radicals oxidize organic substances according to reactions as shown in Equations (5) and (6). Therefore, organic pollutants are degraded into H_2O, CO_2, and less harmful inorganic substances via the photocatalytic activity of catalyst material.

$$h^+ + \text{organic pollutant} \rightarrow CO_2 + H_2O \quad (2)$$

$$e^- + O_2 \rightarrow \bullet O_2^- \quad (3)$$

$$h^+ + H_2O \rightarrow \bullet OH + H^+ \quad (4)$$

$$\bullet OH + \text{organic pollutant} \rightarrow CO_2 + H_2O \quad (5)$$

$$\bullet O_2^- + \text{organic pollutant} \rightarrow CO_2 + H_2O \quad (6)$$

In recent years, the usage of CB and VB potentials for initializing and explaining redox-based reactions for both of these routes in photocatalysts is commonly used. It should be taken into consideration that in the case of a perfect crystal, CB of CuO predominantly originates from Cu 3p, and VB of CuO is derived from Cu 3d and O 3p [71]. Due to the difference in the energy level of various orbitals in the CuO structure, the pin-pointing of potential value for VB and CB is not viable due to the presence of defects that are induced during the synthesis of CuO. In addition, VB and CB of CuO also contain various energy levels derived from the orbitals of O, P, and vacancies. Therefore, the determination of VB and CB values to obtain the exact generation of $\bullet O_2^-$ and •OH from e^- and h^+, respectively, can be quite misleading as the higher energy level which can not be obtained through empirical analysis can produce strong e^- and h^+ for initializing the generation of $\bullet O_2^-$ and •OH as evidenced in our previous study on non-metallic co-doped copper oxide derived from *Mangifera indica* leaf extract [72 - 73]. It should be

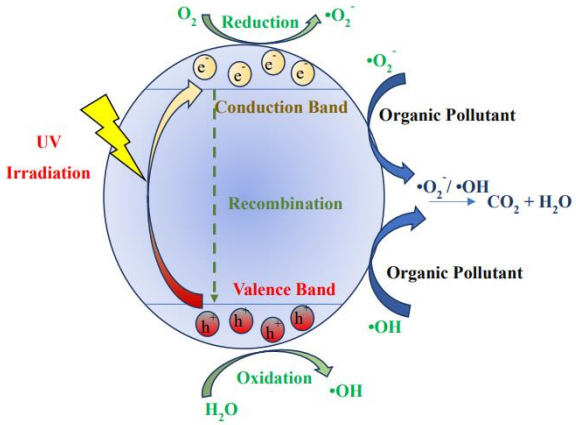

Figure 11. The photocatalytic mechanism of CuONPs [74].
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taken into consideration that the potential of VB and CB of the obtained CuONPs can differ from each study as the formation of defects and the incorporation of other heteroatoms may induce shifting in the potential of the VB and CB of the synthesized CuONPs. Moreover, with the recent advances in material, CuO either is often loaded onto another photocatalyst for the synergistic formation of a heterojunction material or is doped with other heteroatoms to effectively harvest sunlight and prolong the lifetime of photogenerated charges rather than being used alone. Li et al. reported that Ni-doped CuO can degrade 91.4 % of alura red with the initial concentration of 10 ppm under 48 min under sunlight, which was deemed to be in alignment with green chemistry and far superior to other CuO-based nanomaterials [75]. In another work presented by Bano et al., a CuO/ZnO heterojunction catalyst was prepared for the degradation of tetracycline and ciprofloxacin. It is revealed that the heterostructure between CuO and ZnO managed to degrade 94.6 % and 93.5 % for tetracycline and ciprofloxacin with the initial concentration of 25 ppm after 50 min under sunlight [76]. Such a result reveals the potential coupling of CuO with another active photocatalyst to enhance the activity of the combined structure.

Furthermore, it should be taken into consideration that many organic pollutants' color originates from the long conjugated carbon chains, therefore, decoloration of dyes, which is feasibly performed on an ultraviolet-visible spectrometer, can be extremely deceiving. According to the work of Herrmann, the decolorization of an organic compound may result from the limited stoichiometric transfer of electrons from the dye molecules to the photocatalyst, resulting in the lost color of the organic compound as the regular occurrence of the conjugated bonds is disrupted. Therefore, analysis related to the identification and the quantification of intermediates in post-catalysis solution is highly required to confirm the actual photocatalysis activity of the photocatalyst [77]. Zhang et al. demonstrated the removal of methylene blue, which is an organic pollutant, using pinewood biochar-CuO nanocomposite through the analysis of the total organic content of the post-catalysis solution. They further confirmed the actual degradation of methylene through the analysis of intermediates and chronic toxicity of these on fish, daphnids, and green algae. Overall, they reported a removal efficiency of 90% under the presence of PI as a co-oxidizing agent.

3.2. Antibacterial activity

Recently, nanotechnology has offered great possibilities in various fields of science and technology. Pharmaceutical nanotechnology with numerous advantages has growingly attracted the attention of many researchers [78]. The application of nanomaterials in drug delivery systems has been investigated for more than twenty years bringing about innovation of dosage

forms with improved therapeutic effects and physicochemical characteristics. Several types of nanoparticles and their derivatives have received great attention for their potential antimicrobial effects. Metal nanoparticles such as Ag, silver oxide (Ag_2O), titanium dioxide (TiO_2), silicon (Si), copper (II) oxide (CuO), zinc oxide (ZnO), Au, calcium oxide (CaO) and magnesium oxide (MgO) were identified to exhibit antimicrobial activity. In vitro studies revealed that metal nanoparticles inhibited several microbial species [78 - 79].

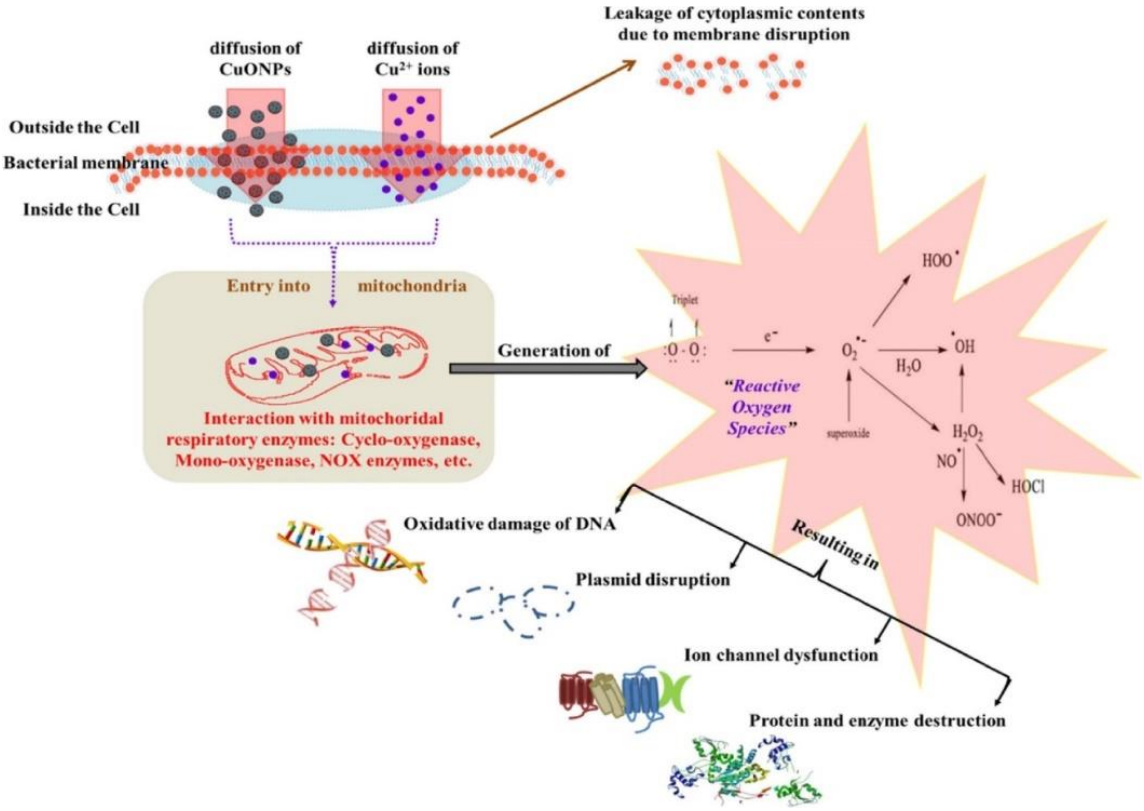

Figure 12. The antibacterial mechanism of CuONPs [80].
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The antibacterial mechanism of CuONPs is a complex mechanism that involves the diffusion of the nanoparticles, the generation of Cu^{2+} ions, and the creation of reactive oxygen species. These phenomena may occur individually or concurrently in the exterior, on the cell membrane, and in the interior of the bacteria cell. In the exterior area of the bacteria, all the aforementioned phenomena occur simultaneously. The generated Cu^{2+} ions and reactive oxygen species can disrupt the cell membrane to cause the leakage of the cytoplasm. In addition, the penetrations of the nanoparticles, ions, and reactive oxygen species also occur either at the cell membrane or at the disrupted sites. Once the nanoparticles manage to get into the interior of the bacteria cell, a domino effect occurs, in which reactive oxygen species and Cu^{2+} are constantly generated. Cu^{2+} ions have been reported by Kim et al. to bond with reactive sites of proteins and DNA in microbial cells [81]. Meanwhile, the reactive oxygen species causes further oxidative stress to the biomolecules inside the bacteria. These phenomena all contribute to the

dysfunctioning of the biomolecules inside the bacteria, causing the inhibition of the growth and proliferation of the bacterial species which eventually leads to the death of these cells. In addition, the generation of the reactive oxygen radicals can be further augmented through photocatalysis activity that is embedded within the CuO nanostructure. Such results were observed with the work of Karim et al., in which they report that the concentration of reactive oxygen species increases by twenty-fold under the illumination of sunlight [82]. The probable antibacterial toxicity is shown in Figure 12. Even though there has been a lot of research reported on the antibacterial performance of CuO nanostructure, the exact mechanism is not exactly determined. Most studies confirm the generation of reactive oxygen species through the scavenging experiments. The exact attacking mechanism of the reactive oxygen species onto the biomolecules of the bacteria has not yet been fully established.

3.3. Other applications

3.3.1. Supercapacitors

Recently, due to the ever-growing requirement for an abundant source of energy, several electrochemical storage devices have been produced with high performance, including fuel cells, lithium-ion batteries, supercapacitors, etc. Among numerous advances in technology, supercapacitors have been broadly regarded as a promising approach thanks to their long lifetime, ultra-high power density, high applicability within a wide temperature range, etc. Concurrently, several studies have been also conducted to investigate the application of metal oxides in the fabrication of electrodes for supercapacitors due to their high capacitance, ease of fabrication process, good stability, and high specific surface area. It has been reported that several metallic oxide nanoparticles such as TiO_2, ZnO, or CuO possess typical properties of pseudocapacitors, which can exhibit energy storage performance via the Faradaic reactions at the surface of the electrodes [83]. Regarding the CuONPs, it was widely found that the physicochemical properties of this p-type semiconductor oxide can be potentially utilized as an efficient component of a supercapacitor thanks to its low cost, low toxicity, and abundance of synthesis precursors [84]. For instance, Sackey *et al*. reported a green fabrication of CuONPs using *Euphorbia pulcherrima* extract as a reducing agent. The resulting nanomaterial exhibited strong electrochemical properties, in which the maximum areal capacitance reached 39.45 mF/cm under the optimal synthesis conditions, which confirmed the potential of the CuONPs in the production of supercapacitors [85]. It is also noteworthy that the storage capacity of the CuONPs can be significantly influenced by several factors, including morphology, crystallinity, or hydrous state. Thus, some recent studies have also been carried out for the modification of the CuONPs in order to obtain the resulting material with more efficient supercapacitor properties. Indeed, Kumar et al. reported a green synthesis of nanoporous CuO using *Piper nigrum* extract, which showed a superior pseudocapacitance property when compared to commercial CuNPs [86]. Particularly, the analysis indicated that the resulting porous CuO can achieve a specific capacitance of 218 $F.g^{-1}$, compared to only 60 $F.g^{-1}$ for the commercial counterpart. On the other hand, Ravichandran et al. also successfully synthesized the CuONPs decorated graphene oxide for application in the production of supercapacitors [87]. The electrochemical analysis results also indicated a high electrochemical performance with a high specific capacity of 82.1 $F.g^{-1}$ at a scan rate of 10 $mV.s^{-1}$, which was also higher than the conventionally pristine CuONPs. The enhanced electrochemical properties of the CuONPs in the study can be attributed to the participation of the carbonaceous structure, which possesses the typical property of electric double-layer capacitors. As a result, the electrochemical performance of the

nanocomposite can be significantly enhanced thanks to the synergistic effects of both charge transfer mechanisms, including pseudocapacitance and charged double layers [88].

3.3.2. Solar cell

Previous studies also investigated the applications of CuONPs-based nanomaterials in the production of solar cells. Generally, a typical solar cell comprises a photoactive layer that facilitates light absorption to promote the electron transfer process, which is responsible for the generation of electron and hole pairs [89]. It has been reported that with a low band gap energy at approximately 1.5 eV, CuONPs can be suitably utilized for the enhancement of visible light absorption as well as the improvement of electron transfer activity [90]. Indeed, Wanninayake *et al*. have successfully utilized the CuONPs to improve the energy conversion activity of the polymer solar cell containing an active layer of blends of poly(3-hexylthiophene) (P3HT) and phenyl-C71-butyric acid methyl ester (PCBM) [91]. The study indicated that thanks to the participation of the CuONPs, the power conversion of the modified solar cell was improved by 24 % under the optimal CuONPs dosage. On the other hand, Siddiquia *et al*. also successfully improved the performance of the bulk-heterojunction solar cells by incorporating the CuONPs onto the photoactive layer of P3HT and PCBM [92]. The study showed a significant improvement of the modified solar cell in the power-conversion efficiency from 2.85 to 3.82 %, as well as the increment in the current density from 9.43 mA/cm^2 to 11.32 mA/cm^2, which implied the enhancement in the energy conversion performance. Additionally, Sharma et al. also utilized the green fabricated CuONPs to improve the performance of the dye-sensitized solar cells (DSSCs) [93]. In the study, CuONPs were successfully synthesized using the *Calotropis gigantea* leaf extract as a reducing agent, which was subsequently incorporated onto the counter electrode of the DSSCs containing a dye-adsorbed TiO_2 photoanode. The results revealed an efficacious improvement in the DSSCs' performance with a higher energy conversion efficiency of 3.4 %, a short circuit current density of 8.13 mA/cm^2, and an open circuit voltage of approximately 0.676 V.

3.3.3. Catalyst for energy production

It has been reported that CuONPs have been also employed for a wide range of catalysis applications, especially in the photocatalysis degradation in organic pollutants and photoconversion of different types of fuels. Generally, the photocatalysis activity of the CuONPs can be explained by the low band gap energy of approximately 1.5 eV, which effectively stimulates the electron transfer from the valence band to the conduction band under the illumination of visible light, eventually promoting the formation of electron-hole pairs. Particularly, the photogenerated holes can electrochemically interact with water molecules, leading to the formation of several hydroxyl radicals. Meanwhile, the electron from the conduction band can strongly react with oxygen to form superoxide radicals. Subsequently, these reactive radicals can participate in numerous redox reactions, catalyzing the degradation of organic pollutants to more benign products, or enhancing the reaction efficiency in the generation of many inorganic products, such as H_2O_2 and NH_3. On the other hand, Singh *et al*. also reported an eco-friendly fabrication of CuONPs using Psidium guajava leaf extract as reducing agents, which showed a great photodegradation of Nile blue and reactive yellow 160 molecules with a high removal efficiency of 93 and 81%, respectively [94]. In terms of the application in fuel photoconversion, Chen *et al*. have utilized CuONPs to enhance the photocatalysis hydrogen production performance of the pristine TiO_2 nanoparticles [95]. Herein, the nanocomposite of CuO/TiO_2 was successfully fabricated via the complex precipitation method. The resulting nanomaterial possessed a great catalysis performance for the production

of hydrogen from the mixture of ethanol and water, which showed a hydrogen production rate of 20.3 mmol/g/h. The general mechanism of hydrogen production is attributed to the oxidation of sacrificial agents (ethanol and water), leading to the formation of H^+. Subsequently, H_2 was eventually produced via the reduction of protons by exciting electrons. During the reaction process, TiO_2 acts as the main catalyst thanks to the suitable valence and conduction bands, which are more positive and negative than the potential of O_2/H_2O and H_2/H_2O redox couple. The participation of CuONPs can promote the electron transfer from TiO_2 to CuO due to the difference in the conduction band, which gradually leads to the negative shift of the Fermi level, preventing the rapid recombination of electron-hole pairs in TiO_2 [96].

4. CONCLUSIONS

Owing to its unique structure, nanostructured CuO has long captured the attention of various researchers around the world. It should be taken into consideration that the long-term sustainable synthesis of CuONPs still remains a lingering question. Chemical and physical approaches for the synthesis of CuONPs have dominated for a prolonged period even though there are major flaws in these approaches. Meanwhile, the emerging biological approach is gaining a reputation over the aforementioned approaches, it is fairly new and has not yet been implemented in a more actual implemented process. Moreover, the combination of various approaches for the synthesis can be deemed to be advantageous when the overall requirement for the resulting nanostructured CuONPs is stricter on an industrial scale. More in-depth study should be made to further validate the practicality of the biological approach, meanwhile, flaws of the chemical and physical approaches should be further alleviated to give out a more objective outlook for the synthesis of CuONPs. Misconception on the utilization of CuONPs in the degradation of dyes should be avoided especially decoloration as well as the study on the interaction between the CuONPs-induced radicals and the biomolecules of bacteria should be emphasized. In overall, the synthesis of CuONPs would create viable options for various applications such as antibacterial-related applications, energy production, and photocatalysis.

5. FUTURE PERSPECTIVE

Given many methods for the synthesis of CuONPS as well as applications, there are still questions left unanswered. These questions should be taken into consideration and unwavering efforts should but put into future research covering the following to address the limitations and advance the synthesis and potential application of CuONPs and possibly their derivatives.

Synthesis efficiency as well as the influences of defect sites in the lattice of CuO synthesized with different methods are reported at a surficial level. In addition, the effect of defects on the overall performance of CuONPs in a specific application is not well documented.

The exact mechanism behind the synthesis of CuONPs using phytocompounds in the plant-based extract has not been thoroughly studied. The exact compounds that are responsible for the synthesis of the nanostructured CuONPs are not pointed out. In addition, the variation in the concentration of the compounds in the extract due to differences in geological location should also be considered.

Even though CuONPs possess various outstanding properties for photocatalysis-based applications, their full potential for these applications such as gas sensing and photo-supercapacitors has not yet been fully studied.

The application of CuONPs in a solar cell has not also been fully explored as the heart of solar cells is still metal oxide that is UV-operated with modification. Therefore, the design and adoption of CuONPs for a fully operational solar cell is a must.

CRediT authorship contribution statement. Le Minh Huong: Methodology, Investigation. Le Tan Tai: Methodology, Investigation. Nguyen Huu Hieu: Investigation, Formal analysis, supervision. Nguyen Hung Vu: Formal analysis,Investigation. Nguyen Thanh Hoai Nam: Formal analysis. Nguyen Minh Dat: Investigation. Nguyen Thuy Diem Thao: Methodology, Investigation.

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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RAPHICAL ABSTRACT