Review

Recent Advances in Copper-Based Materials for Environmental Remediation

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Recent Advances in Copper-Based Materials for Environmental Remediation

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Abstract: Copper-based nanomaterials in the last decade attracted many researchers due to their extensive practical applications, unique, inexpensiveness, and wide availability. In addition to this, copper-based nanomaterials possess good thermal stability, and selectivity and also possess high activity. This review emphasis on the recent advances in the synthesis of copper nanomaterials and their wide applications in the field of environmental catalysis. This review aims to fill a significant knowledge gap in the different areas of environmental pollution management. Also, the paper concentrates on the recent applications of copper-based nanomaterials for environmental remediation, including the removal of heavy metals, and degradation of organic pollutants such as pharmaceuticals, and other environmental contaminants. Also, it will be helpful to young researchers in improving the suitability of implementing the Copper nanomaterials in the right way establishing and achieving sustainable goals for environmental remediation.

Keywords: copper; nanomaterials; organic pollutants; sensors; antimicrobial; photocatalysts; environmnetal remediation

1. Introduction

The economical and feasible design of nanomaterial catalysts for cutting-edge applications, as well as environmentally friendly catalytic processes and sustainable methods for developing synthetic strategies for catalysts, have got a huge amount of attention from researchers in recent years. In this respect, scientific research is continually enhancing and enabling the synthesis of novel materials and applications [1]. Noble metal nanoparticles (NMNPS) have a high degree of functionality due to their unique physical-chemical properties [2]. The high stability, surface functionalization, and easy chemical synthesis makes the noble metallic nanoparticles, such as PtNPs, AuNPs, and AgNPs in their extensive utilization [3]. However, some earth-abundant and inexpensive metals have been attracted the attention in this regard over the expensive noble-metal catalysts that are used widely in conventional commercial chemical processes.

Owing to the high natural abundance, low cost, numerous and practical simple syntheses, Copper based nanomaterials and nanocomposites are particularly appealing for research [4] Due to their unique properties, copper nanoparticles are progressively becoming a key component in a variety of industries such as energy, pharmaceutical, electronics, construction, machinery, construction, engineering, environment, etc. In recent years, researchers focussing on sustainable approaches for environmentally friendly catalytic processes for various advanced applications. This review paper does not promote various chemical methods for synthesis, however, helps the future

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research for an overall idea about the various synthesis and various applications of copper nanomaterials and copper-based nano in a sustainable way.

Dennis et al. reviewed the use of nanomaterials and plant extracts for the removal of micropollutants from wastewater streams. Also analyze their efficacy in removing these contaminants, as well as their cost-effectiveness and sustainability [5]. Khalaj et al. reviewed the investigation of the toxicological, environmental, and operating effects of copper-based nanomaterials for the treatment of persistent effluents such as dyes and their effects on the nanomaterial's reactivity [6]. Crisan et al. made a recent review paper that investigates the potential of copper nanoparticles as an alternative to antibiotics in the fight against multi-resistant bacteria strains [7]. Sandoval et al. reviewed the generation of copper-based particles aimed to discuss the pretreatment, milling, and post-treatment steps, as well as the characterization methods used to analyze the resulting particles [8]. Hong et al. investigated the effects of bimetallic catalysts on the selectivity of carbon dioxide reduction reaction (CO_2RR) and analyzed the effects of different ratios of metal atoms in the bimetallic catalysts on the CO_2RR of different ligands. [9] Naz et al. overviewed the synthesis, biomedical applications, and toxicological assessments of copper nanoparticles which aimed to provide core knowledge to researchers in this field, in order to conduct future studies [10]. Therefore, this present review article explores the potential of copper in various areas of environmental remediation such as the degradation of dyes, pharma products, wastewater treatment, and pesticides, and as a sensor for detecting various pollutants and reducing carbon dioxide (CO_2) emissions. Copper has been identified as an effective tool in these areas due to its high reactivity and low cost. The article reviews the recent research in these areas and highlights the potential of copper in each application. For example, the use of copper in dye degradation has been shown to be effective in reducing water pollution, while copper can also be used in wastewater treatment to reduce levels of heavy metals. The article also emphasizes the need for further research in order to fully understand the potential of copper in these applications.

The review paper also discusses potential challenges and future opportunities for the use of copper-based nanomaterials in environmental remediation.

2. Materials and Methodology

In comparison with other metals, Copper being less toxic, and inexpensive metal, and copper-based materials can be recycled and reused again [11]. Copper nanomaterial synthesis is simple but proper experimental conditions with respect to time are somewhat challenging in comparison. Copper nanomaterial synthesis can be done by using green, chemical, and physical methods.

2.1. Synthesis of Cu Nanoparticles

This review is concentrated on various chemical methods involved recently in the synthesis by varying different experimental conditions and the materials can be categorized into copper and copper-based nanoparticles further into: (i) copper and copper oxide (CuO) nanoparticles, (ii) hetero metal doped copper nanomaterials, (iii) graphene oxide-copper nanomaterials, and (iv) copper-based metal-organic frameworks.

2.2. Synthesis of Copper and Copper Oxide Nanoparticles

There are two widely used approaches for synthesizing these nanomaterials that include atomic-level precursors are utilized to synthesize nano-sized material and bulk solids broken into smaller components. The second approach is widely used for its advantage in controlling the shape of the nanoparticles [12–15]. The synthesis of copper and the copper oxide nano particles are designed based on the final derivative which centers or depends on four chemical reactions namely oxidation, reduction, hydrolysis, and condensation. A diagram outlining the formation of CuO nanoflakes through nucleation growth, orientation attachment, and the Ostwald ripening process is presented in Figure 1.

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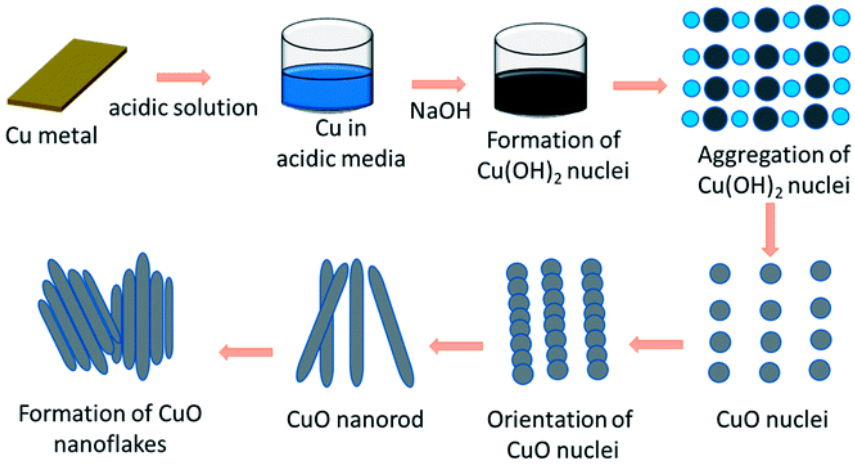

Figure 1. Illustration of the formation of the CuO nanoflakes. Adopted from the article [16].

The following table gives about the various chemical synthesis procedures adopted for the synthesis of copper nano particles. Depending on the desired final nanomaterial, the synthesis can be proceeded with different precursors, the reaction environments, and adopted synthetic methods (such as wet chemical, reverse micelle, Microwave-assisted, etc.) can be changed and is tabulated in Table 1.

Table 1. Reported experimental conditions for the Synthesis of Cu and Copper Oxide NPs.

Synthesized Nano material	Method	Solvent	Precursor	Reducing agent	Stabilizer/binding agent	Conditions	Product description	Ref.
CuO nanoflakes	Chemo-thermal	Water-Acidic medium	Recovered Cu foil from FPCBs, Cu (OH)2	NaOH	-	Decomposed at 520^{0}C	Width ~10 to 50 nm; Length ~30-80 nm	[16]
Cu_2O	Reduction	Water	$CuSO_4$ $5H_2O$, NaOH, D-glucose, PVP, ethylene glycol	NaOH	Ethylene glycol	Heated at 80°C for 1 h, drying for 5 h in a vacuum oven at 55° C.	150-200nm	[17]
Cupric oxide	Simple reduction	Ethanol	Cupric chloride ($CuCl_2$),	NaOH	Polyethylene glycol	Heating for 16hrs, centrifuged, dried.	20nm	[18]
CuNPs	Wet chemical	Octyl ether	Cu (II)	1,2-hexa decanediol	Oleic acid+ Oleyl amine	105^{0}C, 10 min;150 to 200^{0}C, 30min	5-25nm	[19]
Cu/Cu_2O	Chemical reduction	Ethylene glycol	acetyl acetonate Ethylene glycol, PVP, CuSO4, Ascorbic acid, Acetone, NaOH	Ascorbic acid	PVP	80^{0}C at 350rpm for 36hrs. Dried at 6h at60^{0}C	28/29nm	[20]
CuO nanorods	Chemical precipitation	Water	SDS or SLS, Copper nitrate	KOH, Ammonia	-	Stirring 700rpm, Centrifuged 3k rpm for 15min, Dried for 12h at60^{0}C, calcination 400^{0}C,4h	20-40nm	[21]
Cu nano	Chemical reduction	Water	Copper chloride,	Ascorbic acid	-	10k rpm for 10 min.	650nm	[22]

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sheet			Ascorbic acid, CTAB, NaOH				length/ 150nm diameter	
CuO NPs	Simple chemical reduction	Water	Copper acetate monohydrate,	NaOH		Stirred 900rpm, 4hr at 80^{0}C, centrifuged for 20min at 10krpm, dried at 100^{0}C for 3hrs	6.2nm	[23]
Fluorescent CuO NPs	Aggregation induced luminescence	Water	Glutathione, Copper nitrate, NaOH	NaOH	Glutathione	pH 2.7, centrifuge 20min and stored at 4^{0}C	-	[24]
CuS	Microwave hydrothermal	Water	Copper acetate, Thiourea	Thiourea		6 min, 2 min on and 30s off, repeat for 3 cycles. Filtered, dried 60^{0}C for 6h	1.9nm	[25]
Cu NPs	Agitation	Water	Copper sulphate, PEI, NaOH	NaOH	PEI	pH at 12.0, stirred continuously for 60min at 60^{0}C, centrifugation 13k rpm at RT, Dried 70^{0}C for 5h	25nm	[26]

FPCBs- Flexible printed circuit boards; PVP-Polyvinyl pyrrolidone; SDS—Sodium dodecyl sulfate; Sodium lauryl sulphate; CTAB-cetyltrimethyl ammonium bromide, PEI- Polyethylenimine.

2.3. Synthesis of Heterometal Doped Copper-Based Nanocomposites

Various loadings of metal doping are done in nanomaterial synthesis to tailor the materials' cost, availability, dispersibility, control the morphology, adjust the materials' conductivity, mechanical and magnetic properties, etc.

Khlifiac et al. [27] describes heterometals (Fe, Mn, Co, Zn and Ni) are doped to CuO which is designated as CuO:Fe, CuO:Mn, CuO:Co, CuO:Zn and CuO:Ni respectively are synthesized using copper sulfate as the primary precursor through coprecipitation method.

CuO nanoparticles can be synthesized by chemical reduction method with the aqueous solution of 1M copper sulfate solution and sodium hydroxide, while maintaining the pH and temperature with constant stirring and other experimental conditions. A similar procedure is followed for doping of all the hetero metals into CuO. The precipitate hence formed is annealed at 500°C for 4 hours to obtain a pure nanomaterial to enhance the crystalline quality of the synthesized powder. In another modified chemical reduction [28] method for the synthesis of Cu_2O nanoparticles, the dopant elements such as La, Mg and Mn are doped while using the 20mM ethanolic solutions of lanthanum nitrate, magnesium nitrate and manganese nitrate respectively [29–31]. Ce doped CuO is synthesized by using microwave irradiation method to find microstructural changes from spherical to rod-like structure with optical band gap variation from 3.63 to 3.13 eV [32]. A study disclosed the synthesis of Zr doping on CuO via the Pechini method and enhanced antibacterial properties were investigated [33].

Similarly, many synthesis methods are adopted to obtain doped Cu_2O nanostructures such as electrodeposition [34], chemical displacement [35], hydrothermal synthesis [36], biosynthesis [37,38], chemical vapour deposition [39],[40], pulsed laser deposition [41], solvothermal synthesis [42,43] and spray pyrolysis [39,44]. Table 2 reports the various experimental conditions for the synthesis of heterometal doped copper nanomaterials.

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Table 2. Reported experimental conditions for the Synthesis of heterometal dopped Copper NPs.

Nano material	Method	Solvent	Precursor	Reducing agent/ Stabilizer	Conditions	Product description	Ref.
h-BN (Ag/Cu)	Agitation followed by growing	Water	$CuCl_2$, h-BN, Tri-methoxy silane,	Hydrazine hydrate	6h stirring at room temperature, drying overnight at 60^{0}C	-	[45]
CuNPs /DA	Co-pre capitation	Ethanol	$CuSO_4.5H_2O$,1% chitosan, ascorbic acid,	Sodium hyroxide	Stirring and followed by irradiated at 20kGy linear accelerator and dried at 800C	20nm	[46]
SnO_2 /CuNPs	Co-precipitation	Water	tin dichloride dihydrate, Copper acetate monohydrate,	Ammonia	pH maintained at 9.8 and heated at 50^{0}C for 2 hours	25nm-35nm	[47]
Cu-TiO_2	Reverse micelle sol-gel	Water	Copper nitrate trihydrate, triton X-114, TTIP, Toulene, Hexane	TTIP	Stir for 15hrs at 700 rpm. Centrifuging 10 min at 8krpm, 18hrs 130^{0}C dry, calcination 4hrs at 400^{0}C	5.79 nm/0.0839 cm^3/g	[48]
CeO_2-CuO	Flame spray pyrolysis (FSP)	1:2 xylene and 2-ethylhexanoic acid	Cerium (II) ethyl hexanoate, Soligen copper 8, Xylene, 2-ethylhexanoic acid	-	FSP followed by annealing at 500^{0}C, 5h	13.6nm	[49]
CuO-GdO	Hydrothermal	Water	Gadolinium chloride, ammonium hydroxide, copper chloride	Ammonium hydroxide	Autoclave 150^{0}C, 16h; Calcined at 500^{0}C		[50]
CuS QDs@ ZnO	Microwave assisted hydrothermal	Water	Zinc nitrate, HMT, Copper acetate monohydrate,Thiourea	Thiourea	Stirring, 6min irradiated and dried the sample in oven 70^{0}C for 10h	36.5nm	[25]
Cu/CuO-ZnO	Solution combustion synthesis	Water	Copper nitrate trihydrate, Zinc nitrate, polyvinyl alcohol, Urea	Urea/ PVA	Dehydrated by heating to 110^{0}C, powder obtained calcined 500^{0}C for 3h.	15-50nm	[51]
CuO@ AgO/ZnO	Hydrothermal synthesis	Water	Zinc acetate, sodium hydroxide, copper sulfate, silver nitrate	NaOH	Autoclave 185^{0}C for 12h, desiccated at 70^{0}C for 8h, calcinated at 600^{0}C for 5h.	85nm	[52]
Ni/CuO	Hydrothermal synthesis	Water	Copper sulphate, NaOH, Nickel sulphate	NaOH	Hydrothermal 180^{0}C for 12h, dried at 80^{0}C,12h	19 to 28nm	[53]

h-BN: Hexagonal boron nitride; APTES: 3-amino propyl triethoxysilane; Diatomite (DA) with the main component of silica (SiO2); TTIP-Titanium tetra iso propoxide; PVA-Polyvinyl alcohol.

2.4. Synthesis of graphene-oxide (GO) based Copper nanocomposites

For the synthesis of efficient heterogeneous catalysts, graphene has been widely used as a stable and suitable substrate for Nanocatalysts [54,55]. During transformations, its high conductivity can accelerate up the transfer of electrons. [56]. As a result, metal Nano catalysts based on graphene may perhaps promote electrons to facile the reduction efficiency. In fact, when graphene is combined to less reactive Nano catalysts can also produce highly active hybrid nanocomposite catalysts [57]. In an article, $CuCl_2$ and GO solutions were taken as precursors and synthesized by using hydrothermal process by heating up to 150 °C for 12 h to obtain CuO-GO nanocomposite. The catalyst is affective for the successful reduction of nitro aromatics [58].

In another synthesis of rGO-Ag nanoparticles, $AgNO_3$ is used and rGO solution is added to $AgNO_3$ and reduced while using Na [BH_4]. For the rGO-Cu nanoparticle synthesis, $AgNO_3$ was replaced with Cu $(CH_3COO)_2$. [59]

In another modified synthesis [60] for non-enzymatic biosensor to detect glucose, the GO-CuO-FTO nanocomposite is prepared. The initial synthesis is comprised of nano belt formation of GO-CuO with a hydrothermal reduction of GO and CuO. This is followed by preparing GO-CuO-FTO prepared using a fluorine-doped tin oxide (FTO) substrate. The following Table 3 reports the recent procedures and the experimental conditions for the synthesis of GO-based copper nanomaterials.

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Table 3. Reported experimental conditions for the Synthesis of GO based Copper NPs.

Nano material	Method	Solvent	Precursor	Reducing agent /Stabilizer	Conditions	Product description	Pollutant Degradation/ Sensing/Reduction	Ref.
/GO-DE	Ultrasonic impregnation method	Water	Copper nitrate	NaOH	Ultrasonication 30min with reducing agent, filtered, dried 110^0 for 2h	0.52699 (μm) (Pore diameter)	Ciprofloxacin	[61]
CuO-rGO	Simple liquid approach	Water	Copper acetate	Ammonia	Reflux 2h, agitated 1h. Centrifuged, dried 10h at 80^0C	21.68nm	Ascorbic acid	[62]
CPA/N-SWCNTS-GO-CE/CuO nano composite	Chemical oxidative copoly-merization	0.5M H_2SO_4 /Water	CuO, Graphene, PPDA, TPA, Aniline	Ammonia	Ultra Sonication for 30min, stirring at 0-4^0C in N_2 atm. 24hr, black powder dried at 60^0C for 24hr.	-	Methyl orange	[63]
CuO@GO	Reflux	Water/iso propono l	Copper acetate, graphite, Sodium nitrate, $KMnO_4$, NH_4OH,	NH_4OH/ $KMnO_4$	Stirring at 82^0C for 2h, dried at 60^0C in hot air oven overnight	-	Synthesis of Alcohols to carbonyl compounds	[64]
CuO-GO-Ag	Chemical reduction		Copper sulphate, ammonia, SDS, GO nanosheets, Ag nanoparticles	Ammonia/SDS	The entire solution is Sonicated for 1h, pH set to 10.0, heated in oil bath, kept at 112^0C for 30min, dried in hot air for 10h, annealed 4h at 400^0C	5-10 μm	Antibacterial properties	[65]
GO/CUO	Simple chemical reduction	Water	Copper oxide, graphite powder, NaOH	NaOH	Stirring for half an hour to 100^0C,	70-200nm	Glucose	[66]
CuO-Cu2O/GO	Hydrotherma l synthesis	Water	Copper acetate, CTAB	CTAB	Autoclave 160^0C for 12h, dried at 60^0C for 24h	0.21-0.24nm	Organic dyes and tetracycline pollutants	[67]
rGO-ZnO/CuO	Microwave irradiation	Water	Graphite powder, Zinc acetate, copper	NaOH /PEG	Stirring for 20min at 70^0C with the successive addition of	Length 230–780 nm; Diameter 30-96nm	4-nitrophenol, methylene blue	[68]

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			nitrate, NaOH, PEG		each precursor at pH 10, MW 10min, dried 80^0C for 6h and then 200^0C for 2h			
Cu@Ni/rGO	Ultrasonication	Water	Graphite powder, $NaNO_3$, potassium permanganate, nickel chloride hexahydrate, copper sulphate, NaOH, hydrazine hydrate	NaOH	ultrasonicated for 15min, N2H2.H2O with NaBH4 added under Nitrogen atm. For 30 min and filtered, washed and dried at RT.	-	4-nitrophenol hydrogenation	[69]
rGO/bimetallic Fe_xCu_y	Reflux	Water	Iron acetate, copper acetate, graphite oxide, sodium borohydride, ethylene glycol, NaOH	Ethylene glycol	The contents refluxed 5h at 85^0C. Centrifuged. Freezed for later use.	34.7 to 44.5nm	Cyclo Phophamide degradation	[70]

GO-DE: Graphene oxide-diatomaceous earth; PPDA- p-phenylenediamine; TPA-Triphenylamine; SDS: Sodium dodecyl sulphate; CTAB-cetyltrimethylammonium bromide; PEG-Polyethylene glycol; MW-Microwave.

2.5. Synthesis of Copper-Based Organic and Metal-Organic Frameworks

In a study, copper metal–organic framework (Cu-MOF) has been synthesized via hydrothermal method from $Cu(NO_3)_2{\cdot}3H_2O$ and diphenylamine ligand following a solution-based method. The experimental procedure was regular; however, the homogenous mixture was kept for 3 days aside to get the precipitate [71].

In the preparation of CuO Nanoparticles/$Ti_3C_2T_x$ MXene, the solution containing CuO nanoparticles was placed in an ultrasonic bath and sonicated at room temperature for 20 minutes in order to disperse them. Afterwards, a designated amount (10, 20, 30, 40 wt %) of Ti3C2Tx MXene powder was added to the solution, followed by stirring at 500 rpm for 10 minutes. The mixture was then filtered, washed with ethanol, and dried at 70 °C for 12 hours. The sample with 30 wt. % of Ti3C2Tx-MXene was chosen for further characterization [72].

Development of an electrochemically activated copper nitroprusside (CuNPr)-based sensor for the ultra-trace detection of acetaldehyde (AcH). 0.1 M sodium nitroprusside was added dropwise to a copper chloride solution of equal concentration and stirred for 30 minutes at room temperature. Thus, the formed greenish-blue colloid precipitate was washed and then dried at 50°C. The oxidation of AcH to acetate ions by CuNPr was studied using in-situ Spectro electrochemical analyses. The sensor CuNPr/GCE exhibited a limit of detection towards AcH as low as 41×10^{-8} M. The sensing is successfully employed on red wine sample [73].

A study demonstrated the potential of (4-hydroxyquinoline)4HQ-rGO/Cuas a room-temperature acetic acid gas sensor in practical application. This research studied a graphene-based composite, 4HQ-rGO/Cu^{2+}, prepared through supramolecular assembly of graphene nanosheets, 4-

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hydroxyquinoline (4HQ), and copper (II) ions. When acetic acid was attached, the supramolecular assembly showed an enhanced sensing performance at room temperature due to the accelerated charge transfer between the graphene nanosheets and 4HQ molecules. The copper (II) ions also acted as the main active site for gas adsorption and the as-fabricated sensor exhibited a high response time within 5s at room temperature [74].

A research study has focused on the magnetic adsorption material polyaniline (PANI) with an amino functional group combined with $CuFe_2O_4$ ($CuFe_2O_4$/PANI nanocomposite). Coprecipitation technique is adopted for preparation of $CuFe_2O_4$ nanoparticles. $CuFe_2O_4$/PANI nanocomposite was prepared by chemical in situ polymerization. The material showed that it has an extremely high maximum adsorption capacity of 322.6 mg/g for the removal of uranyl ions from wastewater at a pH of 4. The adsorption process followed the quasi-second-order kinetic equation. Also stated that the material has stable adsorption performance for uranyl ions after five cycles of recovery in acid medium [75].

The study presents a novel approach for the synthesis of Pd-Cu alloy nanoparticles encapsulated in carbon nanopillar arrays (Pd–Cu@HPCN) which are promising oxygen evolution electrocatalysts. Figure 2 shows by using Cu-based MOF materials as a framework, the author disclosed a versatile technique to produce a Pd-Cu alloy enclosed within porous carbon nanopillar arrays.

Figure 2 shows the synthesis involves the preparation of a core-shell structured MOF@imidazolium-based ionic polymers (ImIPs) template and the subsequent decomposition of the inner Cu–MOFs when an anion exchange occurs between sodium tetrachloropalladate in solution and bromides in the external ImIP shell. The resulting Pd–Cu@HO-ImIP array is then topotactically transformed to generate Pd–Cu@HNPC [76].

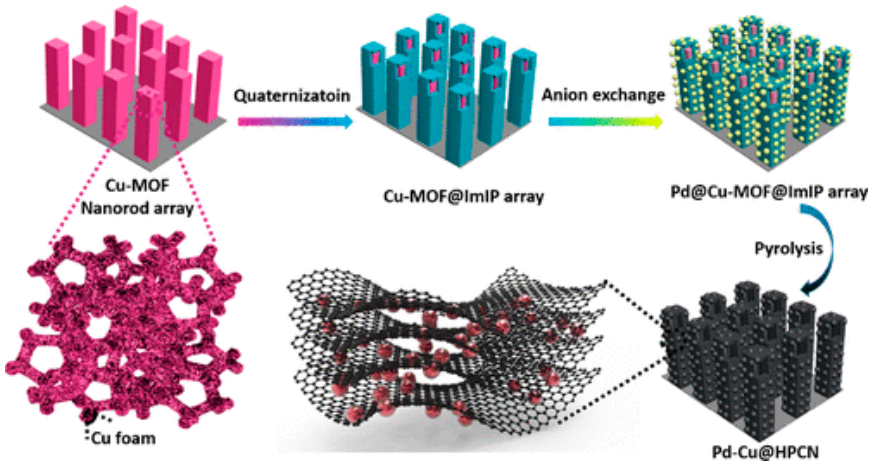

Figure 2. Scheme Illustrating the Fabrication of the Hollow Carbon Nanopillar Arrays Encapsulated with Pd–Cu Alloy Nanoparticles [76].

3. Characterization Methods for Copper-Based Nanomaterials

Various techniques for the characterization of copper oxide and its composites were found by using elemental composition analysis (such as Scanning electron microscopy, Energy dispersive X-ray spectroscopy EDS), structural characterization (such as X-ray diffraction) Morphological analysis (such as TEM), Surface area and pore size distribution (such as Brunauer–Emmett–Teller (BET) measurements) and optical properties (such as UV-Vis spectrophotometer, UV-Vis-Near IR) [31].

Various techniques have been used for the characterization of nanomaterials based on the properties such as size and shape, etc. which are needed to be measured and that are characteristic of the nanomaterial which can be used for further reproducing the experiments. Figure 3 shows the copper nanoparticle characterization techniques [77].

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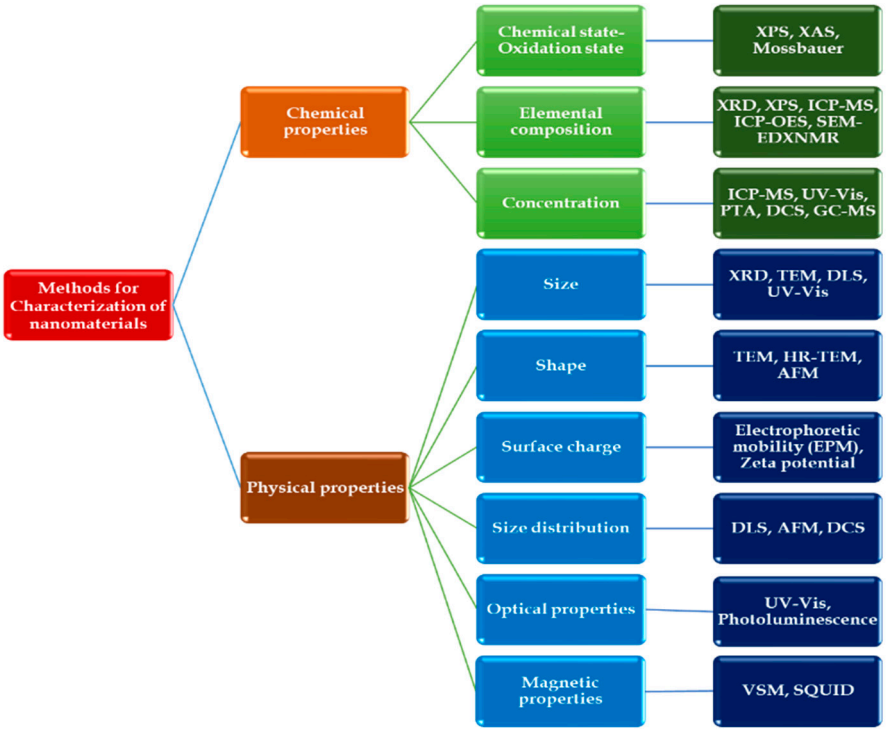

Figure 3. Various nanoparticle characterization techniques with respect to the physical and chemical properties, Atomic force microscopy (AFM), Superconducting quantum interference device magnetometry (SQUID), Photoluminescence (PL), Dynamic light scattering (DLS), Atomic force microscopy (AFM), Differential centrifugal sedimentation (DCS), Dynamic light scattering (DLS), UV-Vis Spectroscopy (UV-Vis), X-ray Diffraction (XRD), Transmission electron microscopy (TEM), High-Resolution Transmission Electron Microscopy (HRTEM), Electrophoretic mobility (EPM), Vibrating sample magnetometry (VSM).

4. Copper-Based Nanomaterials for Environmental Pollution Management

4.1. Copper-Based Nanomaterials in Photodegradation of Industrial dyes/ Removal of Dyes

Recent advances in the food, paper, leather, and textile industries have rapidly increased the usage of Organic dyes. Due to this high usage of dyes which are the main sources of organic pollution in various industries lead to a global concern [78–80]. Since these dyes are extremely persistent, and carcinogenic to humans and other living things, even very low quantities of chemical pollutants in wastewater cannot be eliminated easily by regular methods such as sedimentation and ordinary chemical degradation [78,81]. Hence removal of these effluents is important. Therefore, a sustainable technique for the removal of such effluents is essential to get rid of these hazardous pollutants and therefore efficient catalytic reduction and photocatalytic degradation are essential [82–84]. The two oxidation states of copper Cu^{2+} and Cu^{+} acts as electron trapper leading to higher degradation efficiency of copper nanoparticles. The catalytic property of CuNPs was observed in the reduction activity of Xanthene dye that could be applicable in biological sensing [85]. In a study, to treat textile wastewater, it was observed that the degradation activity of CuO NPs was higher than Ni@Fe_3O_4 against organic dyes such as Congo red, methylene blue and Rhodamine B [86], and also showed reduction of 4-nitrophenol [87].

Hamed et al. concluded that the copper nanoparticles decorated alginate/cobalt-doped cerium oxide composite beads are a promising photocatalyst for the reduction and photodegradation of organic dyes. his composite material is effective at degrading a wide range of organic dyes, with no additional energy source required [88]. Table 4 shows the comparison of the photocatalytic efficacy of the copper-based nanomaterials concerning various dye pollutants.

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Table 4. Table showing the photocatalytic efficacy of copper-based nanomaterials for various dyes.

SI.No	Copper Based Nanoparticles	Synthesis Method	Pollutant	Degradation time	Rate constant (min^{-1}) Degradation efficiency	Ref.
1	Cu@Alg/Co–CeO_2	One-pot synthesis	ArO (0.07mM)	300min	75.26%	[88]
			CR (0.07mM)	270min	33.65%	
			MB (0.07mM)	180min	49.70%	
			MO (0.07mM)	240min	45.54%	
2	Cu/GO/TiO_2	Quartz boat sealed in a furnace and argon gas is flown.	MB/ Cu (1%)-TiO2-GO	141.1min	4.91 min^{-1}	[89]
			MB/ Cu (2%)-TiO2-GO	112.7min	6.15 min^{-1}	
			MB/ Cu (3%)-TiO2-GO	60.8min	11.40 min^{-1}	
3	NiO/ CuO	Co-Precipitation	RB-5	120min	93%	[90]
			RR-2		92%	
			O-II		96%	
4	2D Cu nanosheets	Oriented attachment mechanism	MB	20min	95%	[91]
5	CuO	Thermal decomposition	RhB	150min	93%	[92]
6	Porous CuO nanosheets	Precipitation	AR	6min	96.99%	[93]
7	Copper sulfide NPs	Precipitation	CV	CuS1	120min	56.9% (0.0066)	[94]
				CuS2		72.8% (0.0104)	
				CuS3		84.6% (0.0145)	
			MB	CuS1	180min	31.8% (0.006)	
				CuS2		60.1% (0.0078)	
				CuS3	100min	99.2% (0.0481)	
			RhB	CuS1	120min	26.5% (0.0025)	
				CuS2		53% (0.0062)	
				CuS3		81.4% (0.0127)	
8	Cu_2O		Congo red		180min	90%	[95]
9	CuO	Simple chemical reduction	MB		60min	55.5%	[96]

Allura red (AR), Methyl orange (MO), Reactive red (RR), Orange-II (O-II), Acridine orange—ArO, Congo red (CR), Rhodamine B (RhB), Reactive black- (RB), Crystal Violet (CV), Methylene blue (MB).

4.2. Copper in Reduction of other Heavy Metals Contamination

In developing countries, the industrial sector is rapidly increasing and the heavy harmful metals from these industries such as metal and mining, batteries, paper, pesticides, chemical and petrochemical, textile, leather, cement, etc are released into water bodies. These toxic heavy metals such as lead (Pb), chromium (Cr), cadmium (Cd), arsenic (As), etc. which do not break down further in the environment and accumulate into the vital organs of the animals and cause various chronic diseases and death in extreme cases [97–101].

A highly porous material is synthesized Cu-DPA MOF [102] for the removal of heavy metals from wastewater. The adsorption parameters such as pH value, contact time, initial metals concentration, Cu-MOF dosage exhibited significant adsorption processes in the removal of heavy metals such as Pb, Cd, and Cr. The effect of adsorbent dose, pH, metal ion concentration, contact time and time of mixing to reach equilibrium for these heavy metals by Cu-DPA MOF is determined through batch adsorption experiments. An optimized procedure is performed in order to carry this procedure on wastewater containing Cd, Cr, Pb [102]. An overview of some of the copper nanomaterials associated with the removal of heavy metal ions are tabulated in Table 5. The adsorption capacity and removal efficiency were calculated using equations [i, ii] respectively, where q_e is heavy metal ions concentration adsorbed on adsorbent at equilibrium (mg of metal ion/g of adsorbent), C_o and C_e are the initial and equilibrium concentration or final concentration of metal ions in the solution (mg/L), V is the initial volume of metal ions solution used (in L) and m is the mass of adsorbent (in g).

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$$q_e = \frac{(C_e - C_e)V}{m} \quad \text{(i)}$$

The removal efficiency was calculated using Eq. (ii), where C_0 and Ce are the initial concentration of heavy metals (mg/L) and the equilibrium concentration of heavy metals (mg/L), respectively.

$$\text{Removal} = \frac{(C_o - C_e)}{Co} \text{ X } 100 \quad \text{(ii)}$$

Table 5. Table showing the adsorption capacity/ removal of heavy metal ions.

Nano material used	Target ions	Temperature	pH	Contact time	Ion Concentration	The capacity of Adsorption and removal/ detection limit	Ref.
Copper doped zeolite	Cr^{3+}	Room temperature for 60min and kept in refrigerator prior to analysis	7.5 to 2 before analysis	60min	0.658 mg/L	100%	[103]
	Pb^{2+}				0.696 mg/L	100%	
	Cd^{2+}				0.795 mg/L	99.37%	
CuO NPs	Hg^{2+}	Room temperature	7.27	180min	1 g/L	82%	[104]
	Cr^{6+}					85%	
Cu NPs	Cr^{6+}	25^{0}C	3	180min	20 mg/ml	13.1mg/g (65.6%)	[105]
$CuFe_2O_4$	Ba^{2+}	25^{0}C	7	120min	10mg in 25ml	87mg/g	[106]
$CuFe_2O_4$/ rGO	Ba^{2+}	25^{0}C	7	120min	10mg in 25ml	162 mg/g	[106]
$CuFe_2O_4$/PANI	UO_2^{2+} (Uranium ions)	25^{0}C	4	60min		322.6 mg/g	[107]
CuO NPs	Pb (II)	Room temperature	6	60min	0.33g/L	88.80mg/g	[108]
	Ni (II)					54.90mg/g	
	Cd (II)					15.60mg/g	
	Co (II)					73.2%	
CuO NPs	Pb (II)	Sunlight	6.6	200min	2mg/ml	80.8%	[109]
	Ni (II)					72.4%	
	Cd (II)					64.4%	
	Cr(VI)					91.4%	
Fluorescent CuO NPs	Bi^{3+}	Room temperature	2.7	15min	50 µ L	10 mmol L^{-1}	[110]

4.3. Copper-Based Nanomaterials in Wastewater Treatment

As a result of rapid industrialization, the volume of pollutants had been increased apparently. Industrial by-products often include dangerous and cancer-causing synthetic organic dyes, pesticides, pharmaceuticals, and textile waste. If these materials are not disposed properly, they can have a detrimental effect on the environment. Manufacturing processes often use synthetic organic dyes which are highly stable and do not break down easily. As a result, the wastewater can be toxic to humans, animals, and plants, and it can contaminate surface and groundwater. This can lead to serious environmental issues due to the compounds' ability to remain stable in the environment [25].

Many conventional methods such as photocatalytic degradation, coagulation, advanced oxidation processes, etc have been used to remove pollutants from water and wastewater. These methods are less effective in meeting the stringent standards of water quality, and many emerging technologies have been evolved [111]. Due to the pore size, the high surface area of the nanomaterials that has unique properties such as photosensitivity, antimicrobial activity, catalytic activity, magnetic, electrochemical, and optical properties provide a wide range of applications in the field of remediation of pollutants, detection, and water quality monitoring [112,113]. Many persistent pollutants after long-term exposure cause chronic diseases in animals and humans. For instance, 4-nitrophenol is widely used in the manufacture of drugs, dyes, insecticides and fungicides, and leather

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industries. Organic material has acute effects in humans that cause headaches, nausea, cyanosis, and irritation to the eyes [114,115]. Detection of such organic chemicals is highly needed in drinking and other sources of water. In a study, the copper oxide-reduced graphene oxide nano composite is synthesized for the enhanced catalytic activity towards reduction of 4-nitrophenol [116].

A research study discusses the synthesis of CuS QDs@ ZnO hybrid nanocomposites as an environmentally friendly preparation to improve the performance of the ZnO nanorods photocatalyst for the degradation of dyes, pharmaceuticals, and pesticides in water under simulated sunlight. The XRD, SEM, and TEM analysis results exhibited the CuS QDs@ZnO hybrid nanocomposite had a high crystallinity and smaller sphere size of 2 nm. It was further found that the crystallinity and light absorption as well as degradation activity increased with increasing the ratio of CuS up to 3%, but then decreased with further increase. The 3% CuS QDs@ZnO hybrid nanocomposite had the capability to reduce the electron–hole recombination rate, which enhanced its degradation rate of organic pollutants. [25]

4.4. Copper-Based Materials as Biosensing Materials

Graphene oxide (GO) and copper oxide (CuO) nanocomposites were used to successfully create an enzyme-free amperometric glucose biosensor using a fluorine-doped tin oxide (FTO) substrate [60]. In the presence of phosphate buffer solution at pH 7.0, glucose sensing is performed. It is drafted that the prepared sensor exhibited excellent electrical conductivity, and low detection limit in human serum in comparison, which is perhaps due to the large superficial area that leads to good catalytic activity. The glucose sensing mechanism is given in Figure 4.

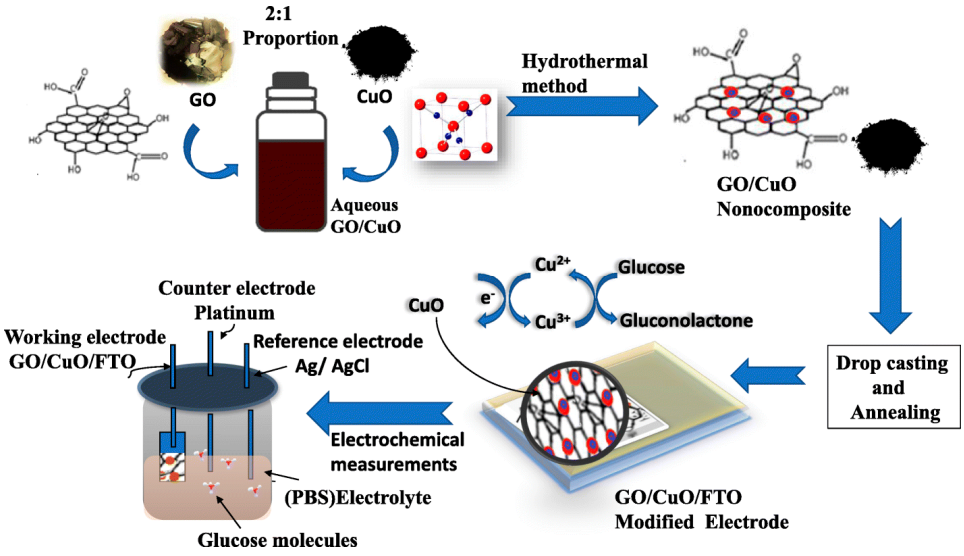

Figure 4. Biosensing mechanism of GO-CuO-FTO modified electrode [60].

The study of the biological process called DNA methylation is important, without changing the sequence, the activity of the DNA segment can be changed with methylation. DNA methylation often inhibits the transcription of genes when it occurs at a gene promoter. DNA methylation is crucial for proper growth in mammals and also associated with aging, genomic imprinting, carcinogenesis, X-chrome inactivation, etc… In a study, modified reduced graphene oxide (rGO) which is decorated on CuNPs is used as the framework for a label-free DNA-based electrochemical biosensor that might be employed as a diagnostic tool for a DNA methylation assay [117]. Table 6 provides an outline of the recent research showing the copper nanomaterial's response towards bioanalytes.

Some small molecules such as H_2O_2 is a key players in the design of many biosensors. It is a substrate in enzymatic reactions and can be used as an electron mediator or oxidizer in electrochemical reactions. It is also used to detect the activity of certain enzymes, such as glucose

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oxidase, in biosensors. Additionally, H_2O_2 can be used to detect the activity of certain proteins, such as cytochrome c, in biosensors. [118,119].

Table 6. Copper nanomaterial as a biosensor and its response towards bioanalytes.

Nano material	Analyte	LOD/ Detection limit	Linear Range(mM)	Sensitivity (μAcm^{-2}/ nM) /Response time	Electro chemical method used	Ref.
CuO/rGO	Ascorbic acid	189.05 µM	500-2000 µM	-	CV	[62]
CuO.GdO NSs/Nafion/GCE	Glutamate	166×10^{-6}	166×10^{-6} to 100×10^{3}	0.567	I-V	[50]
Cu-TiO_2	Enzyme less myoglobin	14pM	3nM-15nM	61.51 /10ms	CV-EIS	[120]
Cu/Cu_2O	Cholesterol oxidation	2.6µM	0.5 to 1mM	850	CV	[20]
Cu_2O	Glucose	1.37 µM	0.28-2.8mM		LDI-MS	[17]
Cu/ZnO	Enzyme less myoglobin	0.46nM	3nM-15nM	~2.13-10.14	CV-EIS	[121]
CuO-MWCNTs/ SPCE	Glutamate	17.5 µM	20-200 µM	8500	LSV	[122]
Cu-ZnO nanorods	Hydrogen peroxide	0.16 µM	0.001-11mM	3415	CV	[123]
CuO	Non enzymatic lactic acid	0.04 mM	0.05-40mM	14.47	CV	[124]
Copper phthalo cyanine-borophene nanocomposite	Non enzymatic Urea	0.05 µM	250-1000 µM	10.43	CV	[125]

CuO.GdO NSs/Nafion/GCE = CuO.GdO nanospikes/Nafion/GCE, CuO-MWCNTs/SPCE = CuO-multiwall carbon nanotubes/screen-printed carbon electrode. CV– Cyclic voltammetry; CV EIS—Cyclic voltammetry Electrical Impedance Spectroscopy; LDI MS—laser desorption/ionization mass spectrometry.

4.5. Copper-Based Nanomaterials in Pesticides Remediation in Soil

Despite being officially prohibited in many countries, several pesticides and insecticides are still in use today, for instance, endosulfan and carbofuran [126]. One of the most frequently used sulfur-containing organic molecules is dithiocarbamates with major applications in the production of sugar, rubber manufacture, antioxidants and antislime in paper making [127,128]. Between 25,000 and 35,000 metric tons are estimated to be consumed annually in this manner [129,130]. These dithiocarbamates are categorized into different classes such as zineb, ferbam, maneb, etc. based on the carbon skeleton and properties [131]. In a report article, an advancement demonstrated for sensing dithiocarbamates (DTCs) Ziram, Zineb, and Maneb pesticides by using cetyltrimethyl ammonium bromide (CTAB) capped copper nanoparticles as the colorimetric probe. This economical probe is used for the detection of these pesticides in various juice samples [132]. In recent advances in agrochemical research, nano fertilizers provide nutrients to plants and even replace many fertilizers, to improve crop yield and quality. Bollworm is a serious pest in the cultivation of cotton. In a study, an engineered CuNPs has the potential of insecticidal activity in as low dose (10mg/L) to regulate the exogenous bacillus thuringiensis microbial protein coded through BT toxin in plant tissue to improve resistance against bollworm [133].

4.6. Copper-Based Nanomaterials in the Degradation of Pharmaceutical Products

The three major sources of drugs and their metabolites entering the environment is the pharmaceutical industry, where they are released during the production of drugs. Poor waste management from industries, hospitals, and homes can also cause these substances to be discharged without being treated. Wastewater and sewage sludge from municipal wastewater treatment plants

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are considered a "dispersed" source, with drugs excreted by humans in homes, hospitals, and other health facilities entering these systems. The use of effluents and biosolids for fertilizing purposes also contributes to the release of pharmaceuticals into the environment [134].

One of the most used strategies to detoxify contaminants of emerging concern (CECs) is bioremediation. Bioremediation involves the use of microorganisms to break down the CECs molecules into harmless by-products. Similarly, another approach to detoxifying CECs is Nano remediation. Nano remediation involves the use of nanomaterials, such as nanoparticles, to absorb and trap the CECs molecules. Nanoparticles can be engineered to specifically target CECs molecules and have been used in a variety of environments, including soils, sediments, and aquatic systems. Nanoremediation has been shown to be more effective than bioremediation in some cases, as it can target specific CECs molecules more effectively by using physio-chemical treatments that include adsorption, oxidation, and filtration. Adsorption involves using particles, such as activated carbon, to absorb the CECs molecules from an environment. Oxidation involves using chemical oxidants, such as ozone, to break down the CECs molecules into harmless by-products. Filtration involves the use of membrane filters to remove CECs molecules from an environment. Overall, the most effective and efficient way to detoxify CECs depends on the specific environment and the type of CECs molecules present. In some cases, a combination of different strategies may be needed to achieve the desired results. All strategies used to detoxify CECs must be environmentally friendly and use sustainable resources [135].

For example, reverse micelle synthesized Cu-TiO_2 nanomaterials towards levofloxacin under visible light emitting diode (LED) light. The reaction rate constant of the nanomaterials was 0.0347 min^{-1}, and the highest degradation efficiency achieved was 93.3%. The results indicate that the nanomaterials were able to adsorb, oxidize, and degrade levofloxacin under visible LED light [48].

Table 7 summarizes the performance of copper-based nanomaterials used in pharmaceutical drug degradation. The recorded concentration of the drug, catalyst loading, temperature/pH, and degradation source, degradation efficiency were all given. The results suggest that copper nanomaterials are promising for the degradation of pharmaceutical drugs.

Table 7. List of Degradation results of some important pharmaceutical drugs using CuO NMs.

Nano material	Pharmaceutical drug	Concentration of drug	Catalyst loading	Temperature/pH	Degradation source	Degradation Efficiency	Ref
CuO NPs	Thiazolyl blue	100mg/L	20mg/10ml	300K/pH 8.0	Sonication /120min	84.1%	[136]
	Paracetamol			300K/pH 7.0		81.2%	
M Mn dopped Cu_2O	Amoxicillin	15mg/L	1g/L	pH 9.0	Sunlight	92%	[137]
ZnO-CuO/ clinoptilolite	Mefenamic acid	0.1g/L	0.1g/L	RT/ pH=5.6	Hg Lamp 200 min	70%	[138]
Zeolite/HDTMA-Br/CuS	Metronidazole	10mg/L	0.01g/L	pH 7.0	Sunlight	100% (200min)	[139]
CuO-GO-DE/H2O2	Ciprofloxacin	50mg/L	2g/L	50^0C/ pH 7.0	Ultrasonic impregnation	240min	[61]
Sulfite activated Fe-Cu	Sulfamethazine	5mg/L	80mg/L	298K/pH 6.0	Advanced oxidation process	87% (60min)	[140]
Cu-TiO_2	Levofloxacin	50mg/L	1g/L	pH 7.0	Visible LED	75.5% (6h)	[48]
Ba/Bi/Fe/CuO	Paracetamol	50mg/L	0.75g/L	pH 9.0	Metal halide lamp J(HQI-T250/OSRAM GmbH)	98.1% (120min)	[141]
CuS QDs@ZnO	ceftriaxone		0.2g/L	RT	Solar simulator	100% (90min)	[25]

HDTMA- Hexadecyltrimethylammonium; GO-DE—Graphene oxide diatomite.

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4.7. Copper-Based Nanomaterials as VOCs Sensor

VOCs (Volatile Organic Compounds) sensing is necessary in industries to ensure that the air quality is safe for both employees and on the roads, to ensure safe driving of individuals as alcohol intoxication is the primary cause of road accidents in the U.S. and worldwide [142]. By monitoring levels of VOCs, industries can ensure they are compliant with safety regulations and that their workers are not exposed to dangerous levels of these compounds. Prolonged exposure to VOCs can lead to respiratory problems and kidney damage, some VOCs have been linked to an increased risk of certain types of cancers such as leukemia and lymphoma and long-term exposure leads to headaches, dizziness, memory loss and other neurological effects [143]. Some molecules such as ammonia, hydrogen sulfide, hydrogen peroxide, etc are considered VOC biomarkers and their detection plays a vital role. For instance, ammonia in the exhaled breath indicates several diseases such as type-II Alzheimer, kidney failure, hepatic encephalopathy, and liver dysfunction [144]. Copper has been used as a sensor for VOCs for over a decade and has proven to be a reliable and cost-effective method for detecting these compounds. Table 8 shows various techniques for deposition and applications of copper sensors to sense volatile organic compounds (VOCs).

Table 8. List of some pure and doped copper sensors for the detection of Volatile Organic compounds.

Materials	Fabrication Technique/Detection system	Response time/ Response (Rg/Ra) /Sensitivity	Linear range	Analytes	Retention Time/recovery time /LOD	Ref
SnO_2-CuO	Slurry coated on ceramic tube	4s	50 to 300ppm	Ethanol	10s	[145]
CuO-rGO	Gas sensor	10.54	100ppm	Ethanol	25s	[146]
CuO/Ti_3C_2TxMXene	Drop casting on printed IDE	11.4	2.3 to 50ppm	Toluene	10s	[72]
CNNS-Cu	Deposited on glassy carbon electrode	Immediate detection	0.1–100 µmol L^{-1}	p-nitro toluene	0.13 µmol L^{-1}	[147]
NiO-CuO/NH_3 sensor	Drop casting on printed IDE	11.7s	25ppm to 500ppm	NH_3	21.5s	[16]
PEDOT-CuO	Drop casting on GCE	2s	40-10000ppm	H_2O_2	8.5µm	[148]
CeO2/CuO	Deposited on Al2O3sensor substrate on IDE		90-457ppb	Acetone	670s	[49]
PNIPAM-Cu@CP	Electrodepositing Cu particles on carbon paper elctrode	72.8 µA cm^{-2} mM^{-1}	1-300mM	Methanol	0.3mM	[149]
Copper nitro prusside	Deposited on the glassy carbon electrode	15s	2.5×10^{-8} to 2.5×10^{-1} M	Acetaldehyde	41×10^{-8} M	[150]
4HQ-rGO/Cu^{2+}	Deposited on IDE	5s	1000ppm	Acetic acid	24s	[151]
AgCu/TiO_2	Coated on Alumina substrate for KSGAS6S KENOSISTEC	22/33	100ppm	Xylene	33.2s	[152]

IDE- Interdigitated electrodes; CNNS- Graphite carbon nitride nanosheets; GCE-Glassy carbon electrode; PNIPAM-Polymer N-isopropylacrylamide, 4HQ- 4-Hydroxyquinoline.

4.8. Copper-Based Nanomaterials in Carbon Dioxide Reduction

CO_2 electroreduction (ER) can transform intermittent energy sources into high-energy chemicals, reducing dependence on fossil fuels and pollution. Products like hydrocarbons and methanol, with

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high energy density, are compatible with existing infrastructures and can substitute for fossil fuels [153].

Use of CuO-ZnO nanomaterials as catalysts to convert carbon dioxide into methanol. This study determined that bimetallic systems combined with porous supports, such as zeolite and activated carbon, had a greater efficiency when compared to unsupported materials. The hydrogenation at different temperatures is carried in a stainless-steel-packed bed reactor for the conversion to methanol which indeed is to reduce the environmental emissions of carbon dioxide emissions [154].

In certain CO_2 reduction experiment, which is conducted electrochemically in two compartments of H-cell in ethylene production, while copper oxide nanoparticles as the catalyst. The ethylene production is dependent on the morphology of the catalyst. The CuO nanoparticles are deposited on conductive carbon materials which will be activated, and the copper species converted to Cu+ which eventually results in the formation of 70% ethylene and 30% of Hydrogen Faradaic efficiency (FE) without any other by-products in an aqueous solution [155].

Listed data reveals the surface morphology of various copper catalyst surfaces on the faradaic efficiency of carbon products that had been reported in Table 9.

Table 9. Comparison of reported Faradaic efficiency of C products on various copper surfaces with the proposed catalyst.

Nanomaterial	Experimental Condition	Potential	Products	Faradic Efficiency	Ref.
Cu_{2-x}-Se_y	41.5 mA/cm²	-1.815V	Methanol	77.6%	[153]
Por-Cu	0.25 mg/cm² 49 mA/cm²	-0.976V vs RHE	Methane Ethylene CO	27% 17% 10%	[156]
Cu-X X=Nafion, PVDF	0.1M $KHCO_3$ -0.6V	-1.4V(vs RHE)	HCOOH, CH_4	30%	[157]
CuPc/C	0.5 M $KHCO_3$ aq.	-0.4 V vs. RHE	Ethylene	42.6%	[158]
Cubic Cu2O and branched CuO nps	0.1M $KHCO_3$ 5mA@2KeV 3.0 V (vs Ag/AgCl)	-	C_2H_4	64%	[159]
Cu/NC	-4.9 mA/cm²	-0.8V vs RHE	Formate Acetate	40.9% 16%	[160]
$Cu_{95}Sn_5$	0.1 M $KHCO_3$ 6.58 mA/cm² 0 V to −1.1 V vs. RHE	−0.9 V vs. RHE	CO	93%	[161]
CuO	0.1 M $KHCO_3$ 50 mA/cm2	-1.1V	C_2H_4	41%	[162]
3D Cu skeleton	-2V(vs. Ag/AgCl); -3.0 A/cm2; 0.5M $NaHCO_3$	-1.0 V vs RHE	C_2H_4, C_2H_6	-	[163]
Cu/Cu_xO PCC	0.5 M $KHCO_3$ -0.1V to -1.1V vs RHE	-0.5V vs RHE	C_2H_5OH	50%	[164]

RHE-reversible hydrogen electrode; Por-Cu: copper (II)-5,10,15,20-tetrakis(2,6-dihydroxyphenyl) porphyrin (PorCu); CuPc/C- Copper phthalocyanine on carbon; Cu/NC- N-doped carbon nanosheets supported copper nanoparticles; Cu/Cu_xO PCC: Cu/CuxO nanoparticles embedded on porous carbon cuboids.

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Figure 5 shows CO_2 reduction to ethanol production over Cu/Cu$_x$O PCC electrocatalyst at low over potential. The amount of Cu/Cu$_x$O nanoparticles embedded in the carbon-nitrogen network turned into altered through varying the leaching time with nitric acid. Leaching the cuboids for 1 h (Cu/Cu$_x$O-PCC-1h) led to 1.93 at% copper and leaching for 6 h (Cu/Cu$_x$O-PCC-6h) ended in 0.86 at%, while the unleached cuboids showed 16.93 at% Cu content material determined from evaluating copper to carbon peaks in XPS spectra. The leaching effect was studied towards CO_2 reactivity and turned into proven to significantly increase the materials' surface area, increase the porosity, adjust the nitrogen nature, and dissipate the Cu nanoparticles. The impact of these parameters became meditated inside the materials' electrochemical performances. It is display that improving the materials' porosity and surface region cannot have a positive effect without owning sufficient number of catalytic active sites. Similarly, pyridinic nitrogen content regarded to be correlated to improved electrocatalytic overall performance.

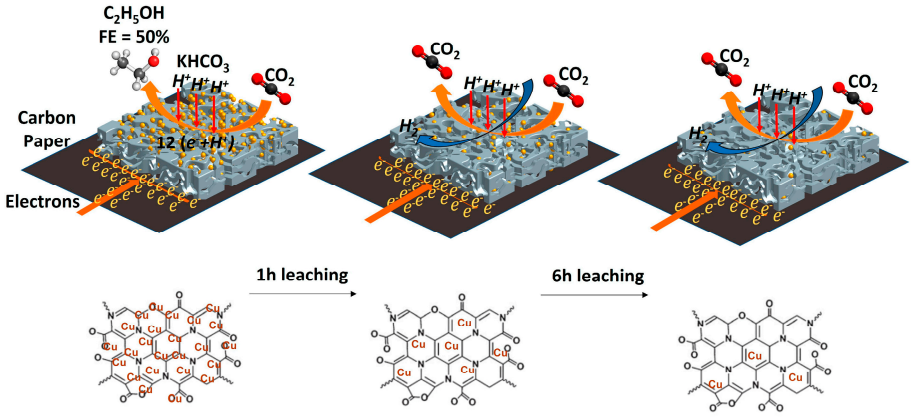

Figure 5. Cu/Cu$_x$O PCC catalyst for electrochemical CO_2 reduction to ethanol production [164].

5. Conclusions

In conclusion, copper-based nanomaterials have shown great promise for environmental remediation such as waste water treatment (dyes, pesticides, and heavy metal removal), biosensing, VOC sensors, and CO_2 reduction, etc. This extensive article summarizes many efficient methods proposed mainly to examine and assess recent publications on Cu-based materials and give an overall view and identify potential future work areas in the remediation of the environment. Even though many promising biological methods are found to be safer, Cu NPs are biocompatible and non-toxic, and are capable of removing hazardous metals from contaminated water, soil, and air, as well as breaking down toxic organic compounds, making them ideal for use in environmental remediation. However, for perfect environmental management, research should not be confined to detection, but potential future work and further investigations shall be extended in different areas of synergetic effects in environmental management in the areas of reduction, degradation, reuse, recycling, etc. With further research, copper-based nanomaterials could be used to effectively clean up many types of contaminated environments, ultimately leading to a healthier and safer world for all of us.

Abbreviations

AFM - Atomic force microscopy
BET- Brunauer–Emmett–Teller
CNTs - carbon nanotubes
CuO - copper oxide (CuO)
CVD-chemical vapor deposition
DCS - Differential centrifugal sedimentation
DLS - Dynamic light scattering.
DRS- Diffuse reflectance spectroscopy

EPM - Electrophoretic mobility
FESEM -field emission scanning electron microscopy
FT-IR- Fourier transform infrared.
FTO - fluorine-doped tin oxide
GO -Graphene oxide.
HRTEM - High-Resolution Transmission Electron Microscopy
LSPR- localized surface plasmon resonance
MA-SiO2 - methacrylate-functionalized silica
MOFs- metal organic frameworks
MRI-magnetic resonance imaging
NPs - Nanoparticles
PEC- photoelectrochemical
PEG- polyethylene glycol
PEO- polyethylene oxide (PEO)
PL - photoluminescence
PLA- polylactic acid
PNP- polymer nanoparticle
PVD-physical vapor deposition
RET- resonant energy transfer
SERS- Surface enhanced Raman spectroscopy
SQUID - Superconducting quantum interference device magnetometry
TEM- transmittance electron microscopy
TMD-NDs transition-metal dichalcogenide nanodots
UV-Vis – UV Vis Spectroscopy
VSM - Vibrating sample magnetometry
XPS- X-ray photon spectroscopy
XRD- X-ray diffraction

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