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A minireview of copper material applications in electrochemical sensing

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Abstract

Copper is an important metal in analytical and industrial fields as it has excellent thermal and electrical properties. In many disciplines, like electronics, optics, and others, copper nanoforms pay more attention than other noble metals nanoparticles. Attractive are its natural abundance, low costs and high activity toward many analytes with simultaneous physical stability. Extensive use has brought new types of sensors and practical implementations. The objective of this paper is to present crucial developments of copper material in the sensing field. Practical applications in the environmental section, like chemical oxygen demand measurement or carbon dioxide reduction reaction for atmospheric CO_2 reduction; technological sensors like organic light-emitting devices, electronic tongue for alcohol type determination, human skin touch and move sensor; and medical sensors for glucose, alcohol, dopamine or paracetamol detection were presented.

1. Introduction

Copper (Cu) as conductive, transition metal is raising much interest in chemical sensing, mainly for electronic and optical use. Cu as a metal and metal oxides (Cu_xO) is more willingly used in nanostructure form as it provides signal enhancement, excellent electrical and optical properties, high catalytic activity, broad accessibility, and approximately low cost.
Cu/Cu_xO applied to the electrode as nanoparticles (NPs) exceed enzymes and other biosensors due to extended activity, easy storage and temperature resistance. The wide range of modification methods, using different shapes and sizes of CuNPs and its derivatives, forming monolayers or more complex structures, open a new branch of sensors. (Li et al., 2015)

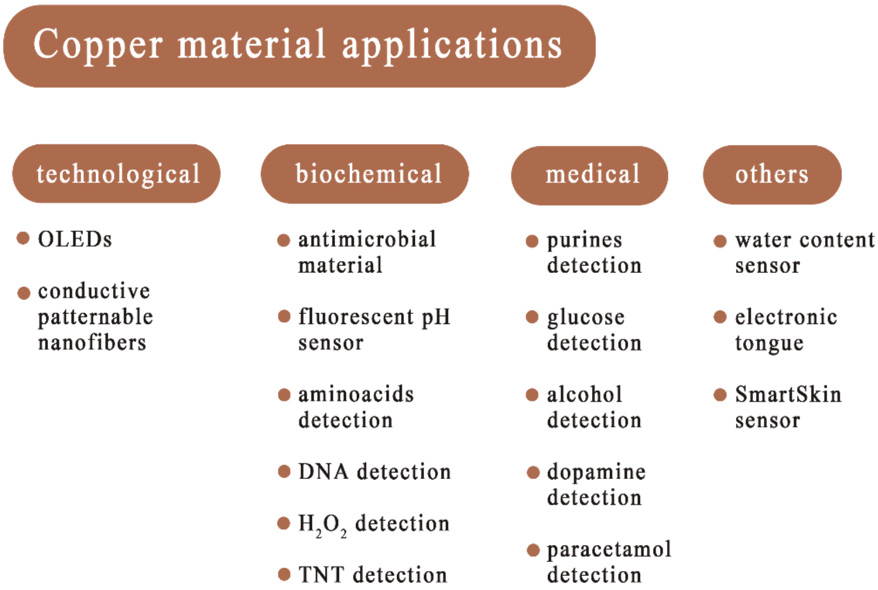
1.1. Copper material characteristics

Copper is commonly used in electrical contact and as an electrode in electrical discharge machining. It is used severally or in alloys like copper-tungsten. Cu is believed to be a better electrode than aluminum or brass, offers greater surface finish, higher electrical conductivity and resistance. (Singh et al., 2004)
Electronic properties of copper and copper oxides strongly depend on the size when functioning as NPs. In the nanosize range of 2-15 nm, a smaller size (<5 nm) leads to higher catalytic activity towards CO_2 electroreduction. Cu properties also vary through the dispersion on the electrode. (Reske et al., 2014) Typical structures are NPs with average size 20-100 nm, nanorods with 200-300 nm length, ~150 nm width and ~20-40 nm thickness, nanowires with an average diameter of 150 nm and length of 53 µm or nanospheres, being single crystals of an average size of 23.4±1.5 nm. (Sahai et al., 2016; Zuo et al., 2017; Dang et al., 2017; Tran et al., 2017; Guo et al., 2014) CuNPs have valuable physical properties- good electrical and thermal conductivity, light absorption with an absorption peak at 570-580 nm. They are more reactive compared to other metallic NPs. (Tamilvanan et al., 2014; Wu et al., 2014)

Among various methods of NPs synthesis, electrochemical one raise much interest due to its simplicity and low costs. NPs are produced *in situ* in the electrochemical cell through metal ions reduction from the electrolyte onto electrode material by the applied potential. This approach is less labor intensive, reduces the number of reagents and time compared to standard laboratory synthesis. Also, there are fewer factors crucial for proper synthesis as most of the reactions occur in room temperature and last few minutes. Electrodeposition can be driven by parameters of electrolyte or the electrode substrate. (Balasubramanian et al., 2017; Yang et al., 2013) Parameters of the electrolyte are pH, the concentration of NP precursors, temperature or applied potential. (Anand et al., 2015; Huang et al., 2005; Salehi, 2014) By this method, it is easy to control the NPs properties, like size and shape. Applying higher voltage causes smaller size and higher density of NPs as more nucleation sites are active. The kinetics of the process is also dependent on temperature: the higher the temperature, the bigger the NPs size and a smaller the amount of particles. (Q. B. Zhang et al., 2014)

Cu/Cu_xO materials require alkaline conditions when used as enzyme-like sensing materials, where are electrochemically oxidized to Cu_xO/$Cu(OH)_2$. Pure copper materials are low-conductive thus are coupled with different conductive materials, mainly carbon. (Xie et al., 2018) Examples of carbon materials for copper-based sensors are graphene, carbon nanoparticles, glassy carbon. (Jin et al., 2017; S. Wang et al., 2018; Lassègue et al., 2017; Tahir et al., 2018; Arévalo et al., 2017) There are also possibilities to combine copper with other metals (nickel, gold, palladium) forming alloy nanoparticles. (X. Ma et al., 2019; Shah et al., 2017; S. Liu et al., 2018)

Table 1 Copper material applications.



Copper material applications

enviromental	technological	biochemical	medical	others
● CO_2RR reaction	● OLEDs	● antimicrobial material	● purines detection	● water content sensor
● COD measurement	● conductive patternable nanofibers	● fluorescent pH sensor	● glucose detection	● electronic tongue
● water treatment		● aminoacids detection	● alcohol detection	● SmartSkin sensor
		● DNA detection	● dopamine detection	
		● H_2O_2 detection	● paracetamol detection	
		● TNT detection		

Several authors have studied characteristic of the metallic copper electrode. Cu electrochemistry in alkaline solutions is very complex as three oxidation states of copper occur: Cu(I), Cu(II) and Cu(III), in soluble and insoluble forms. Marioli et al. showed a full electrochemical scan of the copper electrode under alkaline conditions (0.15 M NaOH). (Marioli et al., 1992) The i=f(E) characteristic (i- current density, E-potential) showed 7 peaks corresponding to: oxygen adsorption, Cu^0/Cu^I oxidation, Cu^0/Cu^I and Cu^I/Cu^{II} transitions, soluble copper forms like CuO_2^{2-}, Cu^{III}/Cu^{II} reduction, Cu^{II}/Cu^I reduction, and Cu^I/Cu^0 transition. Cu(I) and Cu(II) are generated in the anodic scan. Cu(III) is generated close to oxygen evolution potential (-0.6V), where its stability increases with the increase of OH^- ions concentration. (Paixão et al., 2004)

1.2. Copper applications in electrochemical sensors

The main copper applications in electrochemical sensors were presented in Table 1.

1.2.1. Environmental and technological sensors

Copper electrodes raise much interest in technological and environmental processes. Electrochemical carbon dioxide reduction reaction (CO_2RR) to alcohols and hydrocarbons helps reduce atmospheric CO_2 concentration. Producing fuels as methane or ethanol offloads fossil-fuels resources. (Rendón-Calle et al., 2018) Hori et al. first showed that electrolysis of carbon monoxide in aqueous solution is possible on Cu material forming methane, ethane, ethanol, formaldehyde and more. (Hori et al., 1987) The main disadvantages of CO_2 electrolysis are low selectivity and high overpotentials. The reaction in aqueous media has many intermediate species like *CO, *COH, *CHOH, *CH_3 which in experimental techniques cannot be all characterized. Influential on the electrolysis performance is electrode structure, pH, temperature, the applied voltage or current density. (Rendón-Calle et al., 2018) The biggest drawback is fast Cu deactivation, within 30 min of electrolysis, as copper oxidizes in oxygen access. Moreover, poor efficiency of CO_2 reduction is due to the low solubility of CO_2 carbon dioxide and high rates of hydrogen production. Thus, nonaqueous or mixed solvents are used. Acetonitrile is willingly used as preferred due to its high dielectric constant and four times higher CO_2 solubility. In nonaqueous electrolytes, the main reaction product is CO. (Jitaru et al., 1997) Oxidized copper surface can be regenerated by photothermochemical reduction using a laser beam. (Han et al., 2015)

Many articles proved that CO_2 reduction occurs directly on the surface of Cu. This process is very sensitive to the structure of the outer layer of the copper electrode. (Durand et al., 2011; Garza et al., 2018; C. Liu et al., 2012) For the polycrystalline copper, the different structure organization gives various products selectivity, as CO_2RR is a structure-sensitive. Different atoms arrangement forces various adsorption and bonds breaking of the reactant. On Cu(111) facet methane is mainly produced, where Cu(100) yields ethylene. (Arán-Ais et al., 2018) The (211) facet is the most stable. More densely packed layer can enhance reduction in lower potentials. (Durand et al., 2011) Suggested is to synthesize electrodes with altered structures, as nanoparticles have high surface-to-volume-ratio, more active sites, better catalytic activity. Electrodeposition of copper nanostructures can increase the capacitance 13 times compared to polycrystalline copper. (Díaz-Duque et al., 2015) Other ways to regulate electrolysis is introducing copper-complexing chemicals (ammonia) or changing the chemical environment, where cation-exchange membrane selectively forms ethane, and anion membrane- formaldehyde. (Díaz-Duque et al., 2015)

The main disadvantages of Cu is its lability, natural oxidation on air exposure and corrosion in aqueous chlorides. The active surface can be protected from oxidation by chemisorption of organic compounds. A densely packed organic barrier is called SAM (self-assembled monolayer). The basis of SAM is to form strong Cu-S or Cu-N covalent bonds. Many compounds can be used as barriers, like n-alkanethiols, 2-mercapto-1,3,4-thiadiazole, n-tetradecanoic acid as a super-hydrophobic layer, caffeine, Schiff bases, amino acids, surfactants, leaves extract. (H. Y. Ma et al., 2003; Durainatarajan et al., 2018; T. Liu et al., 2007; Fallavena et al., 2006; Quan et al., 2001; D.-Q. Zhang et al., 2008; H. Ma et al., 2003; Valek et al., 2007; Kear et al., 2004)

Another application of copper was found in chemical oxygen demand (COD) measurement. COD is a marker of water pollution level and is defined as oxygen consumption for oxidation of organic compounds using strong oxidizers. For COD determination standard reagents like glycine or glucose are used. Hassan et al. electrodeposited nanolayer of copper on copper cable and disc electrodes. Constant potential and an alkaline medium were used. Copper oxides formed on the surface mediated oxidation of glycine. The higher oxidation current was achieved with an increase of the -OH concentration. The main catalyst were Cu(III) active species. Amperometric detection showed linear range 2-595 mg/L and limit of detection (LOD) 2.6 mg/L. (Hassan et al., 2018)

Cu is also deliberately used in OLEDs (organic light-emitting devices). (Bizzarri et al., 2018) The technology of ultrathin metal layers deposition on flexible substrates is believed to be an alternative for ITO (indium tin oxide) anodes, as ITO is brittle and indium is considered to be poisonous. Xiong et al. have proposed the atomic layer deposition at low temperature (110^0C) for transparent copper film formulation. Transparent conductive copper film has lower resistivity than aluminum. Continuous and smooth morphology of conductive Cu was achieved by the ligand-exchange reaction of two complexes: copper dimethylamino-2-propoxide and diethylzinc. Cu thickness was 10 nm with a 74% transparency at

550 nm and good conductivity 10.2 Ω/sq. This method gave higher luminance comparing to standard OLEDs and ITO anodes. (Xiong et al., 2018)

1.2.2. Simple chemical compounds detection

Copper shows excellent catalytic activity to redox processes of many analytes which are essential from the scientific or industrial point of view. Cu electrode or CuNPs are willingly used for metals detection (zinc, lead) or other simple inorganic compounds like nitrates in water, NO_2 in a gas sensor, glycerol in biodiesel, hydrazine, acetylsalicylic acid, uric acid, urine analysis (determination of tryptophan, acetaminophen and epinephrine), bilirubin and others. (Pei et al., 2014; Kang et al., 2017; Liang et al., 2016; Su et al., 2018; Maruta et al., 2012; Karim-Nezhad et al., 2009; do Socorro Maia Quintino et al., 2002; Sakamoto et al., 2011; Taleb et al., 2018; Noh et al., 2014)

Song et al. have proposed a sensor for hydrogen peroxide (H_2O_2) reduction based on glassy carbon electrode (GCE) moodifiying it with CuNPs and CuONPs. Copper was electrodeposited from $CuCl_2$ solution at -0.4 V for 1 min. The next step was scanning of the electrode in NaOH by cyclic voltammetry (CV) in the potential range of -0.5 to 0.3 V for oxidation of CuNPs to CuONPs. Two-steps modification (Cu@CuO/GCE) showed the best activity forward H_2O_2 comparing to CuO/GCE and bare GCE. The differential pulse voltammetry (DPV) detection exhibited linearity in 0.005-8 mM range. The main advantage of this approach was an enzyme-like activity of Cu@CuO/GCE without using peroxidase, enhancing stability and reproducibility. (H. Song et al., 2015) Other authors also proposed hydrogen peroxide sensors on the carbon substrate. Zhao et al. synthesized Cu@Pt core-shell NPs and deposited onto GCE. Amperometric detection showed a linear range of 0.0005–32.6 mM of H_2O_2 and LOD 0.15 μM. (Zhao et al., 2017) Reddy et al. electrodeposited Cu/CuONPs on pencil graphite using ionic and neutral surfactant templates. Amperometric detection showed linearity in the range 1 μM-13 mM of H_2O_2 with LOD of 0.35±0.04 μM. (Reddy et al., 2017) Liu et al. have elaborated glassy carbon- polydopamine sensor (GCE-PDA) with in-situ reduction of CuNPs (20 nm) from Cu(II) onto graphene oxide sheets. This approach prevented irreversible aggregation or poor adhesion of NPs on sensor. PDA worked simultaneously as reductant and adhesive for CuNPs. Amperometric detection showed a linear response in 5 μM-12 mM H_2O_2 concentration range and 1.4 μM detection limit. (Y. Liu et al., 2016)

1.2.3. Human body analysis application

Detection of the purines adenine (A) and guanine (G) is crucial for proper organism functioning. Unstable purine content can cause anemia, epilepsy and cancer. Wang et al. formed copper-nickel (Cu@Ni) NPs composite layer onto multiwalled carbon nanotubes (MWCNTs) for purines detection. Cu@Ni was deposited by a droplet and left to dry. Bimetallic NPs were chosen for their synergistic effect and high catalytic activities. The scan range 0.6-1.4 V and phosphate buffer of pH=3 were established as optimal conditions. Electrochemical pretreatment by CV before the sensor usage was to prevent NPs aggregation. Linear DPV peaks in ranges of 5-190 μM (LOD 0.35 μM) for A and 8-150 μM (LOD 0.56 μM) for G were obtained in simultaneous detection. The sensor was adequate for real samples from mice brain tissue. (D. Wang et al., 2018) CuNPs have found interest in glucose sensing. The measurement of glucose level is essential in fields as food industry or clinical diagnostics. Alternative enzymatic sensors suffer from poor stability, where enzymes can be deactivated by chemical/thermal treatment. Non-enzymatic NPs-based sensors are a good alternative for sensors commercialization. (Jiaojiao et al., 2015) Song et al. decorated copper foil with CuO nanoflowers for chronoamperometric glucose detection. Cu foil was used simultaneously as a substrate and Cu source. Glucose was oxidized under alkaline conditions. Large surface area gave a high sensitivity of 789.3 $\mu A/mM \cdot cm^2$ and linear detection in range 9.54×10^{-8}- 3.13×10^{-3} M. (M.-J. Song et al., 2013)

Another non-enzymatic glucose sensor was presented by Lin et al. which electrochemically compared three composites: CuO, Cu/Cu_2O, $Cu/Cu_2O/CuO$. Composites were prepared in an aerosol furnace reactor and deposited onto GCE. The sensor showed high selectivity in the presence of human blood interferences: NaCl, KCl, $CaCl_2$, ascorbic acid, uric acid, dopamine. The amperometric detection limit of glucose was 0.39 μM. The sensitivity was on 8726 $\mu A/mM \cdot cm^2$ level for $Cu/Cu_2O/CuO$, where only 1104 $\mu A/mM \cdot cm^2$ for Cu/Cu_2O and 1234 $\mu A/mM \cdot cm^2$ for CuO. The Cu/Cu_2O showed the highest electron transfer resistance but weak electrocatalytic efficiency. $Cu/Cu_2O/CuO$ turned out to have low electron transfer resistance, high surface area, thus the highest electron transfer ability. (Lin et al., 2018; Fang et al., 2018)

Practical application of copper electrodes was found in alcohol sensing. Measurement of breath alcohol concentration (BrAC) is dominating comparing to blood alcohol concentration (BAC) analysis as it is a non-invasive method. The method validation showed a ratio of BAC:BrAC of 2100:1. (Millet et al., 1996) The electrochemical approach enables real-time analysis, low costs, and miniaturization. Alternative techniques have drawbacks, like high costs and no portability (gas chromatography), poor accuracy (colorimetric tests). The principle of the method is the amperometric measurement of ethanol oxidation on the copper electrode. It is possible due to the mediation of soluble Cu(III) species generated from Cu(II) oxide.

Paixão et al. have proposed an alcohol breath sensor. Copper was electrodeposited from Cu^{2+} solution on platinum disc electrode using constant potential -0.1 V. Ethanol vapor in the equilibrium with an ethanol solution of different concentrations was pumped into the electrochemical cell. Amperometric detection showed LOD at 0.005% ethanol concentration level. This method is non-selective in the presence of other organic compounds, however in the breath of people after alcohol consumption they are on relatively low concentrations. (Paixão et al., 2004)

Other essential analytes for health determination are dopamine (DA) and paracetamol (PA), as their abuse have side effects. Devaraj et al. synthesized Cu/Cu_2O-NPs composite for simultaneous detection of DA and PA. The approach of thermal decomposition reaction using a combination of oleylamine and oleic acid gave controlled NPs growth with good shape monodispersity and inhibited NPs oxidation, confirmed by X-ray studies. The Cu/Cu_2O/MWCNTs/GCE sensor showed enhancement and 200 mV separation of oxidation current peaks of PA and DA where bare GCE did not show any meaningful response. DPV measurements gave linearity for DA in range 0.02-0.159 μM (R^2=0.989) with a sensitivity of 22.87 μA/μM and LOD of 3.27 nM. For PA, linearity was at 1-142.9 μM concentration level (R^2=0.998) with a sensitivity of 0.026 μA/μM and LOD of 1.51 μM. Interferential ascorbic acid showed a separate oxidation peak at -0.14 V and did not interfere with analytes. (Devaraj et al., 2016)

Very interesting research of Chen et al. showed CuO nanowires/single-walled CNTs composite applied onto GCE as DNA sensor. After GCE modification three incubation steps were performed: single-stranded DNA linkage by amide bonds to the substrate, complementary single-stranded DNA hybridization, and Adriamycin incubation, which worked as an electrochemical indicator. The DPV peak current of Adriamycin corresponded to the logarithm of double-stranded DNA. Linearity range was 1×10^{-14}-1×10^{-8} M with LOD of 3.5×10^{-15} M. (Chen et al., 2016)

Zen et al. decorated screen-printed carbon electrode (SPCE) with CuNPs for the determination of native 20 amino acids (AA). Authors have used the chronoamperometric method with flow injection analysis. AA were detected at zero potential (vs. Ag/AgCl) in a phosphate buffer solution (pH=8). The SPCE rich in CuO/Cu_2O species worked as a redox pair and turned out to be sensitive to analytes, as Cu_xO-AA electroactive complexes were formed and detected. A linear response was in the range of 24 nM–2.7 mM. (Zen et al., 2004)

1.2.4. Other applications

As copper can be transformed into various forms- foils, conductive patternable nanofibers, elastic transparent and tensile strain materials thus have found application in different types of sensors. (Xu et al., 2005; Jo et al., 2017; Hu et al., 2014) Known are water content sensor for fire resistance tests of cement and concrete or electronic tongue measuring electric resistance for distinguishing types of wines and whiskeys. (Lee et al., 2018; Novakowski et al., 2011) As copper is highly conductive, it can be used as an electrode for the SmartSkin- capacitive sensor for interactive surfaces reacting on human hand touch and move. (Rekimoto, 2002) Cu can also be utilized in the ion-selective electrode for potentiometric Cu(II) and iodide determination down to 1×10^{-5} mol/L concentrations. (Dobčnik et al., 1999)

The high surface-to-volume ratio and reactivity of CuNPs occurred in the antimicrobial properties. They can deactivate viruses- influenza, HIV, bacteria- *Staphylococcus aureus*, *Escherichia coli* and fungi- *Saccharomyces cerevisiae*. (Noyce et al., 2007; Borkow et al., 2008; Różańska et al., 2017; Wilks et al., 2005; Cioffi et al., 2005) The efficiency depends on parameters like temperature, humidity or copper structure. (Vincent et al., 2016) Copper disinfection properties have applications in water treatment, working surfaces or textiles. (Gitis et al., 2018; Parra et al., 2018; Marcus et al., 2017)

A very interesting application of CuNPs was shown by Qiao et al. in a fluorescent pH sensor. Chicken egg white copper nanoclusters were developed in one-step synthesis by mixing reagents in alkaline solutions at 55^{0}C. Chicken egg white has a high content of proteins (10% w/w) which controls the growth and nucleation of NPs. Nanoclusters formulation was confirmed by fluorescence spectrum with strong emission at 417 nm and excitation at 337 nm. Good linearity (R^2=0.9933) was achieved in pH range from 6.14 to 12.08 in Britton–Robinson buffers solutions. The sensor showed great stability up to two months. (Qiao et al., 2015)

Aparna et al. have used polyethylene imine capped copper nanoclusters for trinitrotoluene (TNT) colorimetric and fluorescent detection. Nanoclusters were synthesized by a one-pot microwave method and showed a blue emission at 480 nm. The fluorescent approach utilized vapor phase detection with a LOD of 0.05 nM of TNT. Spectrophotometric detection gave LOD of 14 pM of TNT. (Aparna et al., 2018)

2. Conclusions with the future outlook

The key issues connected to the copper metal electrochemical characteristic and its implementation in biochemical sensing were presented. Its scientific interest derives from good electrical and thermal properties. It turned out that nanoforms of Cu have high catalytic activity towards many analytes like metals, nitrates or enzyme-like properties in hydrogen peroxide sensing. Demonstration of the copper detector for industrial branches proves its essential role in the environmental sector for COD monitoring or CO2 concentration reduction.

Fortunately, the major challenges connected to the high activity and unfavorable oxidation of Cu surface were overcome. Through the control of parameters of Cu nanoforms growth like potential, deposition time, the nanoparticles shapes and sizes are strictly defined. Oxidation issue can be easily overcome by SAM forming using n-alkanethiols, caffeine, amino acids.

The copper electrode was found favorable for many of major electrochemical techniques, like CV, DPV, amperometry. It is difficult to choose a proper technique for Cu-based sensors, as many of them are used simultaneously for sensors characterization. For the highest sensitivities (lowest LODs) DPV is commonly used in DNA detection, where for continuous measurements amperometry is most practical for glucose sensing.

The hopes in the future Cu-based sensing are in its low costs, high activity, and natural abundance. Copper brings simplicity, effectiveness, and cost savings of analyzes. Currently developed prototypes like SmartSkin, electronic tongues or already commercialized OLEDs are the clue for the future diagnostic or hi-tech solutions.

Author contributions

KD, WB, NM made literature research, prepared an original draft and wrote the manuscript. EC, DN edited and supervised the work.

Conflict of interest

The authors declare no conflict of interest.

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