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ORIGINAL ARTICLE

Low cost chemical oxygen demand sensor based on **(**electrodeposited nano-copper film



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Abstract A commercially available copper electrical cable and pure Cu disk were used as substrates for the electrodeposition of copper nanoparticles (nano-Cu). The surface morphology of the prepared nano-Cu/Cu electrodes was investigated by scanning electron microscope (SEM) and energy dispersive X-ray spectrometer (EDX). The bare copper substrates and the nanocopper modified electrodes were utilized and optimized for electrochemical assay of chemical oxygen demand (COD) using glycine as a standard. A comparison was made among the four electrodes (i.e., bare and nano-Cu coated copper cable and pure copper disk) as potential COD sensors. The oxidation behavior of glycine was investigated on the surface of the prepared sensors using linear sweep voltammetry (LSV). The results indicate significant enhancement of the electrochemical oxidation of glycine by the deposited nano-Cu. The effects of different deposition parameters, such as Cu^{2+} concentration, deposition potential, deposition time, pH, and scan rate on the response of the prepared sensors were investigated. Under optimized conditions, the optimal nano-Cu based COD sensor exhibited a linear range of 2–595 mg/L, lower limit of detection (LOD) as low as 1.07 mg/L (S/N = 3). The developed method exhibited high tolerance level to Cl⁻ ion where 1.0 M Cl⁻ exhibited minimal influence. The sensor was utilized for the detection of COD in different real water samples. The results obtained were validated using the standard dichromate method.

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1. Introduction

Assay of organic compounds in water is crucial for water quality assessment and pollution control (American Public Health Association, 1998). COD is a critical marker to indicate the pollution level of water (Association of Official Analytical Chemists, 1990). It is defined as the number of oxygen equivalents consumed in the oxidation of organic compounds using

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strong oxidizing agents. The traditional method estimates COD via the oxidative degradation of organic matter present in water or waste water with strong oxidizing agents such as dichromate or permanganate (Moore and Walker, 1965; Lee et al., 2000; Korenaga and Ikatsu, 1982; Korenaga et al., 1993; Tian and Wu, 1992). Unfortunately, this method involves several disadvantages, such as low sensitivity, low precision, a large sample volume, and a high consumption of expensive (e.g. Ag_2SO_4), corrosive (concentrated H_2SO_4) and toxic (e.g., $HgSO_4$) chemicals. Moreover, the traditional method involves a time-consuming reflux process (2–4 h), which makes it non-applicable for high through-put screening (Lee et al., 1999).

Great deals of efforts have been devoted to improve the traditional method for COD measurement by utilizing ultraviolet spectroscopy (Kong and Wu, 2009), fluorescence spectroscopy (Hur et al., 2010), and chemiluminescence methods (Liu et al., 2008; Yao et al., 2009). Such methods are amenable to flow injection techniques, which greatly improve analysis efficiency. However, digestion procedure with corrosive solvent is unavoidable. Recently, simple, rapid, and sensitive photocatalytic (Zhu et al., 2006; Li and Song, 2009) and photoelectrocatalytic (Zhang et al., 2009b, 2009a) methods have been proposed to determine COD, particularly illuminated TiO_2 materials due to their strong oxidation ability and green credentials. Nevertheless, photogenerated electron hole pairs recombine easily and the use of a UV light source increases the running cost for COD measurement (Yu et al., 2009).

The ability to detect COD in a rapid, sensitive, operationally simple, and cost-effective manner will impact human health and safety. Consequently, increasing attention has been paid to electrochemical methods using different electrodes, because of their high sensitivity, short analysis time, low cost and handling convenience. In many cases, however, the direct oxidation of organic species in aqueous solution using simple metal or carbon electrodes is not possible, because the high electrical potentials required for the oxidation of organic compounds usually result in the oxidation of water. Therefore, a proper choice of a suitable electrode material for this purpose is very important. So far, a number of novel electrode materials have been reported to oxidize organic compounds. For instance, the following electrodes were reported for the electrochemical detection of COD: copper electrode modified with copper nanoparticles (Yang et al., 2011); an activated copper electrode (Silva et al., 2009); a glassy carbon electrode (GCE) coated with Ni nanoparticles (Jing et al., 2012; Cheng et al., 2011), (NiCu) alloy (Zhou et al., 2012), or cobalt oxide film (Wang et al., 2012); boron-doped diamond electrode (BDD) (Yu et al., 2007); Pt electrodes modified with PbO₂ (Westbroek and Temmerman, 2001; Ai et al., 2004; Li et al., 2005), or F-PbO₂ (Li et al., 2005); Ti electrodes coated with nano-TiO₂ (Li et al., 2006b, 2007), Rh₂O₃ (Li et al., 2006a), or TiO₂/PbO₂ (Li et al., 2006b); a graphite-polystyrene composite electrode containing Ag₂O/CuO (Orozco et al., 2008).

The performance characteristics of those electrochemical sensors were assessed using standard reagents (e.g., glucose, glycine and potassium hydrogen phthalate) to evaluate COD values. Since the electrochemical behavior of COD standards is strongly dependent on the substrate and electroactive film deposited on the electrode surface, the study of alternate substrates that may lead to the development of an improved COD sensor is a worthwhile venture. Herein, we report the development of simple, inexpensive, and sensitive electrochemical sensors for the determination of COD using copper cable and pure copper disk substrates coated with nano-copper films prepared using potentiostatic deposition and fast scan cyclic voltammetry (FSCV).

2. Experimental

2.1. Reagents

All chemicals were of analytical grade and used as received. CuSO₄·5H₂O, H₂SO₄, NaOH, K₂Cr₂O₇, Ag₂SO₄, HgSO₄, and (NH₄)₂Fe(SO₄)₂ were purchased from the techno pharma chemicals (Spain). Glycine was purchased from ADWIC laboratory chemicals (Egypt). The stock solution of glycine (75 mg/L) was prepared using doubly distilled water. Doubly distilled water was used in preparation of all solutions.

2.2. Instruments

Electrochemical preparations and measurements were performed on a Potentiostat/Galvanostat (EG&G Princeton Applied Research, Model 273A). A conventional threeelectrode system was employed. The working electrode was either a pure copper disk with a 1.5 mm diameter (1.77 mm²) or commercially available/house-hold electrical Cu-cable with a diameter of 8 mm (50.24 mm²). The reference electrode was Ag/AgCl/(3.00 M KCl) and the counter electrode was a platinum cable. Scanning Electron Microscopy was performed with (SEM; FEI INSPECT S50) and the chemical composition of the modified electrode was determined using energy dispersive X-ray spectrometer (EDX; BRUKER).

2.3. Electrochemical preparation of nano-Cu sensing film

Prior to electrodeposition, Cu-cable and Cu-disk electrodes were polished with 60 mesh emery paper and rinsed thoroughly in bi-distilled water. Then the copper sensing film was electrodeposited under potentiostatic conditions at constant potential (deposition potential, DP) -1.0 V for certain time (deposition time, Dt) 180 s from 4 mM CuSO₄·5H₂O/1 mM H₂SO₄ bath for Cu-electrode and 240 s from 8 mM CuSO₄·5H₂O/1 mM H₂SO₄ bath for Cu-disk electrode.

In case of fast scan cyclic voltammetric preparation (FSCV), the potential scan window was from -0.10 V to -1.30 V for 30 cycles at 100 mV/s for Cu-cable electrode. In case of Cu-disk electrode the potential scan window was from -0.80 V to -1.80 V at 100 mV/s and 20 cycles. The resulting electrodes were rinsed with doubly distilled water to remove any adsorbed species before use.

SEM was employed to investigate the morphology of bare and nano-Cu/Cu modified copper electrodes. Fig. 1 Shows the SEM images of Cu-cable (A) and Cu-disk (B), nano-Cu/Cu-cable (C) and nano-Cu/Cu-disk (D) prepared by potentiostatic conditions, as well as the nano-Cu/Cu-cable (E) and nano-Cu/Cu-disk (F) prepared using the FSCV deposition. SEM images clearly indicated that copper electrodes are coated with copper nano-particles with a diameter ranging from 40 to 125 nm.



Figure 1 SEM images of Cu.cable and Cu.disk electrodes (A, B); nano-Cu/Cu-cable and nano-Cu/Cu-disk prepared by potentiostatic deposition (C, D); nano-Cu/Cu-cable and nano-Cu/Cu-disk prepared by FSCV (E, F), respectively. Inset: shows the diameter of Cu-particles.

The electrodeposited nano-Cu film prepared by FSCV appeared to be continuous and uniform over the entire substrate surface without any noticeable cracks, which could ensure high electrochemical stability of the prepared nanocopper based film.

The chemical composition of nano-Cu film was determined by EDX analysis as indicated in Fig. 2 the EDX spectrum shows that the elements (Cu), (C), and (O) were detected at the surface of nano-Cu/Cu-electrodes (cable, disk).

2.4. Detection of COD using standard dichromate method

The standard dichromate method was used to measure COD value (American Public Health Association, 1998). A 10 mL



Figure 2 EDX analysis of the prepared nano-Cu/Cu-cable electrode (■) and nano-Cu/Cu-disk electrode (■). Where nano-Cu-film prepared by FSCV.

water sample and 10 mL 0.04167 M $K_2Cr_2O_7$ solution were added into a 250 mL round-bottomed flask, and refluxed for 2 h at 160 °C. Then the excess dichromate was determined using titration against 0.025 M Fe(NH₄)₂(SO₄)₂·6H₂O. The value of COD was calculated according to the literature procedures (American Society for Testing and Materials, 1995).

2.5. Determination of COD using the prepared COD sensors

Prior to measurements, the real water samples were filtrated using Sartorius filtration system (Goettingen, Germany), equipped with cellulose nitrate filter paper (pore size $\sim 0.2 \,\mu$ m). The anodic LSV peak current was determined with a standard addition method. Standard COD solutions of different concentrations in the range 20–40 mg/L were added to a series of 100 mL flasks, each containing 5 mL of filtered fresh water sample. Then the volume of each flask was made up to 100 mL using 0.075 M NaOH. The testing solution was placed into an electrochemical cell for the determination of COD. All experiments were carried out at ambient temperature.

3. Results and discussion

3.1. Electrochemical behavior of copper electrode

Copper electrodes in alkaline media electrocatalytically oxidize a wide range of organic compounds mainly responsible for the COD of natural waters. This catalytic action is mediated by surface oxides. As shown in Fig. 3 cyclic voltammetry was employed over a potential range from -1.0 V to +0.8 V. The anodic peak 1 (-0.34 V vs. Ag/AgCl) corresponds to the formation of a first layer of copper (I) oxide (Cu₂O), while the broader anodic peak 2 (-0.12 V vs. Ag/AgCl) corresponds to the formation of a second mixed layer of copper (II) oxide/copper (II) hydroxide (CuO/Cu(OH)₂). Reaching 0.70 V vs. Ag/AgCl indicates the Cu(II)/Cu(III) oxidation. Examining reverse scan could reveal the cathodic peaks 3 and 4 corresponding to the Cu(II)/Cu(I) (-0.54 V vs. Ag/AgCl) and Cu(I)/Cu(0) (-0.86 V vs. Ag/AgCl) reduction reactions, respectively. Several studies for the electrocatalytic oxidation of metallic Cu in alkaline media have been carried out using



Figure 3 Cyclic Voltammetric response of Cu-cable electrode (solid line) and Cu-disk electrode (dashed line) in 0.075 M NaOH solution. Potential scan window -1.0 V to +0.8 V vs. Ag/AgCl/ (3 M KCl), scan rate 100 mV s⁻¹.

different techniques. This electrochemical process is highly dependent on both the hydroxide concentration and the previous formation of a specific layer of Cu(II) oxide. The participation of the Cu(III) species as an electron transfer mediator has been suggested for explaining the good performance of Cu particles in alkaline medium in anodic processes related to several organic compounds (Heli et al., 2010; Liu et al., 2007).

An alkaline medium is required to enhance the electrocatalytic activity of several transition metals (Liu et al., 2007; Burke et al., 1998; Zhao et al., 2011; Silva et al., 2005). Therefore, the effect of the alkalinity on the electrocatalytic oxidation of glycine at nano-Cu/Cu-electrode was investigated. The oxidation current of glycine gradually increases with increasing NaOH concentration from 0.055 to 0.10 M. This could be explained by the ease of oxidation of organic compounds at high pH values (Yu et al., 2007; Zhao et al., 2007). Concomitantly, the over-potential for oxygen evolution would be lowered, and oxygen evolution gradually turned into the main reaction. Therefore, at high NaOH concentrations (>0.1 M) a large background noise was obtained and lots of gas bubbles were observed on the surface of the nano-Cu/Cu(cable, disk) modified electrode, causing difficulty in the measurement of low current signal. These results are consistent with the previous findings (Zhou et al., 2012, 2007; Wang et al., 2012; Yu et al., 2007). A concentration of 0.075-0.1 M NaOH was therefore chosen as the optimal concentrations for the electrocatalytic oxidation at nano-Cu films.

Cu(III) is central in the electrocatalytic oxidation of organic compounds in a basic medium. The expected electrocatalytic oxidation of organic compounds (e.g., glycine) at the copper electrodes in basic medium as follows (Zhou et al., 2012; Heli et al., 2010),

- $Cu + 2OH^- \rightarrow Cu(OH)_2 + 2e^-$
- $Cu(OH)_2 + OH^- \rightarrow Cu(III)OOH^+ + H_2O + e^-$
- Cu(III)OOH + Organics_(red) + H₂O \rightarrow Cu(OH)₂ + Organics_(oxid) + OH⁻

3.2. Optimization of the electrodeposition parameters of nano-Cu film

The effect of different deposition variables on the sensitivity of nano-Cu/Cu electrodes toward glycine was investigated. Controlled potential reduction of nano-Cu particles was achieved at -1.0 V from acidic bath of CuSO₄·5H₂O/1 mM H₂SO₄ at specified reduction time of 180 s. The effect of such variables on the responses of nano-Cu/Cu electrodes toward the oxidation of glycine was investigated by measuring the oxidation peak, observed in LSV, of 75 mg/L glycine, prepared in 0.075 M NaOH. Effect of each variable was represented graphically by plotting the change in this variable vs. the oxidation peak current to determine optimal conditions for the preparation of nano-Cu/Cu modified electrode. Fig. 4 shows the effect of bath composition on the catalytic activity of the prepared nano-sensors. As can be seen in Fig. 4 maximum oxidation current was achieved by electrodeposition



Figure 4 Effect of bath composition on the oxidation current response of 75 mg/L glycine prepared in 0.075 M NaOH in case of nano-Cu/Cu-cable (\blacksquare) and nano-Cu/Cu-disk (\blacktriangle).



Figure 5 Influence of deposition time of Cu particles on the oxidation peak current of 75 mg/L glycine in case of nano-Cu/Cu-cable (\blacksquare) and nano-Cu/Cu-disk (\blacktriangle).

from 4 mM CuSO₄ bath composition for Cu-cable and 8 mM CuSO₄ for Cu-disk (Yang et al., 2011).

The influence of deposition time on the electrocatalytic activity of nano-Cu film based sensors was also studied. As shown in Fig. 5, the oxidation current of glycine increases remarkably when the deposition time extends from 0 s to 180 s at Cu-cable electrode and from 0 s to 240 s for Cu-disk electrode. Longer deposition times then did not enhance the oxidation peak current. Therefore, the electrodeposition was performed at controlled potential of -1.0 V for 180 s from 4 mM CuSO₄/1 mM H₂SO₄ in case of Cu-cable, while for Cu-disk the electrodeposition was performed for 240 s from 8 mM CuSO₄/1 mM H₂SO₄.

FSCV deposition of copper was performed at potential scan window from -0.1 V to -1.3 V for Cu-cable and -0.8 V to -1.8 V for Cu-disk. The LSV responses of 75 mg/L glycine at different repeated scan cycles (*n*) were investigated. As shown in Fig. 6, the optimum oxidation current at nano-Cu/Cu-cable and nano-Cu/Cu-disk was obtained at n = 30 and n = 20 repeated scan cycles, respectively.

Fig. 7 shows the electrocatalytic oxidation (LSV) of 75 mg/L glycine in NaOH at different Cu-cable and Cu-disk based electrodes. It is clear that sensors prepared using FSCV technique exhibit the highest oxidation current. It is worth mentioning that FSCV deposition produces the highest surface area and the most uniform distribution of nano-Cu particles with an average particle diameter of \sim 40 nm (Fig. 1). Those improvements in the surface area and the uniformity of nano-Cu particle in case of FSCV preparation could be responsible for the enhancement of the electrocatalytic oxidation of glycine both in terms of current value and shift to lower oxidation potential. Therefore, nano-Cu/Cu-cable and nano-Cu/Cu-disk prepared using FSCV deposition were selected for further characterization and the detection of COD in real water samples.

3.3. Effect of varying scan rate

Linear Sweep Voltammetric experiments were carried out with the nano-Cu/Cu (cable, disk) electrode to establish the effect of



Figure 6 Effect of repeated scan cycles (n) on the oxidation current of 75 mg/L glycine prepared in 0.075 M NaOH in case of nano-Cu/Cu-cable (solid line) and nano-Cu/Cu-disk (dashed line).



Figure 7 LSVs response of 75 mg/L glycine in NaOH electrolyte solution at 100 mV/s and 22 °C for Cu-cable (solid lines), Cu-disk (dashed lines) electrodes and their nano-Cu films at the optimized condition of potentiostatic deposition (\blacktriangle) and FSCV (\blacksquare).

scan rate (ν) at a constant concentration of 75 mg/L gly/0.075 M NaOH. A shift in peak potential with increasing scan rate was observed (Fig. 8A and B). The anodic oxidation process can be described by Randles–Sevčik equation (Eq. (1)):

$$I_p = (2.99 \times 10^5) n [(1 - \alpha) n_{\alpha}]^{1/2} A C_b (D^{\nu})^{1/2}$$
(1)

where *n* is the number of electron transfer, α is the electron transfer coefficient, n_{α} is the number of electrons involved in

the rate-determining step, A is the electrode area, C_b is glycine bulk concentration (75 mg/L) and D is the diffusion coefficient of glycine. According to Eq. (1) a plot of the peak current (I_p) against the square root of scan rate $(v^{1/2})$ should give a linear relationship for diffusion-controlled process. Indeed, a linear relation was observed for glycine oxidation in 0.075 M NaOH, with a linear regression equation of i_{pa} $(mA) = -0.0024 + 0.0029v^{1/2} (mV/s)^{1/2} (R = 0.989)$ and i_{pa} $(mA) = -0.0017 + 0.0021v^{1/2} (mV/s)^{1/2} (R = 0.994)$ (see data in Fig. 8c) which confirms the diffusion-controlled nature of the oxidation process.

3.4. Amperometric detection of COD

Glycine was chosen as a model compound for amperometric detection of COD. A steady state background current was attained in 300 s, at an applied potential of 0.75 V and an electrolyte solution of 0.075, 0.10 M NaOH for Cu-cable, Cu-disk electrodes, respectively. Upon increasing the concentration of COD (i.e., glycine), the oxidation current signals at nano-Cu/Cu-cable or nano-Cu/Cu-disk prepared using FSCV linearly increases as indicated in Fig. 9. It can be also seen in Figs. 9 and 10 that the proposed sensors exhibited fast responses to the addition of COD values and 2 s for COD values higher than 300 mg/L.

A comparison between the calibration plots of the nano-Cu films modified electrodes prepared using FSCV is shown in Fig. 11. The calibration curve of nano-Cu/Cu-cable electrode is steeper than that of nano-Cu/Cu-disk electrode indicating



Figure 8 LSVs response of the nano-Cu/Cu-cable electrode (A) (\blacksquare), nano-Cu/Cu-disk electrode (B) (\blacktriangle) in 0.075 M NaOH solution containing 75 mg/L glycine vs. the square root of the scan rate ($v^{1/2}$) (C).



Figure 9 (I-t) response curve of nano-Cu film modified Cu-cable electrode, where the nano Cu-film prepared by FSCV, Inset low COD values response. The detected potential is 0.75 V, and the electrolyte is NaOH solution.



Figure 10 (I-t) response curve of nano-Cu film modified Cu-disk electrode, where the nano Cu-film prepared by FSCV, Inset low COD values response. The detected potential is 0.75 V, and the electrolyte is NaOH solution.

higher sensitivity of nano-Cu/Cu-cable electrode compared to nano-Cu/Cu-disk. The linear regression equations are: $J \text{ (mA/mm}^2) = 0.028 + 0.00039 \text{ COD (mg/L)}$ ($R^2 = 0.999$) and $J \text{ (mA/mm}^2) = 0.019 + 0.00019 \text{ COD (mg/L)}$ ($R^2 = 0.979$) for nano-Cu/Cu-cable and nano-Cu/Cu-disk modified electrodes, respectively.

Under the optimized conditions, the linear range and LOD of COD analysis at copper based nano-sensors were



Figure 11 Comparison between calibration plots of the two nano-Cu films modified Cu-cable (\blacksquare) and Cu-disk (\blacktriangle); inset calibration plot for low COD concentrations.

determined and tabulated in Table.1. The LOD was evaluated according to IUPAC regulations (S/N = 3) (Bourais et al., 2004).

3.5. Stability and reproducibility of the proposed electrochemical sensors

The effect of storage medium (air, water) on the response of the prepared COD sensors was investigated. It was observed that storage of the prepared sensors in water enhances the signal stability which could be due to increasing the formation of $Cu(OH)_2$ by time. The signal stability was also investigated. It was observed that signal of the prepared nano-Cu sensors was stable over a period of one week. No practical change was observed in the oxidation current of 75 mg/L glycine when measured in 0.075 M NaOH indicating that nano-Cu modified sensors exhibited high signal stability.

The reproducibility of the proposed electrochemical sensors was evaluated by measuring the LSV oxidation response of 75 mg/L glycine when measured in 0.075 M NaOH for ten times (n = 10). As shown in Table 1, the prepared nano-Cu sensors exhibited a good reproducibility.

3.6. Selectivity toward inorganic interferences

The interference of chloride and nitrite ion must be considered in the measuring of COD, where the presence of Cl^- ions

Table 1	Comparison	between electroanal	ytical features	of nano-Cu	/Cu-cable and	nano-Cu/Cu-disk sensors.
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Nano-Cu sensor	Cu-cable sensors		Cu-disk sensors		
Electroanalytical feature	Nano-Cu/Cu-cable ^a	Nano-Cu/Cu-cableb	Nano-Cu/Cu-disk ^a	Nano-Cu/Cu.disk ^b	
Limit of Detection (LOD) (mg/L)	2.4	2.6	1.5	1.2	
Linear range (mg/L)	2-595	2-595	2-369.9	2-280.9	
Sensitivity (J, mg/L)	3.0E-04	4.1E-04	1.6E-04	2.0E-04	
Reproducibility (RSD%)	2.4	1.1	1.6	1.3	
Tolerance level toward inorganic interference	1.0 M Cl ⁻		0.8 M Cl ⁻		
-	0.01 M NO ₂ ⁻		0.01 M NO ₂ ⁻		

b pa cit i depositio

^b FSCV deposition.

Table 2 Analysis of COD in real water samples using the prepared COD sensors and the standard dichromate method.

Water sample	Standard method	Cu-cable sensor			Cu-disk sensor		
		Nano-Cu/ Cu-cable	Recovery %	Relative error %	Nano-Cu/ Cu-disk	Recovery %	Relative error %
Nile water	40.6	39.9	101.6	-1.6	40.3	100.6	-0.7
Sewage water	121.9	119.9	101.7	-1.7	113.1	107.8	-7.2
Treated waste water	54.2	47.4	114.3	-12.6	48.5	111.8	-10.5
Lake water	30.5	30.6	99.8	0.3	30.3	99.9	0.1
Ibrahimya canal	17.0	17.0	99.9	0.58	17.2	99.1	0.9

 Table 3
 Comparison of proposed COD sensors with the reported nano-material based COD sensors.

Sensor type	Sensing element	Electro active species	LOD (mg/L)	Linear range (mg/L)	Reproducibility (RSD%)
NiCu alloy/GCE (Zhou et al., 2012)	Nano-NiCu alloy	Glucose	1.0	10–1533	3.6
Co-oxide/GCE (Wang et al., 2012)	Co-oxide film	Glycine	1.1	5.7-155.8	5.7
$TiO_2/Ti/TiO_2$ -pt (Qu et al., 2011)	Nano-pt.	KHP	9.5	10-1533	3.6
Boron Doped Diamond (BDD)	BDD	KHP, phenol	7.5	20-9000	1.9
(Yu et al., 2007)					
$Pt-ring + Pt/PbO_2-disk$	PbO ₂	Indigo, KHP	15	10-500 & 500-5000	Not detected
(Westbroek and Temmerman, 2001)					
Nano-Ni/GCE (Jing et al., 2012)	Nano-Ni	Glucose	1.1	10-1533	4.7
F-PdO ₂ Sensor (Li et al., 2005)	Pd (II) particles	Glucose	15.5	100-1200	Not detected
Activated Cu.electrode (Silva et al., 2009)	Cu-disk	Glucose	20.3	53.0-2801.4	Not detected
Nanocomposite-TiO ₂ (Wang et al., 2011)	Nano-TiO ₂	KHP	0.24	3-15	Reused 80.9%
AgO-CuO sensor (Orozco et al., 2008)	Ag ₂ O–CuO	Glucose	4.3	5-1400	Not detected
Activated GCE electrode (Can et al., 2012)	Activated GCE	Lake water	0.3	Not detected	8.7
Nano-Cu/Cu-cable sensor (this work)	Nano-Cu	Glycine	2.6	2–595	1.1

decreases the oxidation current but the NO_2^- eliminates the peak response. The proposed electrochemical sensors based on nano-Cu film modified Cu-electrodes have high tolerance level toward Cl⁻ and NO_2^- interferences as indicated in Table 1.

3.7. Analysis of real samples and recovery study

The analysis of real water samples (e.g., drinking, lake, Nile River, waste water) was carried out using the proposed method and the standard dichromate method for COD. Data obtained indicated good agreement between the prepared COD sensors and the standard method with a low relative error (Table 2). A highly significant correlation (r = 0.997 & 0.9906, p < 0.001, n = 5) was observed for the analysis using nano-Cu/Cu-cable and nano-Cu/Cu-disk sensors. Moreover, the results confirmed that the prepared sensors exhibited good recovery between (99% and 111%) as indicated in Table 2 which could provide a promising tool for the determination of COD in water quality control and pollution evaluation.

3.8. Comparison with reported COD sensors

In comparison with the previously reported COD sensors based on nano-materials, the optimized nano-Cu/Cuelectrode (cable, disk) based COD sensor exhibited lower limit of detection and better sensitivity compared to most of the previously reported electrochemical sensors (Table 3). Moreover, the developed COD sensor is characterized by low cost and operational simplicity since there is no complicated modification procedure for the electrode surface.

4. Conclusion

Electrodeposition via FSCV preparation produces uniform, mono dispersed and stable nano-Cu sensors. The prepared sensors exhibited low limit of detection, excellent reproducibility, high tolerance level toward Cl⁻ as main interfering ion, and fast response time. Moreover the prepared COD sensors are easy to fabricate and operate as well as they exhibit stable responses for a reasonable time. The prepared sensors exhibited a detection limit of about 2 mg/L which could enable the analysis of COD in surface waters (e.g., lakes, rivers). The prepared nano-Cu modified COD sensors were fully optimized in terms of electrochemical parameters. The analytical utility of the optimized nano-Cu modified sensors was demonstrated by the analysis of COD is real water samples. Results obtained were found to be in good agreement with the standard COD method which could enable the use of the prepared sensors in routine analysis of real water samples.

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