Introduction

The industrial revolution is affecting the quality of the available fresh water. Increasing industrial activity is one of the main sources of severe pollution problems globally. Measurement of the amount of organic compounds in water is undoubtedly important for pollution management and this generally is monitored by the measurement of oxygen content or oxygen dissolved in water. Chemical oxygen demand (COD) and biochemical oxygen demand (BOD) are widely used as parameters to evaluate the amount of organic pollutants in wastewater and are the most important index in monitoring water quality.\(^1,2\) COD is defined as the oxygen required for the oxidative degradation of organic compounds by strong oxidizing agents, such as dichromate and permanganate. Potassium dichromate (K\(_2\)Cr\(_2\)O\(_7\)) and potassium permanganate (KMnO\(_4\)) are employed as oxidizers for the conventional measurement of COD. These oxidizers have disadvantages, namely dichromate contains poisonous hexavalent chromium, while permanganate can oxidize organic compounds only partially.\(^1,2\) The conventional method of COD measurements requires a longer analysis time (approximately 3 - 4 h), the use of expensive reagent (Ag\(_2\)SO\(_4\)), and toxic (K\(_2\)Cr\(_2\)O\(_7\), HgSO\(_4\)), and corrosive (H\(_2\)SO\(_4\)) chemicals. Also, the results depend on the measurement accuracy of operator proficiency.\(^3,4\) To overcome the disadvantages of the conventional method of COD measurements, numerous efforts have been made to develop a rapid and environmentally friendly new method for COD measurement. Recently, photocatalytic and photoelectrocatalytic methods have been reported for determining COD using TiO\(_2\) materials.\(^5,6\) Nevertheless, the photogenerated electron-hole pairs easily recombined and the use of UV light source increased the running cost for COD measurement. The other methods such as spectroscopy, fluorescence spectroscopy, and chemiluminescence method make it possible to use flow injection techniques to determine COD, which greatly improves the analysis efficiency.\(^7-10\) However, the digestion procedure using corrosive solvent is unavoidable. The electrochemical method for COD measurement has been considered a promising method due to its advantages such as rapidness, sensitivity, low cost, good precision and accuracy.\(^11-14\) Over the last few decades, electrochemical techniques have been developed for COD measurement, in which the organic substances were oxidized on the surface of a working electrode. Various electrode materials have been investigated for COD measurement. Copper metal in basic media could act as an electrocatalyst for the oxidation of organic species such as carbohydrates and amino acids, which are mainly responsible for COD. However, the direct oxidation
of organic species in aqueous solution using a simple metal electrode is not simple as high potentials are required for the oxidation of organic compounds and usually result in the oxidation of water. Therefore, a proper choice of a suitable electrode material for this purpose is very important. A number of novel electrode materials have been reported for the electrochemical detection of COD, such as copper electrode modified with copper nanoparticles, Cu-cable and Cu-disk electrode modified with Cu nanoparticle, an activated copper electrode, CuO/Cu nanowire and NiCu alloy electrode. The deposition process of metallic nanoparticles on foreign substrates has attracted great attention due to the different properties of nanoparticles compared to those materials. Nanoparticles were reported to improve the surface roughness, provide an increase of conductive area, which corresponds to an improvement in sensitivity, and also enhance electrocatalytic activity. In particular, this condition may lead to an improvement of the ability to amplify the current signal. This research studies the preparation of electrochemical sensors for the determination of COD using Cu-wire and graphite electrode modified with nano-copper films. Cu was selected as the based electrode as it powerfully oxidizes carbohydrates and amino acids, known as a culprit for COD. On the other hand, graphite is cheap, simple, and a well-known carbon electrode. The characteristic of the electrochemical sensors was assessed using standard reagents of glycine and glucose to evaluate COD value. Validation performed by conventional measurements of COD showed comparable results with the prepared electrodes, indicating that the prepared electrodes are promising for COD sensors.

Experimental

Reagents and chemicals
All chemicals were of analytical grade. CuSO₄·5H₂O (≥99.0%), H₂SO₄ (98%), NaOH (≥97%), K₂Cr₂O₇ (≥99.9%), Ag₂SO₄ (99%), HgSO₄ (98%), Fe(NH₄)₂(SO₄)₂ (99.9%), acetone (99.8%), glycine (99.7%), and D-glucose (97.5 - 102.0%) purchased from Merck were used for modification of the electrode. A commercially available Cu wire (0.5 mm diameter), carbon powder and liquid paraffin were used for fabrication of the electrode.

Apparatus
Electrochemical measurements were performed in a three-electrode cell system (EDAQ E-Corder 410). A platinum wire (Nilaco, Japan) was used as a counter electrode and Ag/AgCl electrode (BAS System) as a reference electrode. Analytical instruments used in this research were Ultrasonic (NOVA) and scanning electron microscope-energy dispersive X-Ray (SEM-EDX JEOL/EO JCM-6000 Plus Japan).

Preparation of nano-Cu/Cu and nano-Cu/C electrodes
Nano Cu on Cu wire (nano-Cu/Cu) and nano Cu on graphite (nano-Cu/C) electrodes were prepared by electrochemical deposition. Firstly, Cu wire was polished with metal polish solution and rinsed thoroughly with pure water. Cu wire and graphite were sonicated using ultrasonic in the mix of water and acetone solution with a ratio of 1:1 for 5 min afterward. The carbon paste was made from carbon powder and liquid paraffin (1:3). The electrode was fabricated by following the previous publication about the microelectrode. Briefly, the carbon paste was inserted into micropipette tip. The Cu wire and graphite was then inserted through a micropipette tip with a carbon paste inside (Fig. 1). The copper sensing film was prepared by using a solution of 4 mM CuSO₄·5H₂O/1 mM H₂SO₄. Two types of methods were applied, i.e. electrodeposition with chronoamperometry at constant potential (–1.0 V) for 120 s and cyclic voltammetry in the potential range from –0.1 to –1.30 V for 30 cycles at 100 mV/s. CuSO₄·5H₂O with various concentrations of 4, 8, 12, 16, and 20 mM were used to evaluate the optimum Cu²⁺ concentration. Deposition time was also optimized. The resulting electrodes were rinsed with pure water to remove any adsorbed species.

Electrochemical measurement and determination of COD
The electrochemical measurements were performed in one compartment cell containing three electrodes, nano-Cu/Cu or nano-Cu/C, Pt, and Ag/AgCl, respectively, as the working, counter, and reference electrodes. As standard solutions, 0.075 M NaOH containing glycine and glucose (ratio of 1:1) with different concentrations in the range 32 - 256 mg/L were used. The detection was performed with amperometric detection technique at a potential of +680 mV for 450 s. A steady state background current was attained at 120 s in tap water containing 0.075 M NaOH electrolyte. Then, the testing solution was added into an electrochemical cell for the determination of COD. All experiments were carried out at ambient temperature.

Fig. 1  Schematic drawing and real pictures of the fabricated electrodes.
Samples for COD measurements were prepared by employing Bogor tap-water samples (PDAM Tirta Pakuan, Bogor, West Java, Indonesia). Analysis of this water, reported on February 24th, 2020, showed the presence of inorganic compounds (in mg/L), including iron (<0.20); fluoride (0.41); cadmium (0.03); potassium (140.22); chromium (<0.025); manganese (<0.04); nitrate (0.01); nitrite (<0.004); selenium (<0.002); zinc (<0.05); cyanide (0.005); sulfate (9.04); lead (<0.04) as well as organic compounds (4.55) and detergent (<0.01). All the COD measurement results of the developed sensors were compared to the conventional COD method.

Results and Discussion

Characterization of fabricated electrodes

SEM was employed to investigate the morphology of bare Cu wire, bare graphite, nano-Cu/Cu and nano-Cu/C electrodes (Fig. 2). SEM images indicate that Cu was covered with Cu nanoparticles with a diameter range of 50 – 500 nm, whereas graphite was covered with Cu nanoparticles with a diameter range of 133 – 355 nm. Overall, the electrodeposited nano-Cu film prepared by cyclic voltammetry appeared in smaller and more uniform particles over the surface prepared by chronoamperometric deposition. This is probably due to the repeated scans that were applied in cyclic voltammetry method. The atomic characterization was also carried out using EDX (Figs. S1a and S1b, Supporting Information). Chronoamperometric deposition could cover the Cu electrode by nano-Cu at around 7.35%, while the cyclic voltammetry one at around 14.35%. Meanwhile, nano-Cu was less deposited on the graphite electrode than on the Cu electrode as 0.81 and 7.81% Cu nanoparticles could be deposited by chonoamperometric deposition and cyclic voltammetry method, respectively.

Electrochemical behavior of copper electrode

Copper electrode in alkaline media electrocatalytically oxidizes organic compounds mediated by surface of metal oxides. Figure 3 shows a cyclic voltammetry of 0.075 M NaOH in a potential range of –1.0 to +0.8 V for nano-Cu/Cu prepared by cyclic voltammetry. A typical peak response was also observed at nano-Cu/C electrode (data not shown). The anodic peak 1 (~0.30 V vs. Ag/AgCl) corresponds to the formation of the first layer of copper(I)oxide (Cu₂O), while the peak 2 (~0.12 V vs. Ag/AgCl) corresponds to the formation of a second layer of copper(II)hydroxide (Cu(OH)₂). In addition,
an increasing current observed at around 0.70 V vs. Ag/AgCl indicates the Cu(II)/Cu(III) oxidation and the cathodic peaks 3 and 4 correspond to the Cu(II)/Cu(I) and Cu(I)/Cu(0) reduction reactions observed at –0.54 and –0.89 V (vs. Ag/AgCl), respectively. The electrochemical process of metallic Cu in alkaline media is highly dependent on both hydroxide concentration and formation of a specific layer of Cu(II)oxide. The participation of Cu(III) species as an electron transfer mediator has been suggested to explain the performance of Cu particles in anodic process related to several organic compounds. Cu(III) is central in the electrocatalytic oxidation of organic compounds in alkaline media. The expected electrocatalytic oxidation of organic compounds at the copper electrode in alkaline medium is proposed as follows Eqs. (1) – (3):16

\[
\begin{align*}
\text{Cu} + 2\text{OH}^{-} & \rightarrow \text{Cu(OH)}_{2} + 2e^{-} \quad (1) \\
\text{Cu(OH)}_{2} + \text{OH}^{-} & \rightarrow \text{Cu(III)}\text{OOH}^{•} + \text{H}_{2}\text{O} + e^{-} \quad (2) \\
\text{Cu(III)}\text{OOH}^{•} + \text{organics (red)} + \text{H}_{2}\text{O} & \rightarrow \text{Cu(OH)}_{2} + \text{organics (ox)} + \text{OH}^{-} \quad (3)
\end{align*}
\]

Optimization of the electrodeposition parameters of nano-Cu film

The effect of different deposition variables was investigated. The applied potential, the concentration of CuSO₄ solution, and the reduction time of the chronoamperometric technique were studied to prepare the electrode. The effect of such variables on the responses of nano-Cu/Cu electrodes toward the oxidation of mixture solutions of 150 mg/L glycine-glucose (1:1) in 0.075 M NaOH was then investigated by measuring the oxidation peak observed in linear sweep voltammetry (LSV). The effect of each variable was represented graphically by plotting the change in this variable versus oxidation peak current to determine the optimal condition for deposition of nano-Cu on Cu wire electrode. Figure 4a shows the effect of Cu²⁺ concentration on the catalytic activity of the prepared nano-Cu sensors. The optimal Cu²⁺ concentration was achieved by chronoamperometry from 4 mM CuSO₄ bath composition. The influence of deposition time on the electrocatalytic activity of nano-Cu film-based sensors was also studied. As shown in Fig. 4b, the oxidation current of glycine-glucose was optimum at deposition time 120 s. The study of the electrodeposition parameters of nano-Cu film was also performed on the graphite electrode (Fig. S2, SI). The deposition time of 240 s to achieve the current of 0.14 mA and the Cu²⁺ concentration of 16 mM was then applied for the next experiments by using the chronoamperometry method (Fig. S2a).

Deposition of nano-Cu on Cu wire and graphite electrode using cyclic voltammetry techniques was performed at the potential range of –0.1 to –1.3 V. The LSV responses in 0.075 M NaOH solution containing 150 mg/L glycine and 150 mg/L glucose were studied to obtain the optimal concentration of Cu²⁺ and number of scan cycles. Figure 5a shows the effect of Cu²⁺ concentration for nano-Cu deposited on the Cu wire electrode prepared by cyclic voltammetry. Figure 5b shows the optimum number of scan cycles for the prepared electrode. The optimum concentration of Cu²⁺ was achieved at 4 mM with number of cycles of 30 cycles. Meanwhile, nano-Cu/graphite electrode required 30 cycles with an optimum Cu²⁺ concentration of 12 mM (Fig. S2c). It is suggested that sensors prepared using the cyclic voltammetry technique exhibit a higher oxidation current than those prepared by chronoamperometric technique due to the smaller and the uniform copper nanoparticles on the electrode surface that are responsible for the enhancement of the electrocatalytic oxidation of glycine-glucose in terms of current value. Therefore, the deposition of nano-Cu prepared by using cyclic voltammetry was selected for further characterization and the detection of COD in artificial water samples. Summary of the current and potential responses of concentration and deposition optimization are presented in Tables S1 and S2 (SI).

Effect of scan rate

The effect of various scan rates was investigated using LSV experiments at a constant concentration of 0.075 M NaOH.
A shift in peak potential with an increasing scan rate was observed (Fig. 6). The Randles–Sevcˇik equation (Eq. (4)) describes the anodic oxidation process:

$$I_p = (2.99 \times 10^5)n^{1/2}(1 - \alpha)n^{1/2}(ACb(Dv))^{1/2}$$

Where, $n$ is the number of electron transfer, $\alpha$ is the electron transfer coefficient, $n_e$ is the number of electrons involved in the rate-determining step, $A$ is the electrode area, $C_b$ is glycine/glucose and $D$ is the diffusion coefficient. According to the Eq. (4), a plot of the peak current $I_p$ against the square root of scan rate $v^{1/2}$ should give a linear relationship for the diffusion-controlled process. A linear relation was observed for glycine – glucose oxidation in 0.075 M NaOH on nano-Cu/Cu electrode, showing a linear regression equation of

$$I_{pa}(mA) = 0.0119v^{1/2}(mV/s)^{1/2} - 0.0125 \quad (R^2 = 0.9926)$$

whereas on nano-Cu/C electrode shows

$$I_{pa}(mA) = 0.0093v^{1/2}(mV/s)^{1/2} - 0.0104 \quad (R^2 = 0.9925).$$

The results confirmed the diffusion-controlled nature of the oxidation process.

**Amperometric detection of COD**

A mixture solution of glycine and glucose was employed as the model compound for the amperometric detection of COD. A steady state background current was attained at 120 s from 10 mL NaOH 0.075 M solution at an applied potential of +0.68 V vs. Ag/AgCl. Figures 7a and 7b show that increasing the glycine-glucose concentrations could linearly increase the oxidation signals at both of the prepared nano-Cu/Cu and nano-
Cu/C electrodes, respectively. Both prepared electrodes showed good linearity ($R^2 = 0.997$) in the concentration ranges of 17.45 - 176 and 32 - 256 mgO/L COD, respectively, at nano-Cu/Cu and nano-Cu/C electrodes. A mixture solution of 1000 mg/L glycine and 1000 mg/L glucose, theoretically, has a COD value of 1280 mgO/L. Accordingly, the concentration range was made by diluting this solution. The LOD evaluated according to IUPAC regulations ($S/N = 3$) was estimated to be 9.02 mgO/L COD at nano-Cu/Cu, while it was 8.90 mgO/L at nano-Cu/C electrode. Electroanalytical performances of the developed COD sensors are displayed in Table 1. Excellent linearity were also successfully demonstrated by using different concentration ratios of glycine-glucose, $i.e.$ 1:9 and 9:1 with a concentration range of 17.45 - 176 mgO/L COD (Fig. S3, SI) indicating that the method can be used in any composition of glycine glucose.

### Stability, reproducibility, and selectivity of the proposed electrochemical sensors

The stability of the current responses was investigated by using LSV. The LSV responses of both electrodes were observed for 10 measurements of 0.075 M NaOH solution containing 150 mg/L glycine and 150 mg/L glucose. Good stability of the current responses was shown by the voltammograms for nano-Cu/Cu (Fig. 8a) and nano Cu/C (Fig. 8b) with relative standard deviations (RSDs) of 3.84 and 2.90%, respectively. Meanwhile, the reproducibility of the proposed electrochemical sensors was evaluated by measuring the LSV oxidation responses of 0.075 M NaOH solutions containing 150 mg/L standard glycine and 150 mg/L standard glucose at nano-Cu/Cu and nano-Cu/C (Figs. 8c and 8d, respectively) in 7 different batch solutions with the same concentrations. RSD values ($n = 7$) of 1.63 and 1.87%, respectively, using nano-Cu/Cu and nano-Cu/C indicated excellent reproducibility of both electrodes.

Furthermore, the interference of chloride and nitrite ion was considered in the measuring of COD. Significant change of the COD sensor’s responses was observed in the presence of chloride and nitrite at nano-Cu/Cu as shown in Fig. 9a. On the contrary, the current was less interfered at nano-Cu/C (Fig. 9b). Reactivity of Cu was the possible reason for the interferences at nano-Cu/Cu. It seems that reducing the size of copper particles in nano-Cu/C can maintain the current from nitrite and chloride.

### Analysis of tap water samples and the recovery study

COD analysis using tap-water samples to produce 0.075 M NaOH with 250 mg/L glycine and 250 mg/L glucose was employed for the real sample approach. Analysis of the tap water indicated the presence of organic compounds ($4.55$ mg/L) and detergent ($<0.01$ mg/L) besides metal ions and inorganic anions. The validation was performed with the conventional dichromate method.

Table 2 shows COD of the tap water containing 0.075 M NaOH with a mixture of 250 mg/L glycine and 250 mg/L glucose measured by the developed sensors in comparison with the conventional dichromate method. Theoretically, this solution has 320 mgO/L COD value. The average of obtained COD at nano-Cu/Cu and nano-Cu/C were 303.69 and 287.59 mgO/L,

| Electroanalytical feature | Details | Nano-Cu/Cu | Nano-Cu/C |
|---------------------------|---------|------------|-----------|
| Limit of detection (LOD)/mgO L⁻¹ | 9.02 | 8.90 |
| Linear range/mgO L⁻¹ | 17.45 - 176 | 32 - 256 |
| Reproducibility ($n = 7$), %RSD | 2.84 | 2.90 |
respectively, which were 92.58 and 87.86% comparable against the measurements by the conventional technique. Comparison with theoretical COD value showed the recovery percentage at nano-Cu/Cu and nano-Cu/C were 94.90 and 89.87%, respectively, while it was 102.51% for the conventional method. Moreover, excellent stability of the results could be achieved at both electrodes with RSDs (\(n = 3\)) of 0.77 and 1.66%, respectively, at nano-Cu/Cu and nano-Cu/C, while it was 1.20% with the conventional method. The results indicated that the developed sensors were promising for the determination of COD in water quality monitoring.

### Conclusions

Modification of Cu wire and graphite electrode with nanoparticles copper film was successfully performed using cyclic voltammetry deposition method. Characterization of the modified electrode by SEM shows the formation of nanoparticles Cu on the surface of Cu wire and graphite. Both nano-Cu/Cu and nano-Cu/C electrodes were applied to determine COD of glycine-glucose mixture in basic medium solution with 0.075 M NaOH as the supporting electrolyte. A positive potential of +0.68 V vs. Ag/AgCl was applied. The results showed that both nano-Cu/Cu and nano-Cu/C electrodes are promising for application as COD sensors and showed comparable results with the conventional dichromate method. Therefore, the less poisonous nano-Cu/C electrode was considered as the better option for a COD sensor.

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### Supporting Information

Supporting information is available for EDX spectra of bare Cu wire and bare graphite in comparison with nano-Cu/Cu and nano-Cu/C prepared by chronoamperometry technique and fast scan cyclic voltammetry, cyclic voltammograms of the optimization in the electrode preparations, as well as the amperometric responses of standard solutions of glycine-glucose measurements by using the developed sensors.

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