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# **Cu-Au/rGO Nanoparticle Based Electrochemical Sensor for 4-Chlorophenol Detection**

Yajing Yang, Ning Ma, Zhaoyong Bian\*

College of Water Sciences, Beijing Normal University, Beijing 100875, PR China \*E-mail: <u>bian@bnu.edu.cn</u>

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Copper, gold or gold/copper nanoparticles loaded on reduced graphene oxide (Cu/rGO, Au/rGO and Cu-Au/rGO) were synthesized as catalysts, using chemical and fractional reduction processes. These materials were characterized by scanning electron microscopy, X-ray diffraction, transmission electron microscopy, Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy. A series of sensitive 4-chlorophenol (4-CP) sensors were fabricated using electrodes modified with these three catalysts. The impedance values of these devices were assessed using an alternating current impedance method, while the detection of 4-CP was investigated by cyclic voltammetry. The Cu-Au/rGO exhibited the best catalytic properties. Under optimized conditions (pH 6.5, scan rate 100 mV/s), a sensor based on a glassy carbon electrode modified with this material exhibited a low 4-CP detection limit of 0.17 µmol/L, and demonstrated good reproducibility and long-term stability. This sensor has high application value in on-line detection of chlorophenol pollutants in wastewater.

**Keywords:** Cu-Au/graphene; glassy carbon electrode; 4-chlorophenol wastewater; electrochemical detection

## **1. INTRODUCTION**

Chlorophenols (CPs) play an important role in the production of herbicides, insecticides and pharmaceuticals, but are also common organic pollutants [1,2]. Because of their resistance to biodegradation, CPs tend to persist in the environment and to accumulate in the food chain, and thus are potentially hazardous to various ecosystems. CPs can also have adverse effects on human health, as they are teratogenic, carcinogenic and mutagenic. For these reasons, 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), 2,4-dichlorphenol (DCP), 2,4,6-trichlorophenol (TCP) and polychlorinated polyphenols (PCPs) and other CP compounds are among the 129 priority control pollutants identified by the US Environmental Protection Agency (EPA) [3]. The Chinese government also listed various CPs in the National Dangerous Goods List in 2008, while the World Health Organization limits the allowable

concentrations of various CPs in drinking water: 2,4-DCP ( $40 \ \mu g \cdot L^{-1}$ ), 2,4,6-TCP ( $300 \ \mu g \cdot L^{-1}$ ) and PCP (9  $\ \mu g \cdot L^{-1}$ ). Therefore, the efficient, accurate, rapid and sensitive monitoring of CPs is important in pollution prevention and environmental management. CPs are typically assessed using spectroscopy [4], chromatography [5,6], chromatography-mass spectrometry [7,8] and electrochemical methods [9,10]. Among these, electrochemical analysis technology has the advantages of fast responses, low cost, simple operation, readily miniaturized equipment and a capacity for in situ analysis. Consequently, this method is widely used in environmental analysis, food safety control and medical diagnosis.

Electrochemical analysis is based on generating a measurable electrical signal from the interaction between the analyte and a material sensitive to this compound. Because CPs are electrochemically active substances (as they contain phenolic hydroxyl groups) they can be analyzed by electrochemical techniques. However, these compounds tend to generate weak responses in conventional electrochemical sensors, and so are difficult to measure directly. Therefore, it would be beneficial to develop new sensors that generate stronger signals in response to CPs. Electrode modification is a commonly used means of increasing the signal. As an example, employing different materials in the electrode of the sensor can both increase the surface area of the electrode and facilitate electron transport, both of which can result in highly sensitive detection of the target molecules. Consequently, determining the optimal electrode modification material is critical to improving the performance of the electrode.

Graphene is a two-dimensional carbon nanomaterial which, like fullerenes and carbon nanotubes, has unique properties [11,12]. Due to the specific optical and mechanical characteristics of graphene, as well as its large specific surface area and high conductivity, it is widely used in sensor construction [13,14]. Functionalized graphene has amphiphilic properties and so is soluble both in water and in organic solvents, and thus is superior to carbon nanotubes in terms of permitting the high-efficiency conduction of electrons [15]. Consequently, graphene is an ideal material for the modification of the surfaces of electrodes in electrochemical sensors as a means of promoting electron transfer. In recent years, many nanomaterials have also been used to improve the properties of the electrode interface. The exceptionally small sizes, large specific surface areas, good biocompatibility and unique bonding abilities of these materials can significantly improve the sensitivity and specificity of detectors. As such, nanomaterials are extremely attractive in the fields of chemical sensing and biosensing. Metal nanomaterials, especially Au nanoparticles [16], have been especially widely researched due to their exceptional physical and chemical properties, including excellent electrical conductivity, good biocompatibility and superior environmental stability. Nanomaterials based on Au can enhance detection signals and also improve sensitivity owing to their special electronic characteristics [17-19]. The design and optimization of electrodes with bimetallic nanoparticles has also become a research emphasis. Bimetallic systems incorporating Au, such as Au/Pt [19], Au/Pd [20], Au/Ni [21], Au/Ag [22] and Au/Cu [23] have been applied to certain catalytic processes, although rarely to the electrochemical detection of CPs. The interactions between the two components of bimetallic nanoparticles often result in properties not observed in the corresponding monometallic counterparts, such as improved catalytic activity, catalytic selectivity and better resistance to deactivation. Cu nanoparticles have been studied extensively because of their high electrical activity and low cost, in addition to the resistance to poisoning of this metal [24-28]. Based on this background, the present work attempted to obtain improved detection results by combining Au and Cu on the surface of reduced graphene oxide (rGO) to prepare a highefficiency electrochemical catalyst. The rGO-supported Cu-Au bimetallic catalyst was applied to the detection of 4-CP, as well as to the electrochemical analysis of a specific dehydrogenation oxidation reaction.

In the present study, Cu/rGO and Au/rGO monometallic catalysts and an Cu-Au/rGO bimetallic catalyst were synthesized using a chemical reduction process. The morphology and compositional changes of the catalysts were investigated by Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The electrocatalytic behaviors of the Au/rGO, Cu/rGO and Cu-Au/rGO catalysts were compared and studied under different conditions. These three catalysts were also evaluated in the presence of 4-CP (as a model CP) via cyclic voltammetry (CV) in a three-electrode system, and were also assessed using an in-situ analysis, which is a potential application for the analysis of 4-CP in wastewater.

## 2. EXPERIMENTS

## 2.1 Synthesis of Cu/rGO, Au/rGO and Cu-Au/rGO nanocomposites catalysts

Graphene oxide (GO) was prepared according to an improved Hummers method [29]. Metal precursor solution was prepared by respectively mixing aqueous solutions of  $Cu(CH_3COO)_2 \cdot H_2O(15.59 \text{ mg}, Beijing Chemical Works)$  and HAuCl<sub>4</sub>·4H<sub>2</sub>O (10.45 mg, Beijing Chemical Works) with corresponding volume of hydrochloric acid solution under constant stirring. Moreover, the pH of metal precursor solution was adjusted to 10 with concentrated aqueous ammonia solution.

To compound Cu/rGO and Au/rGO monometallic catalysts [30], 10 mg of GO was dispersed into 100 ml of deionized water with ultrasound for 2 h to form a homogenous solution. 20 mL of Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O precursor solution and 42 ml of HAuCl<sub>4</sub>·4H<sub>2</sub>O precursor solution were added drop wise under constant stirring, respectively. Then pH was adjusted to 10 with concentrated ammonia solution and magnetic stirring for 2 h. Subsequently, a freshly prepared aqueous solution of sodium borohydride (NaBH<sub>4</sub>, JHD, 2 g into 40 ml distilled water) was slowly added to the reaction mixture under fast and constant stirring condition. The black precipitate was collected by repetitive suction filter washing with water and then vacuum dried at 60 °C and preserved for further experimentation, indicating 1 wt.% Cu/rGO (Cu/rGO) and 1 wt.% Au/rGO (Au/rGO) monometallic catalysts were obtained after experiment above.

The Cu-Au/rGO bimetallic catalyst prepared by a simple fractional reduction method [31]. First of all, Cu/rGO monometallic catalyst was compounded through same method above, but with 10 ml of Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O precursor solution. The Cu/rGO monometallic catalyst was taken in to 100 ml deionized water and ultrasonicated for 1 h to get stable dispersion of Cu/rGO monometallic catalyst (Cu 0.5 wt.%). And then, 21 ml of HAuCl<sub>4</sub>·4H<sub>2</sub>O precursor solution were added drop wise under constant stirring (Au 0.5 wt.%). Subsequently, the following procedures were in accordance with the process of monometallic catalyst above. After repetitive suction filter washing and vacuum dried at 60 °C, the 0.5%Au-0.5%Cu/rGO (Cu-Au/rGO) bimetallic catalyst, metal weight proportion of which is 1:1, was compounded in the end. Deionized water was used throughout the studies.

#### 2.2 Characterization methods

Fourier Transform Infrared Spectroscopy (FT-IR) spectra was carried out to reflect the types of functional groups in three catalysts and its chemical environment, which was observed using an IRAffinity-1 (Shimadzu, Japan). Scanning Electron Microscope (SEM) images were taken on an S-4800 SEM (Hitachi Ltd., Japan) for the sake of observing the surface morphology of the catalysts. Transmission Electron Microscope (TEM) images were obtained with JEM-2010F TEM with an acceleration voltage of 160 kV (JEOL Ltd., Japan) and Energy-Dispersive Spectrometry (EDS) images were examined using EMA X350 (Horiba Ltd., Japan) at a voltage of 160 kV. EDS was performed at a resolution of 138 eV and the analyzable element range was B5-U92. X-ray Diffraction (XRD) patterns were collected to analyze the crystal structures using an X'Pert Pro MPD X-ray powder diffractometer (PANalytical B.V., Netherlands) with Cu radiation between 5 °and 80 ° at a scan rate of 4 °/min and an incident wavelength of 0.15406 nm (Cu K $\alpha$ ). X-ray Photoelectron Spectroscopy (XPS) patterns were recorded to analyze elements in catalysts qualitatively and quantitatively using PHI5300 ESCALAB (Pekin-Elmer PHI, USA) with Mg KII radiation. The pass energy was 2 min, the operand power was 250 W, and the scan step-size was 5 eV/step.

#### 2.3 Electrochemical measurements

Electrochemical experiments were carried out using a CHI 610 electrochemical workstation (CHI Instruments, Shanghai Chen Hua Instrument Co., Ltd., China) and a conventional three-electrode system. The system consists of a bare or modified glassy carbon electrode (GCE), an Ag/AgCl and a Pt wire used as the working electrode, the reference electrode and the auxiliary electrode, respectively. Before every use of glassy carbon electrodes (GCEs) (3 mm in diameter), they were polished with 0.3  $\mu$ m, 0.1  $\mu$ m and 0.05  $\mu$ m alumina slurry, ultrasonic cleaned twice using ethanol and deionized water and dried under a nitrogen environment. 2 mg catalyst (Cu/rGO, Au/rGO or Cu-Au/rGO) was dissolved in 50 ml of ethanol and dispersed uniformly with ultrasonic for 0.5 h. 10  $\mu$ L catalyst dispersion was dropped using a micropipette onto the surface of a prepared GCE and dried under infrared lamp to obtain modified electrode for electrochemical study. Cyclic voltammetry measurements were carried out at room temperature (25 ± 2 °C). The electrolyte was deoxygenated by purging them with highly-purity nitrogen for 30 min and maintained under nitrogen atmosphere during measurements.

## **3. RESULTS AND DISCUSSION**

## 3.1 Characterization of Cu/rGO, Au/rGO and Cu-Au/rGO composite

The FT-IR spectra of the GO, rGO, Cu-Au/rGO, Au/rGO and Cu/rGO are presented in Fig. 1a. The GO spectrum displays peaks at 3413, 1700, 1627, 1455, 1384 and 1060 cm<sup>-1</sup>, corresponding to the O-H stretching of carboxyl groups, C=O stretching of carbonyl and/or carboxyl groups, sp<sup>2</sup>-hybridized C=C groups and O-H stretching, C-OH stretching, and carboxy C-O, epoxy C-O and alkoxy C-O stretching vibrations. These data indicate the successful preparation of GO [32,33]. The majority of the

characteristic absorption peaks for O-containing functional groups on the GO are not observed in the spectra generated by the rGO and metal/rGO (M/rGO) nanocomposites, illustrating that the GO was effectively reduced to rGO, which is a prerequisite for successful catalyst preparation. The M/rGO FT-IR spectra primarily show the C=C stretching vibration peak (1627 cm<sup>-1</sup>) and C-O stretching vibration peak (1455 cm<sup>-1</sup>), demonstrating that the M/rGO catalysts were also fabricated successfully. The morphologies of the Cu/rGO, Au/rGO and Cu-Au/rGO (Figs. 1b, c and d) were characterized by SEM. These images show that the graphene surface was smooth, with white porphyritic metal nanoparticles uniformly supported on the external surface of the graphene and no agglomeration, meaning that the Cu-Au/rGO (Fig. 1d) had the smallest particle size and a uniform distribution. The grain sizes of the Cu nanoparticles in the Cu/rGO catalyst were relatively large while the loading was low. This result demonstrates the advantage of using a precious metal, which avoids agglomeration because oxidation of the Cu shell is suppressed in the presence of Au nanoparticle cores [34].



**Figure 1.** Fourier transform infrared spectroscopy (FT-IR) of GO(a), rGO and M/rGO & SEM patterns of Cu/rGO(b), Au/rGO(c) and Cu-Au/rGO(d)

Fig. 2 presents TEM images of the Cu/rGO, Au/rGO and Cu-Au/rGO nanocomposites. It can be seen that the metal nanoparticles were well distributed throughout the graphene matrix. The average sizes of the metal particles loaded on the graphene surface in the Cu/rGO (Fig. 2a), Au/rGO (Fig. 2b) and Cu-Au/rGO (Fig. 2c) catalysts were 7.89±0.30, 7.33±0.27 and 6.92±0.30 nm, respectively, in agreement with the result from SEM analysis. The relative weight amount of nanometals loaded on the graphene was greater than 70%, demonstrating that the metal atom utilization rate was relatively high

and that each of the three catalysts was prepared successfully. TEM-energy dispersive X-ray spectrometry (EDS) analysis at higher magnification was also performed, and the resulting spectra are shown in Fig. 2d. These data exhibit characteristic peaks for Au, Cu and C. TEM-EDS area mapping of all three samples determined that the Cu and Au concentrations in the Cu/rGO, Au/rGO and Cu-Au/rGO samples were respectively 0.7% and 0.8%, and 0.8% and 0.7% (Table 1). The elemental ratios of Au to Cu on the surfaces of the catalysts were in good agreement with the original inputs, which is one of the major conditions that has to be fulfilled in the design of multicomponent electrocatalysts.



**Figure 2.** TEM patterns and particle size distribution analysis (insert) of Cu/rGO(a), Au/rGO(b) and Cu-Au/rGO(c) & EDS (d) of three catalysts

Table 1. TEM-EDS analysis results of composition and content of M/rGO

M/rGO	C(wt%)	Cu(wt %)	Au(wt %)
Cu/rGO	85.5	0.7	
Au/rGO	84		0.8
Cu-Au/rGO	84.1	0.8	0.7

XPS studies were performed to determine the surface compositions of the Cu/rGO, Au/rGO and Cu-Au/rGO. The wide-range spectra of all three materials are provided in Fig. 3a. These spectra exhibit strong C1s, O1s, Cu2p and Au 4f signals. The Cu nanoparticles on the Cu/rGO and Cu-Au/rGO generated characteristic  $2p_{3/2}$  and  $2p_{1/2}$  peaks associated with the Cu<sup>0</sup> spin system at 932.7 and 952.6 eV,

respectively (Fig. 3b). These peaks could be further deconvoluted into dual peaks at 934.29 and 938.67 eV and 951.40 and 952.04 eV respectively. These results can be attributed to Cu<sup>0</sup> and Cu<sup>2+</sup>, suggesting the presence of copper oxide on the Cu surface. Furthermore, three characteristic 4f signals due to Au<sup>0</sup> nanoparticles on the Au/rGO and Cu-Au/rGO catalysts were observed at 89.42, 87.7, 84.4 and 90 eV. which can be assigned to  $Au^04f_{5/2}$ ,  $Au^04f_{7/2}$  and  $Au^{3+}4f_{5/2}$  (Fig. 3c). It is also evident that the Au in the Au/rGO and Cu-Au/rGO catalysts was present in more than one chemical state (Au<sup>0</sup>, Au<sup>3+</sup>). The percentages of zero-valence metals in the Cu/rGO, Au/rGO and Cu-Au/rGO catalysts are summarized in Tables 2 and 3 to allow direct comparisons. These data show that 51.23% of the Cu<sup>2+</sup> was reduced to  $Cu^0$  in the Cu/rGO and 64.51% of the Au<sup>3+</sup> was reduced to Au<sup>0</sup> in the Au/rGO, while 80.53% of the Cu<sup>2+</sup> and 72.51% of the Au<sup>3+</sup> were reduced to their free forms in the Cu-Au/rGO. Thus, the zero valence reduction ratio of Au<sup>3+</sup> in the Cu-Au/rGO was slight higher than that in the Cu/rGO, although the proportion of Cu<sup>2+</sup> ions reduced in the Cu-Au/rGO bimetallic catalyst was 29.3% greater than in the Au/rGO. These results indicate that the proportion of zero-valence metal atoms in the Cu-Au/rGO was greater than in either of the monometallic catalysts. This higher proportion of zero-valence atoms would be expected to improve the conductivity of the catalyst and to enhance its catalytic performance [35,36]. Fig. 3d presents the narrow C XPS spectra for the GO, rGO and three kinds of M/rGO. It is evident that the C was primarily in the form of -C=C-, C=O-C and O=C-O groups, and a detailed analysis of the chemical state of C in these compounds is provided in Table 4. These data confirm that the C in the M/rGO samples was largely present as -C=C-, indicating that rGO was successfully obtained from the reduction of GO. The Cu-Au/rGO also had a relatively high -C=C- concentration, in agreement with the FT-IR characterization (Fig. 1a). The addition of the metal precursor evidently enhanced the degree of reduction of the oxidized functional groups by the sodium borohydride. Consequently, the graphene component of the catalyst had more double bonds, which is the primary reason for the excellent electrochemical performance of rGO.

The nanometals loaded on the three catalysts were also characterized using powder XRD. The pattern in Fig. 3e shows that the natural graphite had a layered structure with regularly arranged atoms. The characteristic graphite diffraction peak appears at 27°, and the peak shape is sharp, indicating ordered graphite crystals. After oxidation by the modified Hummers method, the characteristic graphite oxide peak is shifted to approximately 12°, while the peak shape is relatively flat and broad and the peak intensity is much lower than that in the graphite pattern. These results indicate that the layered structure of the graphite was degraded following oxidation. In addition, O-containing functional groups such as hydroxyl and carbonyl groups were produced between the graphite layers, so that the original XRD peak positions were shifted.



Figure 3. XPS full spectrum (a), narrow spectrum of Cu in Cu/rGO and Cu-Au/rGO (b), narrow spectrum of Au in Au/rGO and Cu-Au/rGO (c) and C in GO, rGO and M/rGO catalysts

An additional peak appears at  $24^{\circ}$  in all three M/rGO XRD patterns, attributed to graphene. The patterns produced by the Cu/rGO and Au/rGO clearly show one and two major peaks, respectively, at  $43^{\circ}$  and at  $38.1^{\circ}$  and  $44.4^{\circ}$ . These can be assigned to diffraction from the {111} planes of the face-centered cubic lattice of Cu(0) and from the {111} and {200} planes, respectively, of the face-centered cubic lattice of Au(0). The peak at  $38.1^{\circ}$  in the Cu-Au/rGO pattern in Fig. 3e is assigned to Au {111}. Because of the similarity between the characteristic Au {200} and Cu {111} peaks, the peak at  $43^{\circ}$  in Fig. 3e can likely be ascribed to both Au {200} and Cu {111}, although this is not certain. However, the

TEM-EDS results in Fig. 2d do confirm that the peak in the Cu-Au/rGO XRD pattern is related to the coexistence of Au and Cu. These XRD results clearly indicate that Cu and Au nanoparticles were introduced onto the graphene surfaces by chemical reduction. Using the Scherrer formula [37], D values of 13.44, 7.66 and 7.17 nm were calculated based on the experimental results, which are in good agreement with the SEM and TEM observations. Thus, these materials appear to represent an ideal interface for use in an electrochemical sensor.

Catalysts	Spectral Line	Cu <sup>(0)</sup> 2p1/2	Cu <sup>(2+)</sup> 2p1/2	Cu <sup>(0)</sup> 2p3/2	Cu <sup>(2+)</sup> 2p3/2
Cu/rGO	Binding energy/eV	954.39	951.43	937.30	933.79
	Percent (%)	22.26	19.15	26.51	32.08
Cu-Au/rGO	Binding energy/eV	952.00	951.40	938.67	934.29
	Percent (%)	5.09	10.57	14.38	69.96

Table 2. XPS binding energy and state, contents of Cu element

Table 3. XPS binding energy and state, contents of Au element

Catalysts	Spectral Line	Au <sup>(3+)</sup> 4f5/2	Au <sup>(0)</sup> 4f5/2	Au <sup>(3+)</sup> 4f7/2	Au <sup>(0)</sup> 4f7/2
Cu/rGO	Binding energy/eV	89.40	87.78	85.96	84.2
	Percent (%)	10.54	40.75	16.95	31.76
Cu-Au/rGO	Binding energy/eV	89.42	87.70	85.96	84.40
	Percent (%)	13.34	38.38	22.15	26.13

Table 4. State and contents (%) analysis of C1s

Catalysts	C content (%)	284.6 eV (-C=C-)	286.24 eV (C-O-C)	288.7 eV (O-C=O)
GO	73.78	33.31	55.45	11.24
rGO	85.12	56.36	30.62	13.02
Cu/rGO	87.51	67.35	23.53	9.12
Au/rGO	84.50	70.73	20.91	8.36
Cu-Au/rGO	89.31	72.43	20.12	7.45

## 3.2 Optimization of electrochemical detection conditions

To select an appropriate electrolyte, CH<sub>3</sub>COONa-CH<sub>3</sub>COOH, Na<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub>, KNO<sub>3</sub>-HNO<sub>3</sub>, Na<sub>2</sub>HPO<sub>4</sub>-NaH<sub>2</sub>PO<sub>4</sub> (PBS), NaCl, K<sub>2</sub>SO<sub>4</sub> and other common metal salts were respectively employed to make 0.1 mol/l solutions containing 50 µmol/L 4-CP, for use as the supporting electrolyte. Considering that the pH of wastewater containing CPs is typically in the range of 6 to 9, the pH of each electrolyte was adjusted to 6.5. The CV data obtained for Cu/rGO/GCE, Au/rGO/GCE and Cu-Au/rGO/GCE using the different electrolytes while maintaining all other conditions the same are presented in Fig. 4. The

largest 4-CP oxidation peak was obtained in the PBS buffer, with values of 16.6, 18.3 and 27.6  $\mu$ A obtained from the Cu/rGO/GCE, Au/rGO/GCE and Cu-Au/rGO/GCE, respectively. The PBS buffer gave the best results because it has a superior balance between salt ions and buffer components, and the ability to reduce and stabilize the electric double layer on the surface of the electrode, thus improving the electrochemical response to 4-CP. Based on these results, PBS was chosen as the supporting electrolyte for subsequent 4-CP trials, as it also provides pH buffering.



**Figure 4.** CV curves of Au/rGO/GCE(a), Cu/rGO/GCE(b) and Cu-Au/rGO/GCE(c) in 4-CP containing different buffers

With the aim of obtaining the best sensitivity for 4-CP and determining the linear response range, the effect of the pH of the PBS electrolyte was investigated at room temperature. These trials were

performed because the pH of the PBS buffer has been found to significantly affect the current response of the electrode [38]. As shown in Figs. 5a1, a2 and a3, the steady-state current increased with increases in the pH from 5.0 to 6.5, but decreased with further increases from 6.5 to 8.0. The maximum current was achieved at a pH of 6.5, which was close to the optimum pH observed during prior 4-CP determination trials.



Figure 5. CV curves of three modified electrodes in different pH 0.1 mol/L PBS containing 50 μmol/L 4-CP and relationship between pH and I<sub>pa</sub> (a, a1) Cu/rGO/GCE, (b, b1) Au/rGO/GCE, (c, c1) Cu-Au/rGO/GCE

The oxidation peak potential also changed along with the pH, indicating that the 4-CP oxidation reaction was accompanied by the transfer of protons and electrons. The oxidation peak potentials obtained from the three modified electrodes were 16.6, 18.3 and 29.6  $\mu$ A, respectively. These potentials

exhibited the same trends with changes in pH, demonstrating that the catalyst did not affect the relationship between  $I_{pa}$  (peak current) and pH. As a result, we selected 6.5 as the optimum value for 4-CP determination, as this value produced higher sensitivity.

CV trials were used to assess the effect of scan rate on the analysis of a 50  $\mu$ mol/L 4-CP solution in pH 6.5 PBS, using the metal/rGO/GCEs. As shown in Fig. 6, a plot of the 4-CP oxidation peak current (I<sub>pa</sub>) against the square root of the sweep rate (*v*), using scan rates between 25 and 1000 mV/s forms a straight line (insert to Fig. 6). The associated linear equations for the three catalysts are [39]:

Cu/rGO/GCE: 
$$I_{pa} (\mu A) = 2.7763 v^{1/2} - 5.0299 (R^2 = 0.989)$$
 (1)  
Au/rGO/GCE:  $I_{pa} (\mu A) = 2.9342 v^{1/2} - 0.8822 (R^2 = 0.997)$  (2)

Cu-Au/rGO/GCE: 
$$I_{pa} (\mu A) = 2.5177 v^{1/2} + 0.2055 (R^2 = 0.99)$$
 (3)



**Figure 6.** CVs of Cu/rGO/GCE (a), Au/rGO/GCE (b) and Cu-Au/rGO/GCE (c) at different scanning rates and relationship between  $v^{1/2}$  and  $I_{pa}$  (a1, b1, c1)

These outcomes demonstrate that the reaction of 4-CP is controlled by diffusion and by surface reactions, which is beneficial to quantitative determinations [40]. The linear relationship between  $I_{pa}$  and  $v^{1/2}$  can be summarized as  $I_{pa} = nFQv/4RT$ , where n is the number of electrons transferred, F is the Faraday constant (96,485 C/mol), Q is the oxidation peak area in the CV curve, and R and T are the ideal gas constant and room temperature, respectively. This equation suggests that the process is largely dominated by the rate of surface reactions [41]. Using this relationship, the calculated values of n are: Cu/rGO/GCE (0.96), Au/rGO/GCE (0.85) and Cu-Au/rGO/GCE (0.87). These data indicate that the total number of electrons involved in the 4-CP oxidation reaction is 1 [42]. A possible reaction mechanism for 4-CP oxidation over the Cu/rGO/GCE, Au/rGO/GCE and Cu-Au/rGO/GCE can be summarized using the equations [43]:



When graphene modified electrodes used for electrochemical detection, the charging current of electric double layer will increase. Too high scan rate will cause the increasing charging current and reduce the accuracy of determination results. According to the 4-CP test results of scanning rate and considering the needs of sensitive quick experiment, we choose 100 mv/s as the fitting scan rate.

## 3.3 The linear range and detection limit

Fig. 7 shows the CV data acquired from the Cu/rGO/GCE, Au/rGO/GCE and Cu-Au/rGO/GCE specimens at various 4-CP concentrations using the optimal experimental conditions (pH=6.5 in a PBS buffer). The three modified electrodes exhibited oxidation peaks at approximately 0.37 V (Cu/rGO/GCE), 0.41 V (Au/rGO/GCE) and 0.51 V (Cu-Au/rGO/GCE). The oxidation peak current also increased linearly with the 4-CP concentration over the range of 1–100  $\mu$ mol/L 4-CP, in accordance with the differential equations [17]:

Cu/rGO/GCE: 
$$I_{pa}(\mu A)=0.7829C(\mu mol/L)+4.8085(R^2=0.985)$$
 (8)  
Au/rGO/GCE:  $I_{pa}(\mu A)=0.7925C(\mu mol/L)+5.3032(R^2=0.984)$  (9)

Cu-Au/rGO/GCE: I<sub>pa</sub>(µA)=0.7925C(µmol/L)+5.3080 (R<sup>2</sup>=0.984) (10) The limit of detection (LOD) values for the Cu/rGO/GCE, Au/rGO/GCE and Cu-Au/rGO/GCE electrodes (based on a minimum signal to noise ratio (S/N) of 3) were found to be 0.34, 0.17 and 0.10 µmol/L, respectively. The performances of our metal/rGO/GCE sensors are compared with those of other published 4-CP sensors in Table 5. It can be seen that the present sensors exhibit a very fast response, a superior detection limit and a wide linear range.



**Figure 7.** CVs of Cu/rGO/GCE (a), Au/rGO/GCE (b) and Cu-Au/rGO/GCE (c) in different 4-CP concentrations & relationship between  $v^{1/2}$  and  $I_{pa}$  (a1, b1, c1)

The wide linear range obtained from these devices may be due to the high surface-to-volume ratio, which provides more electroactive sites and larger surface areas for 4-CP molecules to adsorb and

react. The rapid, sensitive catalytic performance is attributed to the enhanced electron transfer, while the superior catalytic activity is afforded by the nanocomposite structure of the Cu, Au and Cu-Au nanoparticles and graphene sheets. The lowest detection limit of 0.10 µmol/L was obtained with the Cu-Au/rGO/GCE. This result indicates that the bimetallic modified electrode possessed better sensitivity and stability in the presence of 4-CP compared to previously reported devices. Moreover, the proposed Cu-Au/rGO electrode also demonstrates faster response and a lower detection limit than those provided by typical oxidase-based biosensors, in which oxidase is immobilized on the electrode surface in the presence of graphene sheets and thin-walled graphitic nanocages [44,45].

Electrode material	Linearity range ( $\mu$ mol·L <sup>-1</sup> )	LOD ( $\mu$ mol·L <sup>-1</sup> )	Reference
Cu/rGO	0.5-65	0.23	This study
Au/rGO	0.5-80	0.17	This study
Cu-Au/rGO	0.5-85	0.10	This study
Nafion/CNT	1-25	12.09	Arribas et al. [46]
Ag-PTA NPs/CTS/TiO	1-400	0.34	Zhu et al. [47]
Tyr-MPA-AuE	0.4-40	0.15	Campuzano et al. [44]
Laccase & tyrosinase	1-10	0.09	Renato et al. [45]
CNT/PPy	1.6-14.4	0.3	Korkut <i>et al</i> . [48]
ZnO nanorod microarrays/BDND	1-150	0.2	Zhao et al. [49]

Table 5. Comparison of electrochemical detection of 4-CP

Electrochemical impedance spectroscopy (EIS) was used to determinate the resistance of the bare GCE, Cu/rGO/GCE, Au/rGO/GCE and Cu-Au/rGO/GCE in a 5 mmol/L Fe(CN)<sub>6</sub><sup>3-/4-</sup> solution containing 1 mmol/L KCl. Fig. 8 demonstrates that the impedance associated with the resistance of the units was significant modified after the various catalysts were used to modify the GCE. The impedance spectrum of the bare GCE showed a largest circular arc in the high frequency part, with an impedance of approximately 320  $\Omega$ , while the Cu/rGO/GCE, Au/rGO/GCE and Cu-Au/rGO/GCE showed values of 302, 232 and 205  $\Omega$ , respectively. The GCE modified with the Cu-Au/rGO exhibited the lowest impedance, suggesting that this catalyst had the smallest resistance. This would be expected to enhance the conductivity of the catalyst and improve its performance.

Overall, the characterization data show that the Cu-Au/rGO had the smallest metal particle size (as per the XRD data), highest degree of dispersion (SEM) and the highest relative concentration of zero-valence metals (XPS). After the electrochemical performance tests, this material generated the minimum impedance and maximum CV values under the optimum conditions (PBS, pH=6.5, scan rate=100 mV/s). Furthermore, EIS analyses demonstrated that the Cu-Au/rGO had the lowest resistance, which is

consistent with the other results. Based on these data, the Cu-Au/rGO outperforms the Cu/rGO and Au/rGO and would be preferred for the electrochemical detection of 4-CP.



Figure 8. EIS curves on different modified electrode

#### 3.4 Selectivity, repeatability and stability

The reproducibility of the Cu-Au/rGO/GCE were investigated based on ten successive analyses of a 4-CP solution in 0.1 mol/L PBS. The resulting relative standard deviation (RSD) was 2.10%, indicating a suitable level of performance. Five parallel electrodes with each modifier were prepared under the same conditions and applied to the analysis of this same solution and the relative standard deviation was 2.15%, indicating excellent fabrication reproducibility.



**Figure 9.** Stability (a) and selectivity (b) of Cu-Au/rGO/GCE upon determining 50 µmol/L 4-CP (n=3). Error bar represents the standard deviation of triple measurements.

The storage stability of the modified electrode (Fig. 9(a)) was also studied, and the peak current response was found to decrease by 3.1%, 3.55%, 5.67% and 8.43% relative to the initial current response after 3, 7, 14 and 28 days of storage at room temperature. These results indicate excellent stability. Furthermore, various common inorganic ions and organic compounds (0.1 mmol/L Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>,

 $Zn^{2+}$ ,  $C1^-$  and  $SO_4^{2-}$  and 0.05 mmol/L glucose and ethanol) were added to the electrolyte (0.1 mol/L PBS) to assess the potential for interference with 4-CP detection. The results in Fig. 9(b) demonstrate a relative error of less than 3% and so confirm a negligible degree of interference. Based on the above results, the Cu-Au/rGO/GCE displayed good selectivity, repeatability and stability with regard to 4-CP detection.

#### 3.5 Sample analysis

The proposed sensor was used for the determination of 4-CP in a artificial wastewater. The standard addition method was applied by adding increasing concentrations of 4-CP to tap water to assess the analysis of 4-CP using all three catalyst modified electrodes. As shown in Table 6, which provides the averages from four replicate analyses, the recoveries were all in the range of 98.3%–102.3%. These data demonstrate that these electrodes may have practical applications to the detection of chlorinated organic pollutants.

**Table 6.** Recovery of 4-CP in simulated water samples using Cu-Au/rGO nanoparticle electrochemical sensor

Samples	Input (µmol/L)	Output (µmol/L)	Recovery (%)
1	1.00	$1.01\pm0.03$	98.3~101.8
2	2.00	2.01±0.05	99.0~100.9
3	5.00	4.97±0.06	99.2~102.3

#### **4. CONCLUSIONS**

Cu/rGO and Au/rGO monometallic catalysts and Cu-Au/rGO bimetallic catalysts were successfully prepared by chemical reduction method which is simple and facile. Compared with Cu/rGO and Au/rGO, Au and Cu particles supported on rGO in Cu-Au/rGO had the smallest metal particle size, good dispersibility, the relative most content of zero-valent metals, minimum impedance and possessed larger active surface area. Under the contrast, prepared Cu-Au/rGO/GCE showed good electrochemical properties, exhibited the lowest detection limits (0.10 µmol/L) and could be used in a wider range of 4-CP concentrations (0.50-85 µmol/L). This high 4-CP sensitivity could be attributed to the excellent electrocatalytic activity of Cu-Au bimetallic particle and large specific surface area of the rGO. In addition, the composite electrode displayed good selectivity toward 4-CP, even in the presence of various common ions and familiar organic compounds. The real sample analysis result indicated that the electrode was highly selective and sensitive to 4-CP. The high stability, reproducibility, and shelf-life make this composite electrode a suitable device for the detection of 4-CP in industrial samples.

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