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Sonochemical preparation of carbon nanosheets supporting cuprous oxide architecture for high-performance and non-enzymatic electrochemical sensor in biological samples

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ABSTRACT

Copper (Cu) based metal oxides have high electrocatalytic ability. In this work, we are synthesized stone-like cuprous oxide particles (Cu_2O SNPs) covered on acid functionalized graphene oxide (GOS) sheets using ultrasonic process (50 kHz and 100 W). Besides, the chemical structural and crystalline analyses of Cu_2O SNPs@GOS composites were characterized by transmission electron microscopy, X-ray crystallography and energy-dispersive X-ray spectroscopy. The Cu_2O SNPs@GOS nanomaterials were tested towards detection of 8-hydroxydeoxyguanosine (8-OHdG) in biological samples. As expected Cu_2O SNPs@GOS catalyst modified electrodes performed an outstanding catalytic ability on 8-hydroxydeoxyguanosine oxidation. 8-OHdG is oxidative stress biomarker. Further, it is noted that the detection performance of Cu_2O SNPs@GOS coated electrodes and it's highly enhanced due to the synergistic effect of Cu_2O SNPs and GOS. Besides, the modified materials provide more electro-active faces and as well as rapid electron transport pathway and shorten diffusion. Moreover, oxidation of 8-OHdG sensor is exploring a long linear or working range of 0.02–1465 μM and high sensitivity (8.75 nM). The viability of the Cu_2O SNPs@GOS proposed electrochemical methods have tested, to find out 8-OHdG concentrations in biological fluids (blood serum and urine) with a satisfying recovery ranges.

1. Introduction section

Sonochemical and ultrasound–assisted nanomaterials are considered as an highly effective and robust method compare to other methods such as hydrothermal and chemical vapor deposition methods (CVD synthesis of nanomateriasls) [1,2]. Because, ultrasound based irradiation approach is low reaction time and formation of particle size is high unique [3–5]. Besides, the metal dioxides materials have efficient properties based on electrochemical analysis and energy storage applications. Copper based metal oxides and materials are outstanding performances in various fields such as electrochemical detection and determination, degradation of toxic pollutants, biochemical applications and etc [6,7]. Cuprous oxides have been developed variety of nanocrystal structures using copper(II) sulfate and copper chloride [8]. Recent years, many methods are applied to develop a cuprous oxides based composite such as sol-gel methods, CVD, and hydrothermal methods. Moreover, those methods to synthesis of verity of nanostructures such as nanorods, nanospheres, nanocubes, nanosheets, nanoflower, nanostars and nanowires of cuprous oxides [9,10]. In general, copper based metal oxides have fast-electron transfer, thermal and biocompatible properties [11]. Further, it becomes a high conductor of metal dioxides and their easy agglomeration, increase operating speed to create electrochemical electron-transfer directly. It results are good sensing performances due to catalytic abilities and such

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as metal dioxides are making as a nanocomposites in addition of carbon sheets to improve the electron transfer mechanism of the work (sensing properties). The photochemical and catalytic performances have been various research work using Cu_2O nanoparticles. In this work, Cu_2O NPs based nanomaterials and composition has been developed with acid functionalized graphene oxide nanosheets as an modified electrode material [12,13]. Ultrasonic irradiations and waves are help to growth, formation, collapse of bubbles and acoustic cavitation in nanocomposite.

Moreover, the Cu_2O SNPs@GOS nanomaterial has been modified with GCE and applied an effective electrochemical sensing application towards oxidative stress biomarker of 8-OHdG (8-Oxo-2′-deoxyguanosine) [14]. Because of, an 8-OHdG compound is increased from human cells due to oxidative stress of human body. Further, 8-OHdG is one of the derivatives from deoxyguanosine compounds and biomolecule. It is one of the biomarker for oxidative stress diseases [14–16]. Its levels for body fluids increase for 8-Oxo-2′-deoxyguanosine. A quantitative determination of 8-OHdG in biological samples is more important. Moreover, different analytical and chemical methods are developed for sensing of biomolecules and biomarkers such as capillary based electrophoresis methods, mass coupled HPLC, UV-spectrometry and electrocatalytic methods [16–18]. Herein, Cu_2O SNPs/GOS based nanomaterial has been developed with highly sensitive detection of 8-OHdG by CV and amperometric methods. Preparation of Cu_2O SNPs and GOS has unique and different physical and chemical properties. The electrochemical method is more simples and facile method compare to HPLC and other methods. Many researchers are focusing electrochemical methods; due to simplicity in laboratories for depends on time consumption and cost effective [13,19,20]. Recently, electrochemical determine method has more popular for 8-OHdG sensing using various nanomaterials modified electrodes. Hence, the variety of electrochemical techniques are applied fast years and it's like CV, LSV, DPV and amperometric methods. Because, those methods are sensitivity, low-cost, accurate and reliable analysis.

2. Experimental section

2.1. Facile preparation of cuprous oxide modified with graphene oxide

In this preparation of cuprous oxide decorated acid functionalized graphene oxide nanocomposite was prepared using copper acetate. 400 mg of $Cu(CH_3COO)_2$ (copper acetate) was mixed using 30 mL DI water. Then, the reaction solution was stirred with magnetic pellets for 30 min. Then, the reaction solution was transferred to ultrasound irradiation process (ultrasonic horn; PCI Analytics Pvt. Ltd/50 kHz/power of 100 W) for 30 min. After the reaction time, the change of the solution was from blue to brick-red color precipitate (with solution). In this color of the solution is indicating formation of the Cu_2O materials. Further, the reaction mixture solution was washed with distilled water and alcohol (ethanol). Then, the brick-red color precipitate of the product was centrifuged at 6000 RPM and the colloidal precipitate was dried at electric oven at 80 °C. Moreover, the prepared, Cu_2O powder was analyzed by TEM, EDS, XRD and quantitative analysis (Scheme 1). Furthermore, 20 g of acid functionalized graphene oxide sheets were dissolved in 30 mL of DI water under stirring at 80 °C for 30 min and the solution was obtained. 20 mg of Cu_2O NPs added in above solution. Moreover, the solution was sonicated for 30 min and then, the collected sample was dried and then heated at electric oven for 12 h. After that, the powder is cooling to room temperature and the final Cu_2O/GOS hybrid product was collected.

2.2. Fabrication of Cu_2O/GOS hybrid with glassy carbon electrode (GCE)

Before the fabrication process, the surface of the glassy carbon electrode (GCE) was washed with 0.05 μm alumina slurry and washed with DI water and washed GCE was dried at electric oven. After, 8 μL of Cu_2O SNPs/GOS hybrid was drop by drop casted on the surface of GCE. Then, the Cu_2O SNPs/GOS hybrid covered electrode was dried at electric oven. Finally, Cu_2O SNPs/GOS hybrid/GCEs were and used for electrochemical detection.

3. Results and discussions

3.1. Morphological and X-ray powder diffraction analysis Cu_2O SNPs/GOS hybrid

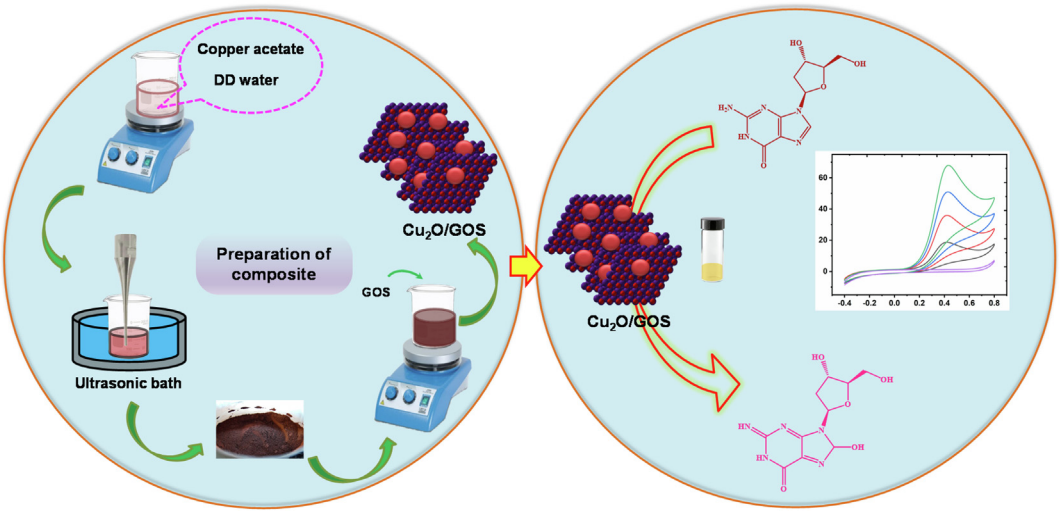
The surface analysis of prepared Cu_2O particles (Fig. 1F) and Cu_2O/GOS hybrid was analyzed by TEM. Fig. 1A-C shows, the TEM images of Cu_2O/GOS hybrid and it's clearly showed a compact arrangement of stone shaped Cu_2O nanoparticle with acid functionalized graphene oxide sheets during the sonochemical process and also it's a nano sized electrode material. The TEM image of Cu_2O/GOS hybrid was also shown in Fig. 1C. Moreover, a sheet like cluster (Fig. 1D and E) was observed for the formation of graphene oxide sheets on the surface of Cu_2O nanoparticle. Notice that the Cu_2O well covered with the sheet liked GOS after the ultrasound method, indicating the successful formation of Cu_2O SNPs/GOS hybrid.

In addition, the EDX analysis of Cu_2O SNPs/GOS hybrid was further measured and shown in Fig. 2. The corresponding each elemental percentage of Cu_2O/GOS hybrid was indicated as follows; Cu = 19.3%, O = 21.2%, and C = 59.5%. Clearly, a uniform scattering of C, Cu and O were displayed for the Cu_2O SNPs/GOS hybrid in elemental analysis and it's confirm that the successful formation of Cu_2O SNPs/GOS composition. The crystal analysis of the Cu_2O SNPs@GO material is presented in Fig. 3. The XRD peaks are located at 29.6, 36.7, 42.4, 61.7, 74.3, and 77.2° corresponds to the crystalline planes of Cu_2O SNPs are (1 1 0), (1 1 1), (2 0 0), (2 2 0), (3 1 1), and (2 2 2) planes of cubic crystal structure (Cu_2O SNPs) with JCPDS number 65-3288 [21–23]. Further, XRD diffraction peaks are detected at 10.0 to 15.0°, consistent to the (0 0 2) plane is attributed to acid functionalized graphene oxide sheets [24,25].

3.2. Electrochemical 8-OHdG oxidation at Cu_2O SNPs@GOS coated electrode

Herein, the electrochemical response of the unmodified electrode (bare GCE), Cu_2O SNPs@GCE, graphene oxide sheets@GCE, and Cu_2O SNPs/GOS@GCE are analyzed at a scan rate of 0.05 V/s. The experimental solution condition is presence of 0.05 M phosphate buffer with 50 μM of 8-OHdG biomarker (pH 7.0). All electrochemical experiments are used as phosphate buffer pH 7.0 (0.05 M). Because, working conditions are optimized such as pH analysis, scan rate analysis and concentrations analysis. Effect of the electrolyte and conditions checked with different pHs (3.0 to 11.0) on the electrochemical oxidation of 50 μM 8-OHdG biomarker at Cu_2O SNPs@GOS nanocomposite electrode. Further, the Cu_2O SNPs@GOS/glassy carbon electrode shows sharp oxidation or anodic peak response at pH 7.0 and it's gradually increased pH 7.0. Nevertheless, after the oxidation peak responses were decreased (higher pH ranges). According to the electrochemical detection of 8-OHdG biomarker and previous articles, the electrochemical mechanism is two protons and two electrons reaction (Scheme 2), which would assist the electrochemical oxidation at pH 7.0 values (phosphate buffer). It's shows higher current response due to catalytic effect of the modified materials and as well as electrolyte conditions. Furthermore, the anodic peak potential of 8-OHdG biomarker was fixed on the pH values. In this work, phosphate buffer was used as a suitable pH conditions.

According to obtained CV analysis, the bare electrode of GCE shows a small electrochemical oxidation peak current and acid functionalized graphene oxide modified GCE shows little high response towards oxidation of 8-OHdG biomarker. Further, Cu_2O SNPs@GOS modified electrode, shows an excellent electrochemical oxidation current



Scheme 1. Ultrasound-assisted preparations and fabrication of Cu_2O SNPs@GOS nanocomposite, and its applications in electrochemical sensing.

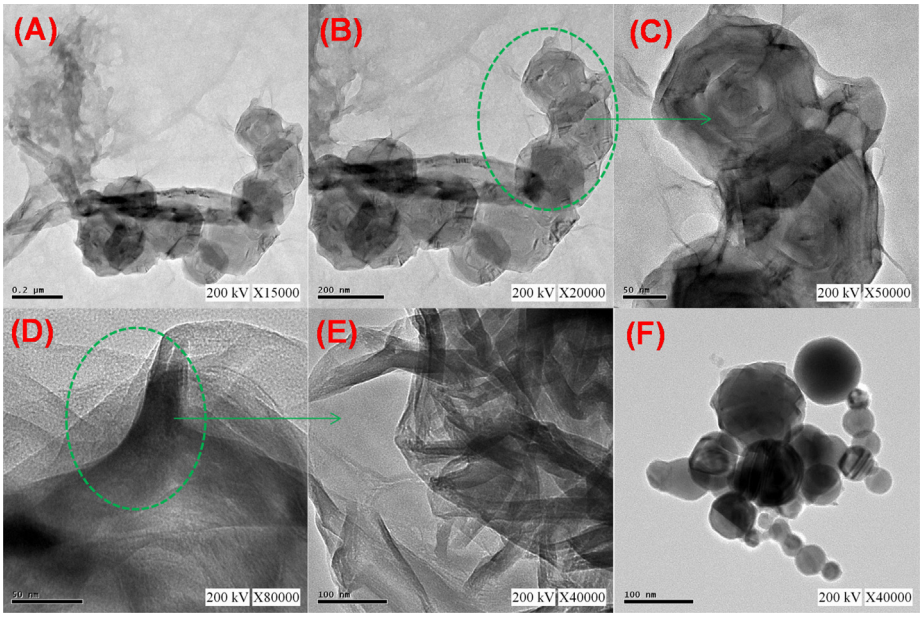


Fig. 1. TEM images of Cu_2O@GOS (A-C). TEM images of GOS (D and E) and Cu_2O NPs (F).

response towards 8-OHdG biomarker (Fig. 4A and B). Because, the electrochemical properties of the modified material and electro-active sites are good and it enhance the catalytic performance of the sensor and work [26]. In addition, corresponding calibration plot of the electrochemical performances was given in Fig. 4B. These results are confirmed that the Cu_2O SNPs@GOS material exhibited valuable performances due to fast electron transfer effect of copper based metal oxide.

Fig. 5A, shows that the electrochemical peaks of the Cu_2O SNPs@GOS covered GCE at different concentrations of 8-OHdG biomarker from 100 to 400 μM in 0.05 M (pH 7.0) phosphate buffer at a scan rate of 0.05 V/s. Furthermore, the oxidation peak and anodic current response of 8-OHdG biomarker is moderately increased without any fouling of the currents (100–300 μM). Moreover, the linear relation and correlation plot of the oxidation performance was analyzed from Fig. 5B (8-OHdG concentration versus peak current. According to Fig. 5B, regression equation is I_{pa} (μA) = 0.1656 [8-OHdG] + 2.08 (μM) with the correlation co-efficient of the equation (R^2) = 0.9952. Therefore, the modified nanomaterial has anti-fouling property. In addition, the Fig. 6A shows, is effect of the scan rate in this work. The Cu_2O SNPs@GOS/GCE at scan rate ranges from 20 mVs to 200 mV/S in 50 μM of the 8-OHdG biomarker (condition: 0.05 M/phosphate buffer/pH 7.0). Besides, the anodic peak responses of the 8-OHdG biomarker were increased linearly with ranges of the scan rate 20 mVs to 200 mV/S. Fig. 6B is explained the calibration plot of the scan rate versus anodic peak current of 8-OHdG sensor. Besides, the regression equation is I_{pa} (μA) = 0.0764 (Vs^{-1}) + 18.181 (μM) and the correlation co-efficient of the reaction is (R^2) = 0.9929. Therefore, these results suggests that the reaction process of the Cu_2O NPs@GOS sensor follows a surface confined process [27–29].

3.3. Electrochemical analysis of 8-OHdG biomarker at Cu_2O SNPs@GOS modified electrode

The amperometric technique (i-t) is one the important method in electrochemical aspect. The electrochemical performances and parameters of the Cu_2O SNPs@GOS modified RDE (rotation disk electrode) was analyzed toward the oxidation of 8-OHdG biomarker by using amperometric method (Fig. 7A). The electrochemical anodic and oxidation responses of the Cu_2O SNPs@GOS/RDE were increases with the

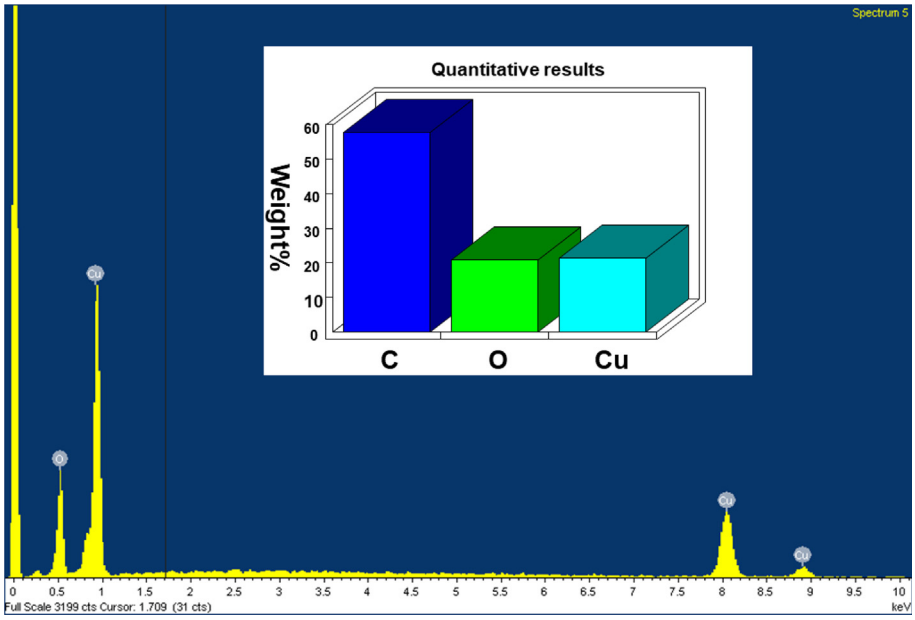


Fig. 2. EDX profiles of Cu_2O SNPs/GOS NC. Quantitative analysis of Cu_2O@GOS NC consists of C, Cu, and O atoms.

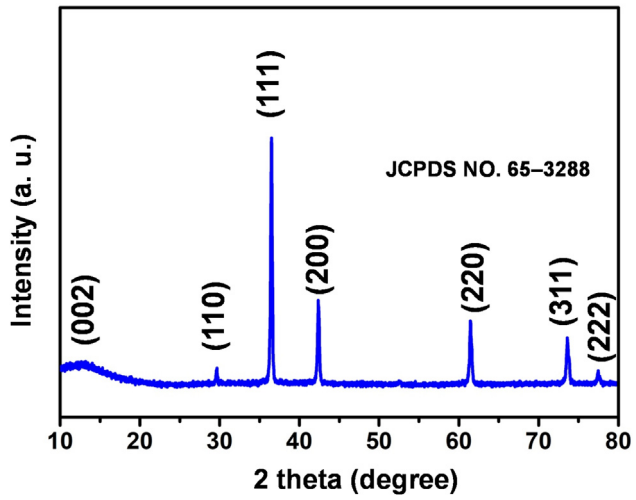
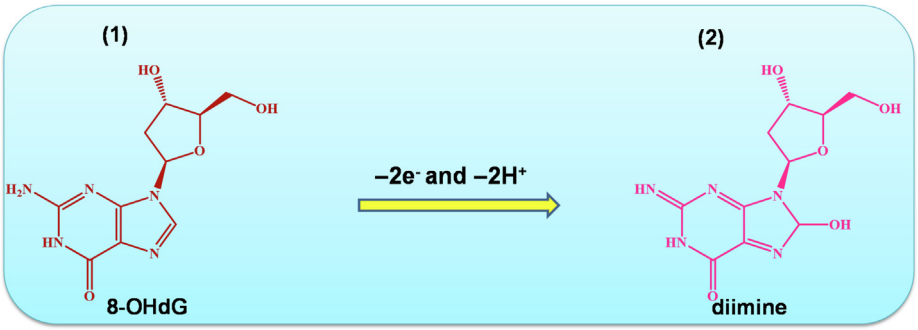


Fig. 3. XRD analysis of Cu_2O SNPs/graphene oxide sheets based nanocomposite.

concentration of 8-OHdG biomarker in the range of 0.02 μM–1565 μM. Further, this experiment can be clearly seen that the oxidation peak of 8-OHdG biomarker and it's exhibited a sharp electrochemical oxidation peaks. In addition, the electrochemical oxidation and currents was increased linearly in the range from 0.02 to 1465 μM as shown in Fig. 7B. Further, the electrocatalytic equation is I_{pa} (μA) = 0.0468 [8-OHdG] + 0.75 (μM) and R^2 = 0.9978. Besides, the limit of detection (LOD) is calculated using as equation $3S_a/s$ [30–32]. Further, 'S_a' is the standard deviation of blank current and sensitivity of the reaction is S [33,34]. According to this reaction and equation, limit of detection is 8.75 nM and the sensitivity of 8-OHdG detection is 0.235 μA μM^{-1} cm^{-2}. Moreover, the electrochemical parameters are compared with other works and materials and given in Table 1. According to Table 1 and comparison of parameters, the Cu_2O SNPs@GOS modified RDE has excellent oxidation property compare than previously articles.

Anti-interference analysis is highly important for electrochemical sensor application. In this work, potentially interfering biomolecules and metal ions such as H_2O_2, dopamine, uric acid, ascorbic acid, hydrazine, serotonin, epinephrine, glucose, 8-nitroquinoline, gallic acid, caffeine and paracetamol has been analyzed by amperometric method [35,36]. The sensor performances were obtained at ten-fold of the biomolecules and metal ion species such as H_2O_2, dopamine, uric acid, ascorbic acid, hydrazine, serotonin, epinephrine, glucose, 8-nitroquinoline, gallic acid, caffeine and paracetamol. The of 8-OHdG sensor peak response not affected (error percentage is less than 8%). Moreover, these experimental analyses are confirmed that Cu_2O SNPs@GOS modified electrodes possessed a good selectivity toward 8-OHdG detection. In addition, the modified electrode stability was checked by amperometric method for electrochemical 8-OHdG sensor. The Cu_2O SNPs@GOS/RDE current is kept about 95.81% from the



Scheme 2. Electrochemical mechanism of 8-OHdG oxidation based on Cu_2O NPs@GOS/GCE in 0.1 M PBS (pH7.0) at 50 mVs^{-1}.

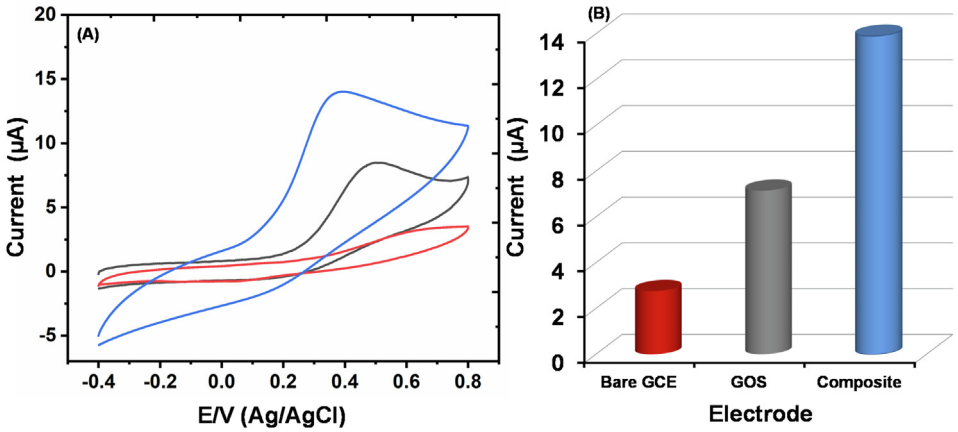


Fig. 4. (A) Electrochemical response of (a) bare electrode, (b) GOS modified GCE, (c) Cu_2O SNPs@GOS/GCE in Phosphate buffer (0.05 M; pH7.0) at 0.05 V/s in 50 μM of 8-OHdG biomarker. (B) Concentration of 8-OHdG biomarker and electrochemical peak current.

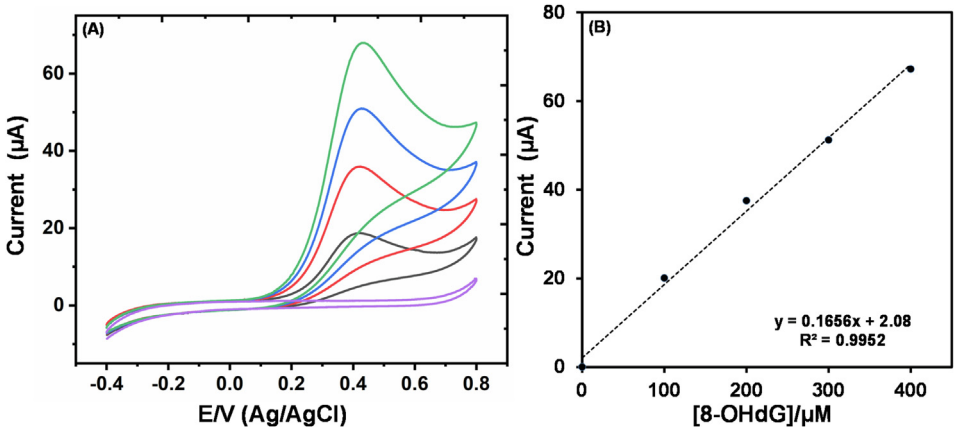


Fig. 5. A) Electrochemical response of Cu_2O SNPs@GOS modified GCE with concentrations of 8-OHdG biomarker (100–400 μM) in phosphate buffer (0.05 M; pH7.0) at 0.05 V/s and (B) peak current against concentration of 8-OHdG.

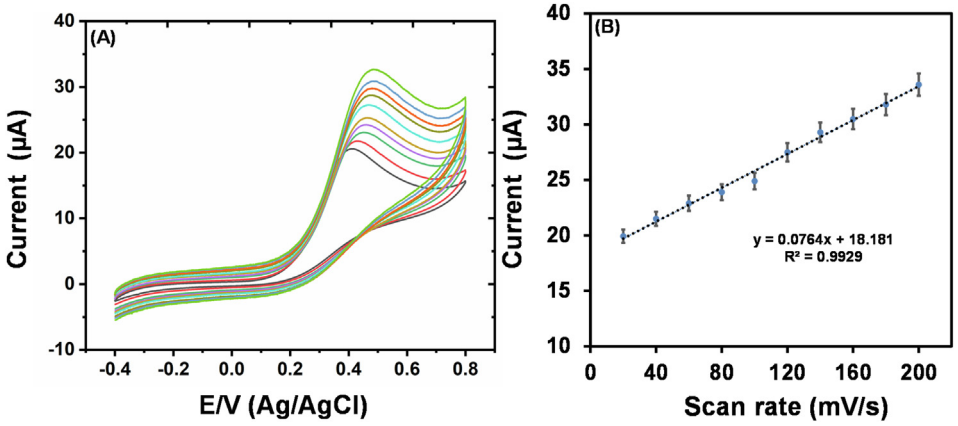


Fig. 6. A) Electrochemical response of Cu_2O SNPs@GOS modified electrode with different scan rate (20 to 200 mV/s) in phosphate buffer (0.05 M; pH7.0) and (B) peak current against scan rate of the experiments.

initial current over 25 days. The reproducibility analysis also checked with Cu_2O SNPs@GOS modified GCE and it's performed at six different electrodes and checked sensor responses towards 8-OHdG biomarker. This result shows a valuable performance towards reproducibility test with the relative standard deviation is 2.91%. Finally, Cu_2O SNPs@GOS modified electrodes are explored high stability, selectivity, and good reproducibility towards the electrochemical determination of 8-OHdG biomarker.

3.4. Real sample analysis

The electrocatalyst modified Cu_2O SNPs@GOS/RDE is checked for real samples analysis in human blood serum (HBS) and urine (HU) samples. Biological samples were collected from medical hospital, Taipei (ROC). The biological samples of HBS and HU samples are directly analyzed then the known concentration of 8-OHdG biomarker was added into HBS solution and HU solution. Then, the samples were analyzed by amperometric method. The electrochemical sensor

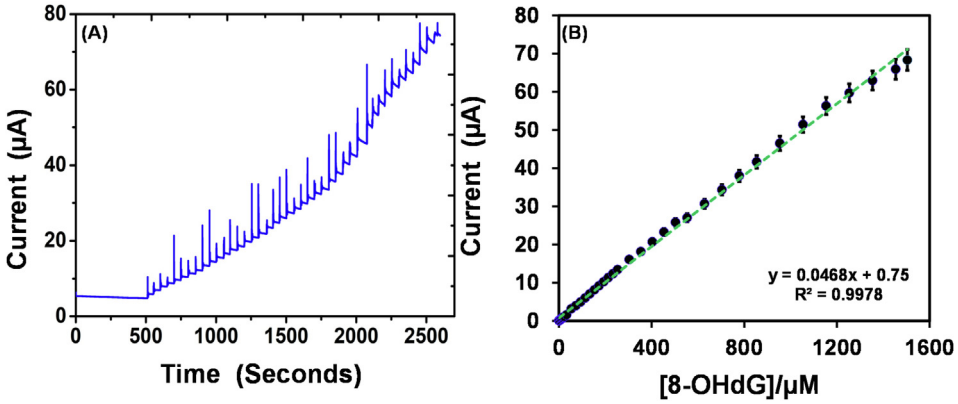


Fig. 7. Amperometric analysis of Cu_2O SNPs@GOS modified RDE addition of various concentrations [0.02 μM–1565 μM] of 8-OHdG biomarker in 0.05 M phosphate buffer (pH 7.0) at 0.05 V/s and (B) [8-OHdG]/μM versus anodic peak current/μA.

Table 1
Comparison of analytical parameters for the determination of 8-OHdG at Cu_2O NPs@GOS NC film modified electrode with reported works.

Modified electrode	LOD (nM)	Linear range (μM)	Refs.
SWCNTs/GCE	990	29–87.0	[37]
SWCNTs-Lysine	97.0	0.3–10.0	[38]
MWCNTs-polyethylenimine	10	0.5–30.0	[39]
MWCNTs/graphene oxide/GCE	35	3–75.0	[40]
ZnO NPs/RGO sheets	1.25	0.05–50	[41]
Poly(3-methylthiophene)/GCE	10	0.7–70.0	[42]
Graphene sheets/nafion	12	0.07–33.04	[43]
Cu_2O SNPs@GOS	8.75	0.02–1465	This work

Table 2
Real sample analysis (8-OHdG biomarker) in biological samples at Cu_2O NPs@GOS hybrid/GCE.

Samples	Added (μM)	Found (μM)	Recovery (%)	RSD* (%)
Urine	0	0	–	–
	5.0	4.91	98.20	3.24
	10.0	9.92	99.20	3.17
	20.0	19.79	98.95	2.66
Blood serum	0	0	–	–
	5.0	4.88	97.60	3.63
	10.0	9.89	98.90	3.07
	20.0	19.83	99.15	3.18

currents were obtained and recoveries of the performance were calculated and data were given in Table 2. Finally, the Cu_2O SNPs@GOS modified GCE indicating that the Cu_2O SNPs@GOS material has excellent practical ability due to electrochemical properties.

4. Conclusion

In this work, Cu_2O SNPs@GOS based composite materials was developed using facile and green method (sonochemical). The Cu_2O SNPs@GOS materials were characterized by TEM, XRD, quantitative and EDS (elemental) analysis. The Cu_2O SNPs@GOS modified electrode explored a nanomolar LOD, wide sensing ranges, excellent sensitivity and stability, rapid responses, remarkably selectivity and good reproducibility. Furthermore, the Cu_2O SNPs@GOS modified GCE and RGE are applied to real sample analysis and the results are high valuable. Besides, its explained electron conductivity of the electrode, electron transfers ability based on the Cu_2O SNPs and graphene oxide sheets. Consequently, the Cu_2O SNPs@GOS material is good electrocatalyst for the electrochemical applications in detection of 8-OHdG sensor in biological samples.

CRediT authorship contribution statement

Tse-Wei Chen: Methodology, Formal analysis, Writing - original draft. **Umamaheswari Rajaji:** Methodology, Writing - original draft. **Shen-Ming Chen:** Resources, Supervision. **Jun-Yu Wang:** Formal analysis. **Zeid Abdullah Alothman:** . **M. Ajmal Ali:** Resources, Supervision, Formal analysis, Funding acquisition. **S. Mohammad Wabaidur:** Resources, Methodology. **Fahad Al-Hemaid:** Visualization, Methodology. **Shih-Yi Lee:** Formal analysis, Supervision, Funding acquisition. **Wen-Han Chang:** Visualization, Methodology.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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