



Investigation of Glucose oxidation at Gold Nanoparticles deposited at Carbon Nanotubes modified Glassy Carbon Electrode by Theoretical and Experimental Methods.

Farhat Saira

National Centre for Physics , Shahdra Valley, QAU campus, Islamabad., fsghaus@gmail.com

Humaira Razzaq

hunza_pk2@yahoo.mail.com

Misbah Mumtaz

misbah_21_39@yahoo.com

Safeer Ahmad


safeerad@qau.edu.pk

Muhammad Aftab Rafiq

aftabrafiq@pieas.edu.pk

See next page for additional authors

Follow this and additional works at: <https://kijoms.uokerbala.edu.iq/home>

 Part of the [Biology Commons](#), [Chemistry Commons](#), [Computer Sciences Commons](#), [Medicine and Health Sciences Commons](#), and the [Physics Commons](#)

Recommended Citation

Saira, Farhat; Razzaq, Humaira; Mumtaz, Misbah; Ahmad, Safeer; Rafiq, Muhammad Aftab; Yaqub, Azra; Dilshad, Nabiha; Ihsan, Ayesha; and ul Hasan, Muhammad Masood (2020) "Investigation of Glucose oxidation at Gold Nanoparticles deposited at Carbon Nanotubes modified Glassy Carbon Electrode by Theoretical and Experimental Methods.," *Karbala International Journal of Modern Science*: Vol. 6 : Iss. 1 , Article 10.

Available at: <https://doi.org/10.33640/2405-609X.1370>

This Research Paper is brought to you for free and open access by Karbala International Journal of Modern Science. It has been accepted for inclusion in Karbala International Journal of Modern Science by an authorized editor of Karbala International Journal of Modern Science. For more information, please contact abdulateef1962@gmail.com.

Investigation of Glucose oxidation at Gold Nanoparticles deposited at Carbon Nanotubes modified Glassy Carbon Electrode by Theoretical and Experimental Methods.

Abstract

In the current research work, AuNPs-CNTs nanocomposite was synthesized chemically and decoration of AuNPs on the surface of MWCNTs was confirmed by UV-Vis, SEM and XPS analysis. Synthesized nanocomposite was utilized for its application towards non-enzymatic glucose sensing by modifying glassy carbon electrode with nanocomposite employing electrochemical techniques. In addition, theoretical calculations were performed by Density Functional Theory (DFT), employing B3YLP with basis set 6-311+G(d,p) in gaseous phase and LANL2DZ basis set. Both theoretical and experimental results predicted Au-CNTs composite as a better candidate for glucose oxidation as compared to CNTs and AuNPs alone, owing to the synergistic effect of CNTs and AuNPs. This preliminary study for predicting possibility of glucose oxidation by different nano hybrids is not reported earlier. This study can find its applications in glucose biosensor and food industry.

Keywords

Carbon nanotubes, Glucose sensing, cyclic voltammetry, computational studies, HOMO, LUMO

Creative Commons License



This work is licensed under a [Creative Commons Attribution-Noncommercial-No Derivative Works 4.0 License](https://creativecommons.org/licenses/by-nc-nd/4.0/).

Cover Page Footnote

Investigation of Glucose oxidation at Gold Nanoparticles modified Glassy Carbon Electrode by Theoretical and Experimental Methods. Farhat Sairaa#, Humaira Razzaqb#, Misbah Mumtaz a, Safeer Ahmadc, M. A. Rafiq, Azra Yaqubd, Ayesha Ihsane, Nabih Dilshadc, M. M. Hasana* aDepartment of Metallurgy and Materials Engineering, Pakistan Institute of Engineering & Applied Sciences (PIEAS), Lehtar Road, Nilore, Islamabad, Pakistan. bNational Centre for Physics (NCP), QAU, Islamabad, Pakistan. cDepartment of Chemistry, Quaid-i-Azam University, 45320 Islamabad, Pakistan. d PINSTECH, Chemistry Division, Lehtar Road, Nilore, Islamabad, Pakistan e National Institute of Biology and Genetic Engineering (NIBGE), Faisalabad, Pakistan. * Corresponding author, email: masoodh@pieas.edu.pk # Equal contribution Declaration No conflict of interest is declared by authors regarding the publication of this research. Acknowledgments Higher Education Commission (HEC) Pakistan is acknowledged for sponsoring this project under SRGP grant. Pakistan Institute of Engineering & Applied Sciences (PIEAS), Dr. Rumana Qureshi and Chemistry Department, Quaid-i-Azam University Islamabad are acknowledged for offering their laboratory facilities and Gaussian software for DFT calculations during this research.

Authors

Farhat Saira, Humaira Razzaq, Misbah Mumtaz, Safeer Ahmad, Muhammad Aftab Rafiq, Azra Yaqub, Nabih Dilshad, Ayesha Ihsan, and Muhammad Masood ul Hasan

1. Introduction

Sensors belong to a class of devices that can be used for multiple purposes, ranging from gas molecules detection to tracing of chemical signals in biological systems. Generally, a sensor consists of two basic elements: a sensing element, responsible for detection of a specific analyte and a signal transducer, which generates an output in the form of a thermal, magnetic, optical or electrical output signal. Biosensors first reported in 1960 [1], vary from conventional chemical sensors in two aspects firstly, the active sensing element is usually biological material such as proteins or microorganisms [2,3] and secondly the biological processes such as oxidation of ascorbic acid, dopamine, uric acid and glucose etc., are being monitored by the sensor. Biosensors can either act as *in vitro* or as *in vivo* detectors. Among all types of biosensors, electrochemical biosensors are presently the most prevalent. Carbon materials are essential constituents in electrochemical biosensors for more than a decade. With the discovery of Carbon nanotubes (CNTs) in 1991, they are considered as potential materials for sensing purpose because of availability of large length-to diameter aspect ratio as well as capability to facilitate electron-transfer kinetics for several of electro-active species. Surface modification of CNTs can be exploited for the attachment of any specific chemical specie to their surface, sanctioning them enhanced solubility [4]. Moreover, chemical and mechanical strength, field emission and electronic transport properties of CNTs make them to initiate pronounced interest in imminent applications [5,6]. Based on these properties CNTs can be used as constituents for composite materials and biosensors [7–13]. Combining the fascinating catalytic properties of gold nanoparticles and excellent electrical, thermal and conducting properties of CNTs composite electrode materials have been introduced [4]. When noble metal nanoparticles like Ag, Au are deposited on carbon nanotubes a composite is produced which has higher available surface of CNTs for numerous nucleation sites, eradicating capping agent which is required to avoid agglomeration of nanoparticles. Moreover, this composite presents advantages like the high catalytic activity, lifetime and easiness of storage [14–19].

Glucose is an essential component of everyday food. It comprehensively exists in pharmaceuticals, food and blood. Glucose is inevitable for living organisms to

maintain their life activities. However, due to accumulation of higher level of glucose in the blood stream, diabetes is caused which is one of the lethal diseases [20,21]. Amongst many other assays, glucose is most frequently performed because of the massive increase in diabetic population [22]. Consequently, developing a sensitive, stable and selective technique for glucose detection is extremely indispensable [23–30].

In the present work we have modified carbon nanotubes by gold nanoparticles (GNPs) using an ultrasonication method [31]. This is a convenient and simple method of solubilizing and stabilizing CNTs for further GNPs deposition. This nanocomposite was utilized to fabricate quite stable and sensitive biosensor for the detection of glucose. In addition to this, DFT calculations were carried out to ascertain Au and CNTs effect on glucose oxidation. Theoretical and experimental results complemented well for gold modified CNTs glucose biosensor.

2. Experimental

2.1. Materials

Carbon nanotubes (110 nm diameter and 10 μm length, Sigma Aldrich), gold salt (Sigma Aldrich) and trisodium citrate (Sigma Aldrich) were used as received. Ultrapure water was used to prepare 1 wt% solutions of HAuCl₄ and sodium citrate.

2.2. Synthesis of Au-CNTs/nanocomposite

For synthesis purpose we used already reported procedure to attach gold nanoparticles over carbon nanotubes [31]. Briefly, 3 mg of multi wall carbon nanotubes (CNTs) were added in 4 ml trisodium citrate solution (1 wt %) followed by 5 min ultrasonication. This will generate sodium citrate shells on the surface of carbon nanotubes with the help of ultrasonication, afterwards 96 ml ultrapure water was added to this suspension [31]. This 100 ml mixture was then heated to boiling point with constant stirring followed by the dropwise addition of 0.5 ml of 1 wt% solution of HAuCl₄. This solution was further allowed to keep stirring and boiling for 5 min. A gradual transformation of colour occurs from blackish blue to reddish purple, indicating formation of Au-CNTs (see Fig. 1 inset). Modified Carbon nanotubes were then washed with ultrapure water and separated by

centrifugation at 6000 rpm for 5 min. For comparison purpose spherical gold nanoparticles were also synthesized by Fren's method [32]. Concisely, to a 20 ml of a 1 mM aq.HAuCl₄ boiling solution, 0.5 ml of a 1% trisodium citrate solution was added under reflux. End point of reaction is appearance of a deep red colour. At this moment turn off heating and let the system cool down. This procedure has many advantages, e.g., it utilizes low reaction temperature (100 °C), does not require organic solvents or surfactant, as well as less than an hour of synthesis time, as well as synthesized nanocomposites are easier to collect from aqueous solution.

2.3. Instrumentation

Cyclic voltammetry was carried out on an Ecochemie Autolab PGSTAT-10 potentiostat/galvanostat at room temperature. A cell equipped with three electrodes i.e., modified glassy carbon, a platinum wire and silver/silver chloride were used as working, counter and reference electrodes respectively. For EIS measurements Ecochemie Autolab PGSTAT-10 potentiostat/galvanostat was also used in the frequency range of 0.1–100 kHz. A UV–Visible spectrophotometer (UV-1601 Shimadzu spectrophotometer) with wavelength range of 190–1100 nm was utilized to collect spectral data. Scanning Electron Microscopy (SEM) used was JSM 7500F with operating accelerating voltage 1–30 KV. XPS measurements were performed using a Scienta-Omicron XPS instrument that was equipped with a micro-focused monochromatic Al KAlpha X-ray source. Data acquisition for the XPS was performed with Matrix software and data analysis was performed with Igor Pro along with XPS fit procedures. The curve fitting of spectra was done using Gaussian-Lorentzian line shape after performing the Shirley background corrections.

2.4. Electrode modification

Alumina powder of different grading i.e., 0.5 μm, 0.3 μm, 0.1 μm was used to polish GCE to a mirror finish on polishing pads, followed by proper rinsing with deionized water. Electrodes were ultrasonicated for 1 min in deionized water after utilizing each grading to remove alumina particles. All electrodes were dried at room temperatures. Clean and dried GCE was spotted with 10 μL of ultrasonicated AuNPs, CNTs and Au-CNTs aqueous solutions. The electrodes were allowed to dry in air for 30 min. These prepared electrodes were used for acquiring electrochemical data.

2.5. Computational details

Computational calculations for the glucose and the two other systems namely CNTs, AuNPs and CNTs-Au nanocomposite were carried out using Density functional theory (DFT), which is more accurate method as compared to other theoretical methods. The molecular geometries of glucose and CNTs were optimized using B3YLP with basis set 6–311 + G(d,p) in gaseous phase. However, for the optimization of CNTs-Au composite, DFT method using LANL2DZ basis set was employed. GAUSSIAN 03W software was used for all calculations.

3. Results and discussion

3.1. Characterization of CNTs and Au-CNTs nanocomposites

3.1.1. UV-visible spectroscopic characterization

UV–vis spectra of MWCNT, AuNPs and Au-CNTs nanocomposite are shown in Fig. 1. MWCNT exhibit no specific plasmon rather a broad band, while AuNPs and Au-CNT nanocomposite indicated an absorption peak around 520 nm. The UV–vis spectrum of Au-CNT nanocomposite is not broader, indicating no aggregated lumps of gold nanoparticles over the CNTs surface [12] (See Fig. 1).

3.1.2. Scanning Electron Microscopy (SEM) imaging

SEM was used to characterize pure CNTs and nanocomposites (Fig. 2A–F). The SEM images 2A–B at different magnifications show pure (CNTs),

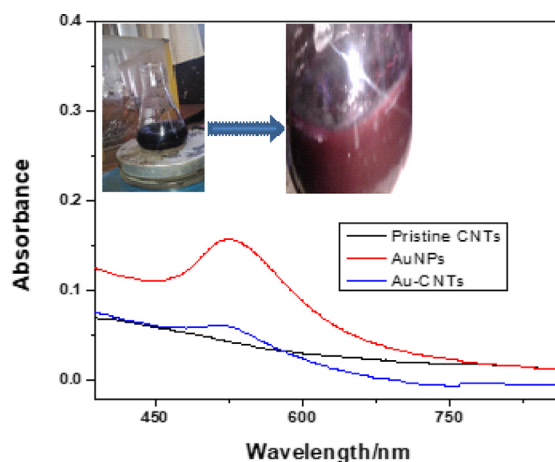


Fig. 1. UV–Visible spectra of CNTs AuNPs and Au-CNTs nanocomposite.

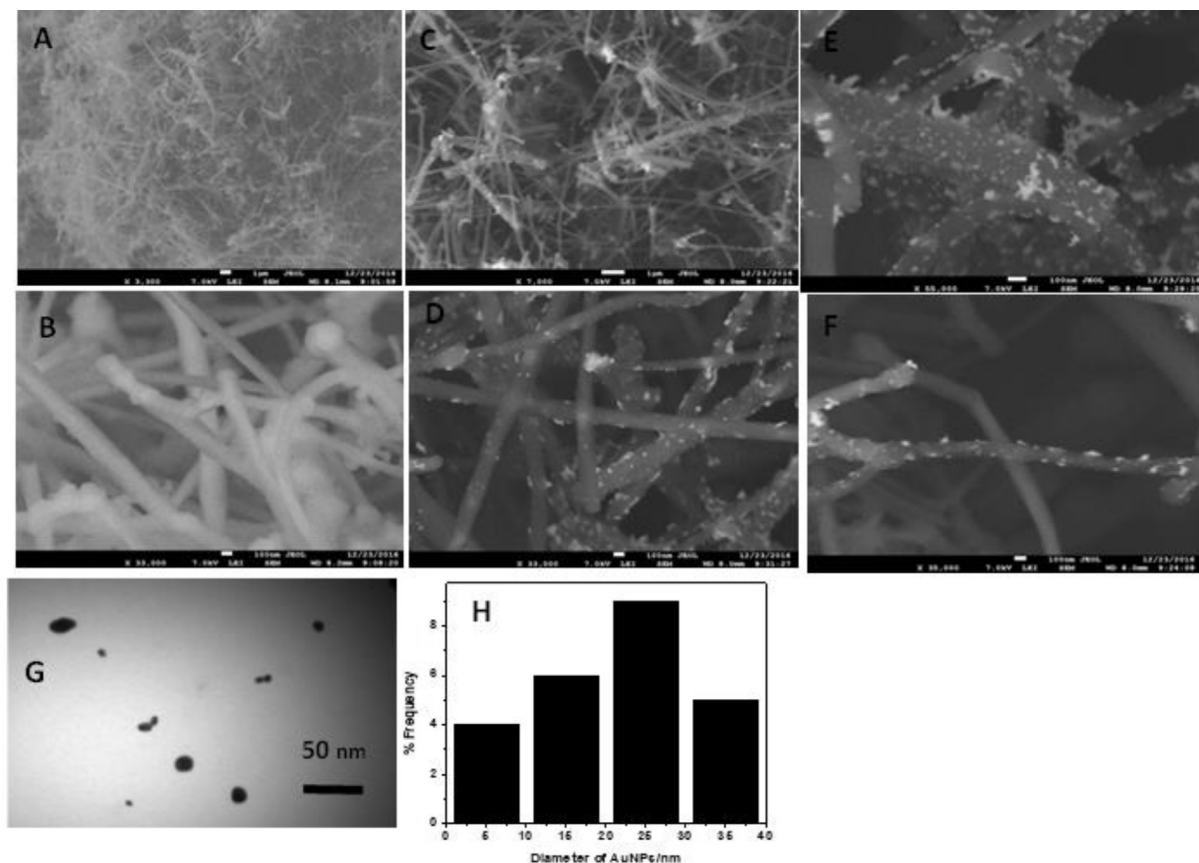


Fig. 2. SEM images of CNTs (A–B) and Au-CNTs (C–F) nanocomposites, TEM image of synthesized AuNPs (2G) and a bar graph for AuNPs (H).

indicative of clean surface of the carbon nanotubes as received. Further Fig. 2C–F shows nanocomposites after decoration with gold nanoparticles. Fig. 2G shows TEM image of synthesized AuNPs for comparison purpose. The size distribution of gold nanoparticles is shown in Fig. 2H, and is estimated to $25 \text{ nm} \pm 5$.

3.1.3. X-ray Photoelectron Spectroscopy (XPS)

Further confirmation of the deposition of gold nanoparticles on the surface of CNTs and information on chemical element states was obtained by XPS analysis (Fig. 3). Results indicated that the nanocomposites were composed of Au, C and O. Two peaks in XPS for Au $4f_{7/2}$ and Au $4f_{5/2}$ at 83.4 and 87.3 eV are depictive of two types of Au electronic states (Au^+ and Au^0), as shown in Fig. 3 whereas the peak C1s for the carbon is located at 280.3 eV. In addition, a strong peak at 530 eV is indicative of the presence of O1s. Pristine CNTs show a strong peak of C at 248 eV from literature [33,34] but as the CNTs get functionalized this peak shifts towards higher energy i.e. 280–285 eV.

Also, the ratio of C to O peak intensity is high in pristine CNTs while in our case O is showing a strong peak indicative of well functionalized CNTs. Also peaks for Au 4f are present in our sample which is not shown in pristine CNTs from literature.

3.2. Glucose oxidation on Au-CNTs/GCE

Non-Enzymatic glucose sensing was performed in the presence of AuNPs, CNTs/GCE and Au-CNTs/GCE as working electrodes vs. Ag/AgCl as reference and Pt as counter electrode. Supporting electrolyte i.e., 0.1 M NaOH solution was used in the potential range from -0.5 V to $+1.0 \text{ V}$ (see Fig. 4A) for modified electrodes without glucose and $0-0.8 \text{ V}$ for modified electrodes with glucose. In the absence of glucose in the applied potential window no significant change in terms of oxidation or reduction current was observed for CNTs/GCE. For AuNPs/GCE and Au-CNT/GCE electrodes show a typical response of gold hydroxide and gold oxide. After addition of glucose into

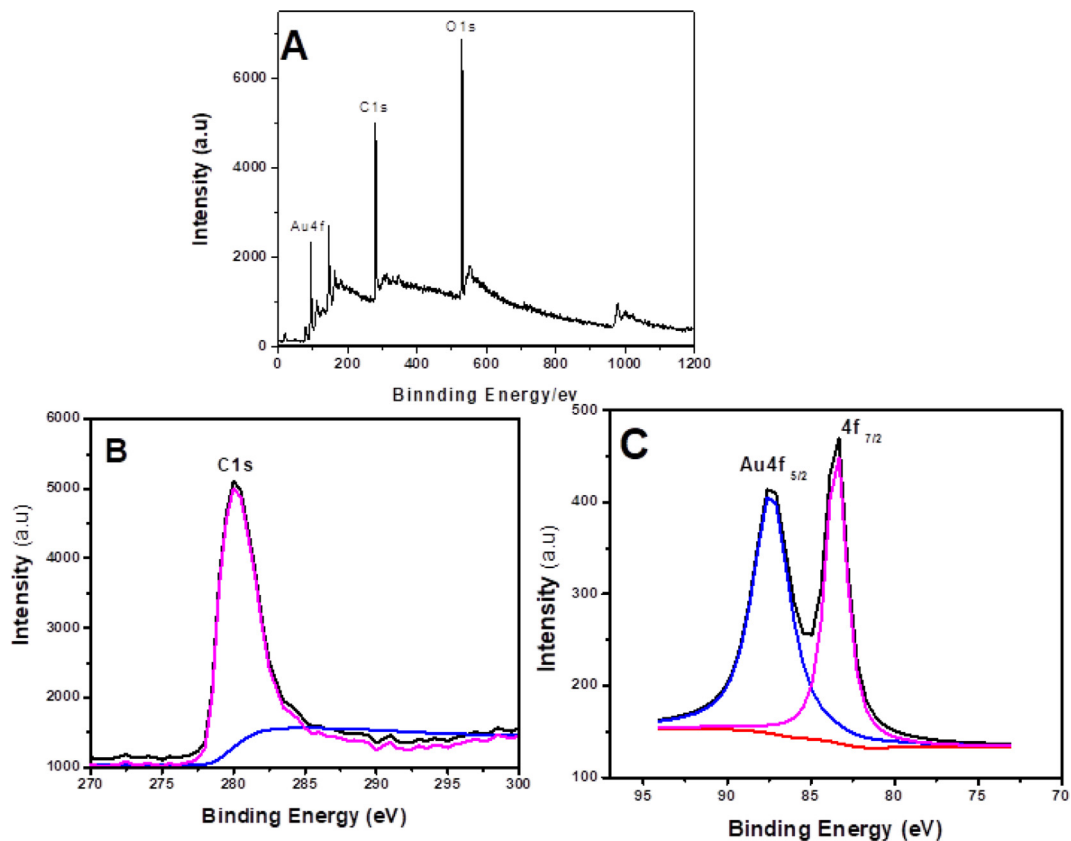


Fig. 3. XPS spectra of Au-CNTs, full spectra (A), while C1s(B) and Au4f(C) are fitted curves.

electrochemical cell see Fig. 4B, four main peaks observed in voltamogram by Au-CNTs nanocomposite and AuNPs while pristine CNTs did not show any response.

Detail of four peaks is that, two in the cathodic scan (forward scan) and two in anodic scan (backward scan). Peak I corresponds to the gold hydroxide formation in the forward scan, followed by a very sharp

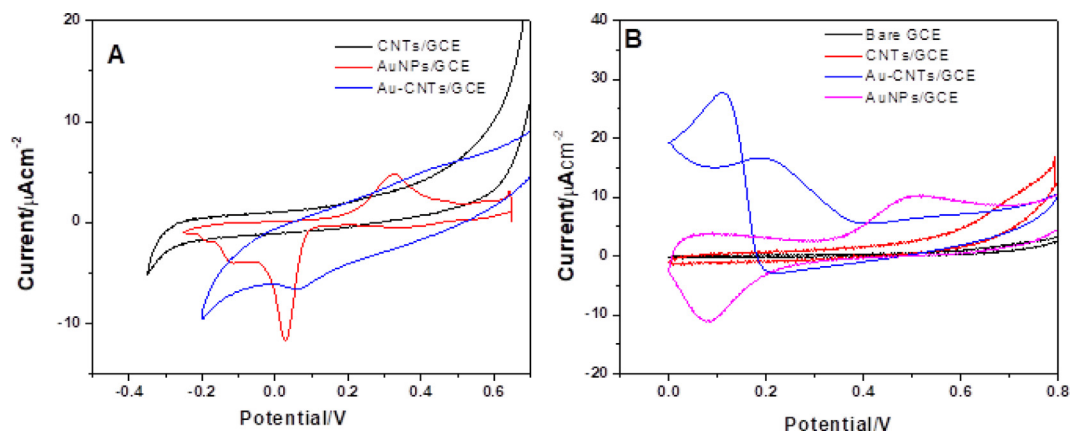


Fig. 4. CV response of CNTs/GCE, AuNPs/GCE and Au-CNTs/GCE Vs. Ag/AgCl reference and platinum as counter electrode in 0.1M NaOH solution as supporting electrolyte (A), CV response for 1 mM glucose at CNTs/GCE, AuNPs/GCE and Au-CNTs/GCE Vs. Ag/AgCl reference and platinum as counter electrode in 0.1M NaOH solution as supporting electrolyte at a 100 mV/s (B).

peak II that corresponds to the adsorption of glucose onto active sites of gold nanocomposite and conversion to gluconolactone. Peak II is basically an anodic peak in cathodic scan. Peak III corresponds to the formation of gluconic acid and peak IV corresponds to oxidation of gold nanoparticles. Peak appeared at i.e. 0.23 V potential during the anodic scan is taken as glucose oxidation peak. This is reported to be the glucose oxidation peak in many literature reports [35–40]. The selection of main glucose oxidation peak is critical. As this oxidation is occurring in basic medium, it can be ventured that AuNPs have high affinity for the adsorption of OH^- ions, which effectively catalyze the process of oxidation of glucose. First, the metal Au(0) was electrochemically oxidized to strongly oxidizing species $\text{Au}(\text{OH})_{\text{ads}}$ under the alkaline conditions, and finally this $\text{Au}(\text{OH})_{\text{ads}}$ specie catalytically oxidizes

glucose and produces gluconic acid. Stability of Au-CNTs electrode was evaluated at ten consecutive cycles and by changing NaOH concentration (see Fig. 5), modified electrode was found stable at 0.1M NaOH concentration.

3.2.1. Possible mechanism of glucose oxidation

Out of three modified electrodes Au-CNTs showed higher sensitivity towards glucose detection. Therefore, this electrode is selected for rest of electrochemical experiments and mechanism evaluation. Linear range of 0.1–3 mM glucose concentration was obtained and Limit of detection (LOD) was evaluated for Au-CNTs/GCE electrode and found to be $0.19 \mu\text{M}$ and sensitivity to be $2.28 \mu\text{Acm}^{-2}$ (See Fig. 6). Glucose oxidation mechanism at gold-CNTs modified

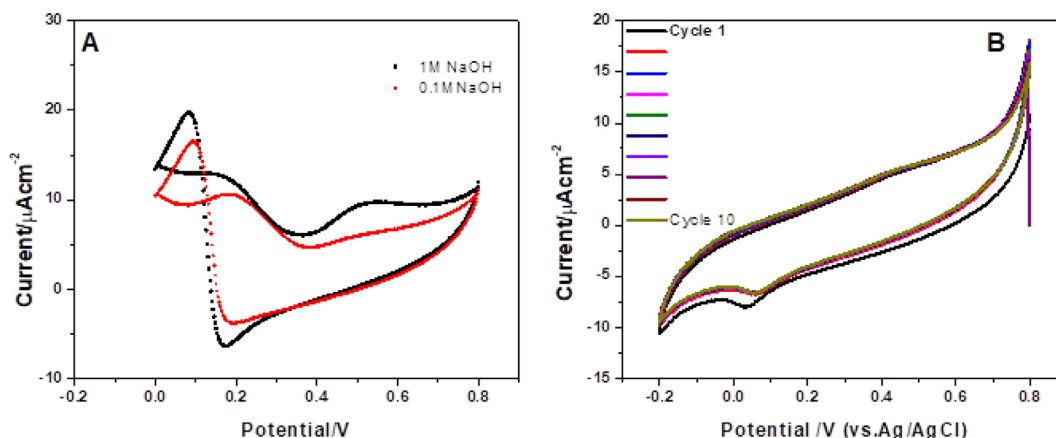


Fig. 5. CV response for 1 mM glucose at modified Au-CNT/GCE at different NaOH molarities, Vs. Ag/AgCl reference and platinum as counter electrode (A) Stability of modified Au-CNT/GCE at ten different cycles Vs. Ag/AgCl as reference and platinum as counter electrode in 0.1M NaOH at a 100 mV/s scan rate (B).

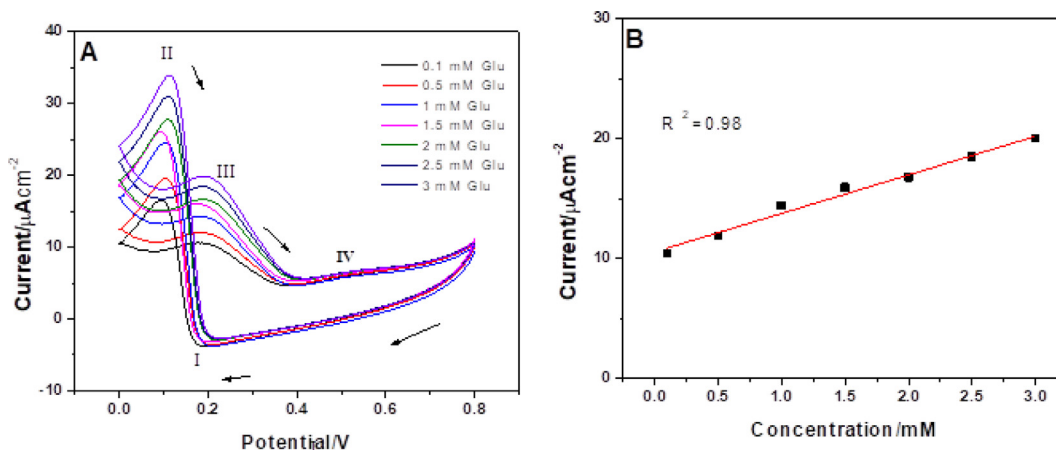
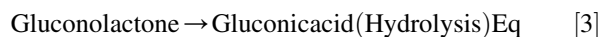
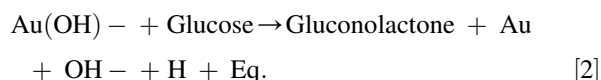
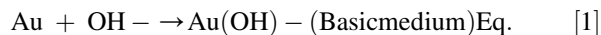


Fig. 6. CV response of modified Au-CNT/GCE at different concentrations of glucose (0.1–3 mM) Vs. Ag/AgCl reference and platinum as counter electrode in 0.1M NaOH solution as supporting electrolyte at 100 mV/s scan rate (A), Linear range for glucose detection at Au-CNTs (B).

electrodes is suggested to be three step processes. It can be narrated as described in below equations.



The enhanced signal of glucose is because of synergistic effect of electroactive sites of AuNPs and huge surface area of CNTs. As gold nanoparticles deposited over CNTs surface offer active reaction sites for electro-oxidation of glucose. Therefore, excellent

conductivity of Au-CNTs nanocomposite is solely responsible for the observed enhancement in electro-catalytic activity of present sensor system i.e., Au-CNTs/GCE towards glucose oxidation. This synergistic effect helps in facilitated charge transfer, better access to vigorous reaction sites and surplus electron transfer routes offered by AuNPs uniformly deposited on the surface of CNTs [41–47].

3.3. Computational analysis of CNTs, AuNPs and Au-CNTs nanocomposite

The computational chemistry gives a good estimate of oxidation and reduction characteristics of molecules.

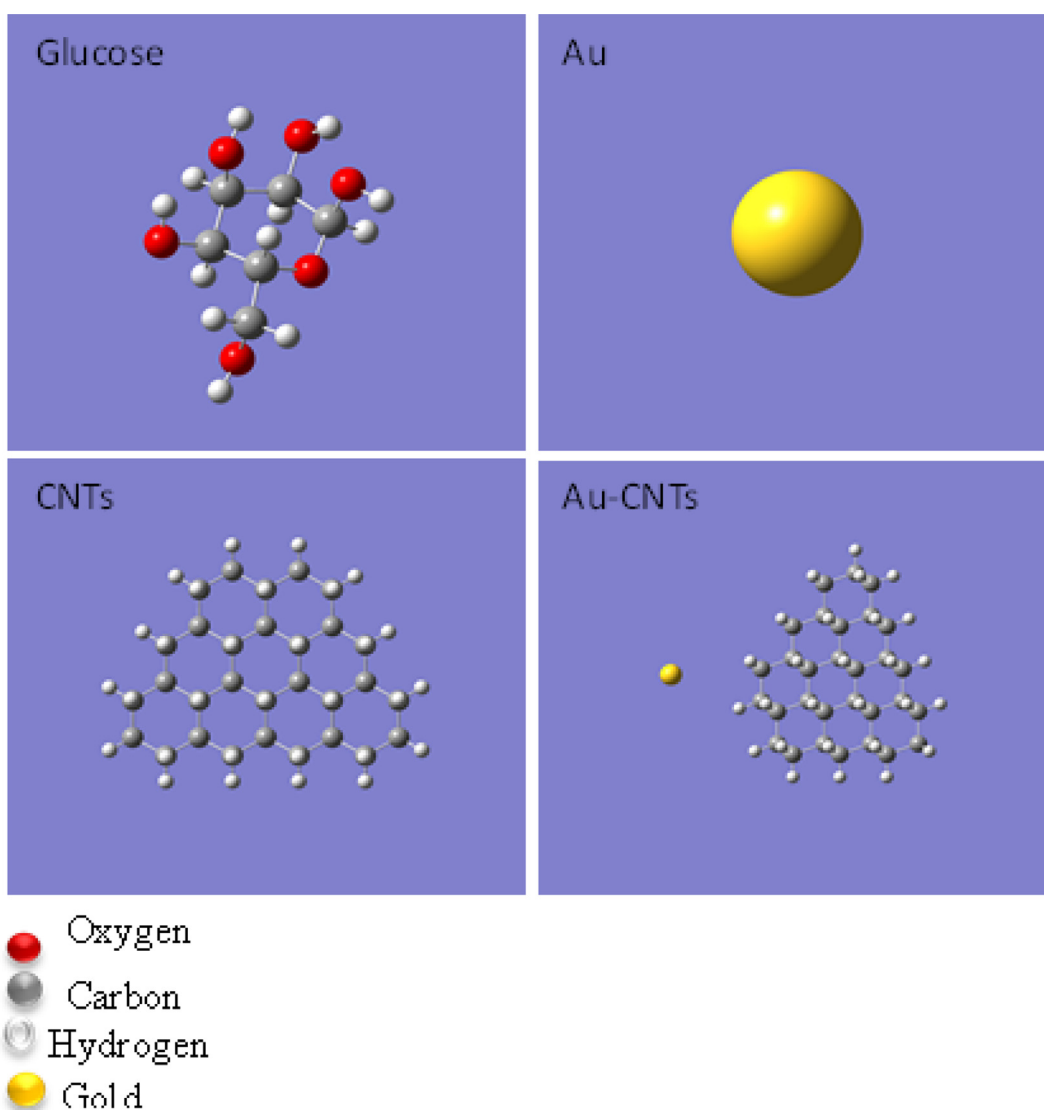


Fig. 7. Optimized structures of glucose, Au, CNTs and Au-CNTs considering B3LYP level using 6-311G(dp) basis set for glucose/CNTs and LANL2DZ basis set of DFT method for Au-CNTs merged structures.

In fact, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are correlated with the oxidation and reduction potential of the molecules. The more negative is the E_{LUMO} , more easily will be the molecule reduced. In the present study, computational calculations were performed in order to predict the feasibility of glucose oxidation on CNTs and CNTs-Au nanocomposite substrates using DFT. To predict the feasibility of glucose oxidation on modified glassy carbon electrode, the HOMO of glucose while LUMO of the modifiers (CNTs and CNTs-Au nanocomposite) systems is considered. Nanoparticles are typically presented by cluster model but their optimization needs super computers. Calculations were simplified by representing gold NPs by monoatomic gold [48] (see Table 1).

LANL2DZ basis set of DFT method is designed for metals optimization [49–51]. The optimized structure is presented in Fig. 7. The molecular geometries of glucose and CNTs (represented as hexagons here for simplicity of calculations) were optimized using B3YLP with basis set 6–311 + G(d,p) in gaseous phase. Hexagons and gold atom containing merged

Table 1
HOMO and LUMO values of Glucose, CNTs, AuNPs and Au-CNTs using semi empirical calculations employing B3YLP with basis set 6–311 + G(d,p) in gaseous phase and LANL2DZ basis set.

Energy/Hartree	Glucose	CNTs	Au	CNTs-Au
HOMO	–0.58813	–0.240872272	–0.24745949	–0.54628
LUMO	–0.54836	–0.0627372768	–0.02410248	–0.54225

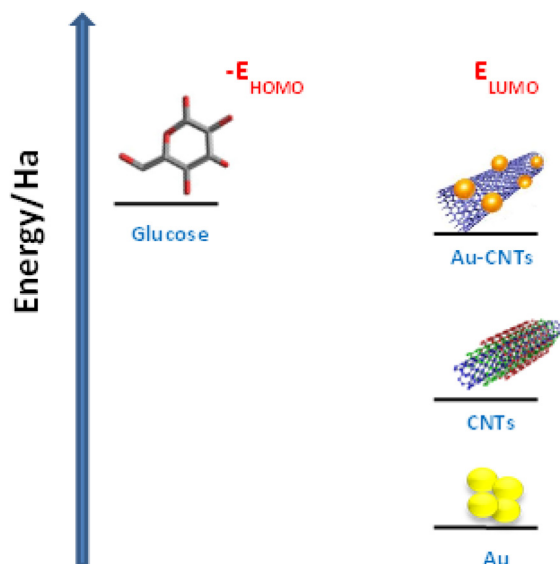


Fig. 8. Energy level diagram of investigated systems. The energy levels are not drawn according to scale.

system was considered as one entity for Density functional calculations. The merged system i.e. Au-CNTs showed more –ive value of LUMO than CNTs and AuNPs, which shows the ease in accessibility of molecules to accept electrons (Fig. 8). Since LUMO of CNTs–Au composite system is more negative as compared to CNTs, depicting a facile glucose oxidation. These results complemented well with our experimental findings (see experimental section) for Au-CNTs hybrid.

The energy level diagram of optimized structures of studied molecules is shown in Fig. 8. Following trend could be observed

$$-E_{LUMO}(\text{Au} - \text{CNTs}) > -E_{LUMO}(\text{CNTs}) > -E_{LUMO}(\text{Au})$$

4. Conclusions

A synergistic effect of AuNPs and pristine CNTs as a sensor on the electro-oxidation of glucose is presented here theoretically and experimentally. We modified GCE with CNTs, AuNPs and Au-CNTs to study their glucose oxidation performance. Pristine CNTs did not show any response AuNPs showed some and Au-CNTs presented prominent response towards glucose oxidation. This report also presents some preliminary results of DFT prediction of glucose oxidation by Au-CNTs hybrids. The synergistic effect of Au-CNTs/GCE provides more active sites and higher electron transfer chances for glucose oxidation. Both experimentally and theoretically Au-CNTs system was found better than CNTs and AuNPs for glucose oxidation. This study may provide a base for predicting theoretically a better candidate for glucose oxidation prior to experiments.

Acknowledgement

Authors acknowledge Higher Education commission (HEC) Pakistan for funding this research by project No:21-1119/SRGP/R & D/HEC and Dr. Mahmoud A. Mahmoud for providing TEM images of AuNPs. Farhat Saira acknowledges Dr. Rumana Qureshi from Chemistry Department QAU, Islamabad Pakistan for providing access to GAUSSIAN 03W software.

References

- [1] L.C. Clark Jr., C. Lyons, Electrode systems for continuous monitoring in cardiovascular surgery, *Ann. N. Y. Acad. Sci.* 102 (1962) 29–45.

- [2] G.S. Wilson, R. Gifford, Biosensors for real-time in vivo measurements, *Biosens. Bioelectron.* 20 (2005) 2388–2403.
- [3] B.D. Malhotra, R. Singhal, A. Chaubey, S.K. Sharma, A. Kumar, Recent trends in biosensors, *Curr. Appl. Phys.* 5 (2005) 92–97.
- [4] K. Balasubramanian, M. Burghard, Biosensors based on carbon nanotubes, *Anal. Bioanal. Chem.* 385 (2006) 452–468.
- [5] M.S. Dresselhaus, G. Dresselhaus, P.C. Eklund, *Science of Fullerenes and Carbon Nanotubes: Their Properties and Applications*, Academic press, 1996.
- [6] H. Murakami, M. Hirakawa, C. Tanaka, H. Yamakawa, Field emission from well-aligned, patterned, carbon nanotube emitters, *Appl. Phys. Lett.* 76 (2000) 1776–1778.
- [7] T. Ebbesen, H. Lezec, H. Hiura, J. Bennett, H. Ghaemi, T. Thio, Electrical conductivity of individual carbon nanotubes, *Nature* 382 (1996) 54.
- [8] M.J. Treacy, T. Ebbesen, J. Gibson, Exceptionally high Young's modulus observed for individual carbon nanotubes, *Nature* 381 (1996) 678.
- [9] A. Merkoçi, M. Pumera, X. Llopis, B. Pérez, M. Del Valle, S. Alegret, New materials for electrochemical sensing VI: carbon nanotubes, *Trac. Trends Anal. Chem.* 24 (2005) 826–838.
- [10] J.-M. Bonard, H. Kind, T. Stöckli, L.-O. Nilsson, Field emission from carbon nanotubes: the first five years, *Solid State Electron.* 45 (2001) 893–914.
- [11] H. Dai, J.H. Hafner, A.G. Rinzler, D.T. Colbert, R.E. Smalley, Nanotubes as nanoprobe in scanning probe microscopy, *Nature* 384 (1996) 147.
- [12] J. Zeng, Q. Zhang, J. Chen, Y. Xia, A comparison study of the catalytic properties of Au-based nanocages, nanoboxes, and nanoparticles, *Nano Lett.* 10 (2009) 30–35.
- [13] R.A. Soomro, O.P. Akyuz, R. Ozturk, Z.H. Ibupoto, Highly sensitive non-enzymatic glucose sensing using gold nanocages as efficient electrode material, *Sensor. Actuator. B Chem.* 233 (2016) 230–236.
- [14] B. Wu, Y. Kuang, X. Zhang, J. Chen, Noble metal nanoparticles/carbon nanotubes nanohybrids, *Nano Today* 6 (2011) 75–90.
- [15] F.R. Caetano, L.B. Felipe, A.J. Zarbin, M.F. Bergamini, L.H. Marcolino-Junior, Gold nanoparticles supported on multi-walled carbon nanotubes produced by biphasic modified method and dopamine sensing application, *Sensor. Actuator. B Chem.* 243 (2017) 43–50.
- [16] H. Yadegari, A. Jabbari, H. Heli, A. Moosavi-Movahedi, K. Karimian, A. Khodadadi, Electrocatalytic oxidation of deferiprone and its determination on a carbon nanotube-modified glassy carbon electrode, *Electrochim. Acta* 53 (2008) 2907–2916.
- [17] S. Majdi, A. Jabbari, H. Heli, H. Yadegari, A. Moosavi-Movahedi, S. Haghgoo, Electrochemical oxidation and determination of ceftriaxone on a glassy carbon and carbon-nanotube-modified glassy carbon electrodes, *J. Solid State Electrochem.* 13 (2009) 407–416.
- [18] S. Majdi, A. Jabbari, H. Heli, A. Moosavi-Movahedi, Electrocatalytic oxidation of some amino acids on a nickel–curcumin complex modified glassy carbon electrode, *Electrochim. Acta* 52 (2007) 4622–4629.
- [19] A. Mujtaba, N.K. Janjua, Fabrication and electrocatalytic application of CuO@ Al₂O₃ hybrids, *J. Electrochem. Soc.* 162 (2015) H328–H337.
- [20] J. Wang, Electrochemical glucose biosensors, *Chem. Rev.* 108 (2008) 814–825.
- [21] A. Heller, B. Feldman, Electrochemical glucose sensors and their applications in diabetes management, *Chem. Rev.* 108 (2008) 2482–2505.
- [22] V.A. Kumary, T.M. Nancy, J. Divya, K. Sreevalsan, Nonenzymatic glucose sensor: glassy carbon electrode modified with graphene-nickel/nickel oxide composite, *Int. J. Electrochem. Sci* 8 (2013) 2220–2228.
- [23] X. Yang, Y. Wang, Y. Liu, X. Jiang, A sensitive hydrogen peroxide and glucose biosensor based on gold/silver core–shell nanorods, *Electrochim. Acta* 108 (2013) 39–44.
- [24] W. Lu, X. Qin, A.M. Asiri, A.O. Al-Youbi, X. Sun, A novel three-dimensional porous sensing platform for sensitive and selective nonenzymatic glucose detection, *Analyst* 138 (2013) 417–420.
- [25] L. Wang, X. Lu, Y. Ye, L. Sun, Y. Song, Nickel-cobalt nanostructures coated reduced graphene oxide nanocomposite electrode for nonenzymatic glucose biosensing, *Electrochim. Acta* 114 (2013) 484–493.
- [26] C. Gong, J. Chen, Y. Song, M. Sun, Y. Song, Q. Guo, L. Wang, A glucose biosensor based on the polymerization of aniline induced by 0a bio-interphase of glucose oxidase and horseradish peroxidase, *Anal. Methods* 8 (2016) 1513–1519.
- [27] E. Reitz, W. Jia, M. Gentile, Y. Wang, Y. Lei, CuO nanoparticles based nonenzymatic glucose sensor, *Electroanalysis: An International Journal Devoted to Fundamental and Practical Aspects of Electroanalysis* 20 (2008) 2482–2486.
- [28] W.-D. Zhang, J. Chen, L.-C. Jiang, Y.-X. Yu, J.-Q. Zhang, A highly sensitive nonenzymatic glucose sensor based on NiO-modified multi-walled carbon nanotubes, *Microchimica acta* 168 (2010) 259–265.
- [29] W. Lv, F.-M. Jin, Q. Guo, Q.-H. Yang, F. Kang, DNA-dispersed graphene/NiO hybrid materials for highly sensitive non-enzymatic glucose sensor, *Electrochim. Acta* 73 (2012) 129–135.
- [30] X. Li, Q. Zhu, S. Tong, W. Wang, W. Song, Self-assembled microstructure of carbon nanotubes for enzymeless glucose sensor, *Sensor. Actuator. B Chem.* 136 (2009) 444–450.
- [31] R. Zhang, M. Hummelgård, H. Olin, Simple and efficient gold nanoparticles deposition on carbon nanotubes with controllable particle sizes, *Mater. Sci. Eng., B* 158 (2009) 48–52.
- [32] G. Frens, Controlled nucleation for regulation of particle-size in monodisperse gold suspensions, *Nat. Phys. Sci. (Lond.)* 241 (1973) 20.
- [33] P.R. Mudimela, M. Scardamaglia, O. González-León, N. Reckinger, R. Snyders, E. Llobet, C. Bittencourt, J.-F. Colomer, Gas sensing with gold-decorated vertically aligned carbon nanotubes, *Beilstein J. Nanotechnol.* 5 (2014) 910–918.
- [34] V.D. Chinh, G. Speranza, C. Migliaresi, N. Van Chuc, V.M. Tan, N.-T. Phuong, Synthesis of gold nanoparticles decorated with multiwalled carbon nanotubes (Au-MWCNTs) via cysteaminium chloride functionalization, *Sci. Rep.* 9 (2019) 5667.
- [35] G. Chang, H. Shu, K. Ji, M. Oyama, X. Liu, Y. He, Direct electrodeposition of gold nanostructures onto glassy carbon electrodes for non-enzymatic detection of glucose, *Appl. Surf. Sci.* 288 (2014) 524–529.
- [36] W. Wang, S. Ying, Z. Zhang, S. Huang, Novel glucose biosensor based on a glassy carbon electrode modified with

- hollow gold nanoparticles and glucose oxidase, *Microchimica Acta* 173 (2011) 143–148.
- [37] H. Zhu, X. Lu, M. Li, Y. Shao, Z. Zhu, Nonenzymatic glucose voltammetric sensor based on gold nanoparticles/carbon nanotubes/ionic liquid nanocomposite, *Talanta* 79 (2009) 1446–1453.
- [38] R. Prehn, M. Cortina-Puig, F.X. Muñoz, A non-enzymatic glucose sensor based on the use of gold micropillar array electrodes, *J. Electrochem. Soc.* 159 (2012) F134–F139.
- [39] H. Shu, L. Cao, G. Chang, H. He, Y. Zhang, Y. He, Gold nanoparticles directly modified glassy carbon electrode for non-enzymatic detection of glucose, *Electrochim. Acta* 132 (2014) 524–532.
- [40] R. Sedghi, Z. Pezeshkian, Nonenzymatic glucose voltammetric sensor based on gold nanoparticles/carbon nanotubes/ionic liquid nanocomposite, *Sensor. Actuator. B Chem.* 219 (2015) 119–124.
- [41] S. Hrapovic, Y. Liu, K.B. Male, J.H. Luong, Electrochemical biosensing platforms using platinum nanoparticles and carbon nanotubes, *Anal. Chem.* 76 (2004) 1083–1088.
- [42] J. Ryu, K. Kim, H.-S. Kim, H.T. Hahn, D. Lashmore, Intense pulsed light induced platinum–gold alloy formation on carbon nanotubes for non-enzymatic glucose detection, *Biosens. Bioelectron.* 26 (2010) 602–607.
- [43] C.H. Kwon, Y. Ko, D. Shin, S.W. Lee, J. Cho, Highly conductive electrocatalytic gold nanoparticle-assembled carbon fiber electrode for high-performance glucose-based biofuel cells, *J. Mater. Chem.* 7 (2019) 13495–13505.
- [44] D.T. Tran, N.H. Kim, J.H. Lee, Cu-Au nanocrystals functionalized carbon nanotube arrays vertically grown on carbon spheres for highly sensitive detecting cancer biomarker, *Biosens. Bioelectron.* 119 (2018) 134–140.
- [45] A. Pani, T.D. Thanh, N.H. Kim, J.H. Lee, S.-I. Yun, Peanut skin extract mediated synthesis of gold nanoparticles, silver nanoparticles and gold–silver bionanocomposites for electrochemical Sudan IV sensing, *IET Nanobiotechnol.* 10 (2016) 431–437.
- [46] H.T. Le, D.T. Tran, T.L.L. Doan, N.H. Kim, J.H. Lee, Hierarchical Cu@CuxO nanowires arrays-coated gold nanodots as a highly sensitive self-supported electrocatalyst for L-cysteine oxidation, *Biosens. Bioelectron.* 139 (2019) 111327.
- [47] T.D. Thanh, J. Balamurugan, N.H. Kim, J.H. Lee, Recent Advances in Metal Alloy-Graphene Hybrids for Biosensors, *Graphene Bioelectronics*, Elsevier, 2018, pp. 57–84.
- [48] A. Shah, M. Akhtar, S. Aftab, A.H. Shah, H.-B. Kraatz, Gold copper alloy nanoparticles (Au-Cu NPs) modified electrode as an enhanced electrochemical sensing platform for the detection of persistent toxic organic pollutants, *Electrochim. Acta* 241 (2017) 281–290.
- [49] H. Jabeen, S. Saleemi, H. Razzaq, A. Yaqub, S. Shakoore, R. Qureshi, Investigating the scavenging of reactive oxygen species by antioxidants via theoretical and experimental methods, *J. Photochem. Photobiol. B Biol.* 180 (2018) 268–275.
- [50] P. Pyykkö, Theoretical chemistry of gold. III, *Chem. Soc. Rev.* 37 (2008) 1967–1997.
- [51] D. Maniu, V. Chis, M. Baia, F. Toderas, S. Astilean, Density functional theory investigation of p-aminothiophenol molecules adsorbed on gold nanoparticles, *J. Optoelectron. Adv. Mater.* 9 (2007) 733.