CHAPTER 6

ELECTROCHEMICAL DETERMINATION OF GLUCOSE BASED ON METAL (Au, Ag, Pt AND Pd) DOPED CuO NANOCOMPOSITES

6.1. INTRODUCTION

Noble metal nanoparticles (NPs) with a narrow size distribution have valuable technological importance because of their unique physiochemical properties and applications in the field of catalysis, information storage, optoelectronics, sensors, fine chemical synthesis, oil refining processes, and fuel cell technology. Uniformly dispersed small size particles can exhibit important properties that are critical in these such as surface chemical activity and magnetic as well as electronic properties (Li et al., 2014; Xiao et al., 2014; Huh et al., 2012; Chen et al., 2014).

Due to the unique size, shape, composition and structure-dependent properties and physiochemical properties, noble metal nanomaterials with narrow size distribution have been applied in various fields of science and technology (Xu et al., 2010; Qiao et al., 2014). Uniformity of particle size minimizes the dispersion of important properties that are critical in these operations, such as surface chemical activity and magnetic as well as electronic properties (Wang et al., 2009; Wang et al., 2007). A combination of noble metal and metal oxide nanoparticles can produce a composite material that possesses complementary properties of the individual components with a synergistic effect or tuned properties (Sun et al., 2001). These materials are being employed in electrochemistry to improve the performance of electrochemical techniques due to the excellent electrocatalytic properties (Kumar et al., 2014). In order to increase the response signal, sensitivity and to achieve a better reproducibility the fabrication of electrodes modified with nanoparticles has been the focus of recent attention. Nanomaterials with good biocompatibility and electrocatalytic activities have been widely incorporated in micro electrode modification (Shu et al., 2014; Zheng B et al., 2014). Using physical and chemical modification of electrode surface, detection performance has been effectively improved and the application scope has been expanded. Because of their low cost, high stability and enhanced glucose oxidation due to the multi-electron oxidation
effect, more efforts have been undertaken onto development of various nanoscale metal oxides (e.g., NiO (Jamal et al., 2013), Co$_3$O$_4$ (Hou et al., 2012), Fe$_2$O$_3$ (Cao and Wang, 2011), and CuO (Cao and Gong, 2012). Among these, nanoscale CuO semiconductor can behave as a promising material for developing non-enzymatic glucose sensor in terms of its good electrochemical activity and capability of promoting electron transfer rate at a low over potential in alkaline medium, based on the redox couple Cu(II)/Cu(III).

Noble metal nanomaterials provide a new opportunity for fabricating electrodes with high electrocatalytic activity, due to their high ratio of surface atoms with free valences to the cluster of total atoms. In order to improve the sensor sensitivity, Au, Ag, Pt and Pd nanoparticles have been used due to its high electrocatalytic activities and excellent biocompatibility (Bo et al., 2010; Yang et al., 2013). Various Pt based binary catalyst have been proposed to increase the amperometric current response towards the glucose oxidation and low interference from other electroactive species. According to the reports (Blaesi and Buie, 2011; Gao et al., 2011), the applications of noble metal nanoparticles in electrochemical sensors and biosensors have witnessed a significant growth in the past few years due to their extraordinary advantages, including good biocompatibility, low cytotoxicity, high stability, conductivity and catalytic property (Yang et al., 2014; Gu et al., 2014; Gholivand et al., 2014). Moreover, the catalytic activity of these materials is highly dependent on surface areas, surface atomic structures, crystal sizes, and shapes (Chen et al., 2009). By controlling the sizes and shapes of the catalysts, large surface areas and abundant catalytic active sites could be realized, thereby favoring enhanced catalytic performance and improving the noble nanomaterials utilization efficiency (Hu et al., 2014).

This chapter demonstrates the facile chemical precipitation route to synthesize the noble nanomaterial-decorated CuO nanoleaves and its application in glucose sensing using amperometric method. The fabricated noble metals (Au, Ag, Pt and Pd) based CuO sensor exhibited notable electrocatalytic performance for glucose oxidation and also showed high sensitivity, linear detection range to glucose. Based on the mechanism, copper oxide catalyzes glucose oxidation and the noble nanomaterials act as a co catalyst to enhance the electron transfer during oxidation of
glucose. The electrochemical properties and electrochemical activity of the fabricated electrode have been investigated in detail.

6.2. RESULT AND DISCUSSION

6.2.1. Structural and morphological properties of metal (Au, Ag, Pt and Pd) decorated CuO nanoleaves

The crystallographic structures of the samples were examined by X-ray diffraction (XRD). The wide-angle XRD patterns of the as-prepared samples were also carried out to further explain the existence forms of the metal elements. Figure 6.1a represents the XRD pattern of Au/CuO nanoleaves and the diffraction peaks could be indexed to (110), (002), (111), (-202), (020), (202), (-113), (113) and (311) phases, which shows the presence of the monoclinic crystal structure of CuO (JCPDS 43-1002). Besides, the remaining peak at 38.2º, 44º, 64º correspond with (111), (200), (220) planes of Au structure (JCPDS 65-2870) (Fang et al., 2014). The average size of the Au decorated CuO nanocomposites calculated based on the Scherrer formula is 30 nm. Figure 6.1b shows the X-ray diffraction (XRD) pattern of the as synthesized composites (labeled as Ag-CuO), indicating that the silver was formed after being reduced by ethylene glycol. The peaks at 20 = 38º, 44º, 65º, and 78º can be assigned to the (111), (200), (220), and (311) crystalline planes of face-centered cubic (fcc) structure of silver, respectively (Balan et al., 2007), which indicate that the silver nanoparticles are composed of pure crystalline silver. However, remaining diffraction peaks indicates the monoclinic crystal structure of CuO. The average crystalline size of the Ag deposited CuO nanocomposites was calculated to be 33.7 nm based on Scherrer’s equation. Figure 6.1c illustrates the XRD patterns of the as-prepared composites exhibiting a high crystalline quality of Pt decorated CuO nanoleaves. The sharp and strong diffraction peaks suggest that the prepared products are highly crystalline and the obtained black precipitate indicates that it consist of both CuO (JCPDS: 89-5895) and Pt (JCPDS: 88-2343) phase in the composite. The diffraction peaks are described to two groups. One group belongs to the cubic phase of the Pt crystal as indexed at a peak position of 39.28º, 45.66º, 66.57º and 80.11º corresponding to the Pt (111), Pt (200) and Pt (311), respectively (Gu et al., 2013). Another indexed group belongs to the monoclinic CuO (space group with lattice constants, a = 4.682, b = 3.424, c = 5.127) with similar peak intensities and shapes, with peaks at 32.5º, 35.8º, 38.9º, 48.8º, 58.1º, 61.5º, 66.3º, 67.9º, 75º indexed to (110),
(002), (111), (-202), (020), (202), (-113), (113) and (311) planes of the CuO nanocrystal respectively (Wan et al., 2013). The average crystalline size of the nanocomposites can be estimated using Debye-Scherrer equation and found to be 39.08 nm. Powder X-ray diffraction pattern of Pd-decorated CuO nanocomposites are shown in Figure 6.1d. As shown in figure, all peaks can be indexed as the pure monoclinic phase of CuO, which agrees well with the reported data (JCPDS No. 43-1002) Pd (111), Pd (200) and Pd (220) are located at 2θ values of 40.0°, 45.7° and 67.7°, respectively (JCPDS 05-0681) (Li et al., 2012), illustrating that Pd-CuO nanocomposites possess the face centered cubic crystal structure. The average size of Pd based CuO nanocomposites can be calculated from the half peak width of the Pd (220) peak according to Scherrer equation. The average size of Pd-CuO nanocomposites was calculated to be 45 nm.

![Figure 6.1 XRD-patterns of (a) Au-CuO, (b) Ag-CuO, (c) Pt-CuO and (d) Pd-CuO nanocomposites](image)

The surface morphology can be illustrated by field emission scanning electron microscope (FE-SEM). Representative FE-SEM images of leaf-like CuO nanomaterials and metal nanoparticles (Au, Ag, Pt and Pd) were decorated on CuO nanoleaves as shown in Figure 6.2a-d.
As could be seen, aligned leaf like CuO platelets with an average length range of 100 nm-130 nm are observed in Figure 6.2a-b. It could be clearly see that the as formed metal nanoparticles are equally distributed and highly dispersed on the surface. The metal nanoparticles could be seen on the surface of leaf-like CuO nanostructures and having roughened surface, which suggests that the metal nanoparticles are highly dispersed with an average size of metal nanoparticle ranging from 20-50 nm. Figure 6.2c and d shows the images of Pt and Pd on the CuO nanoleaf substrate in which it clearly reflects that the nanoparticles are homogenously decorated throughout the leaves of CuO and the distribution of the nanoparticles are almost uniform. Finally from these results, it is evident that the size and morphology for the formation of metal nanoparticles were uniformly decorated on the CuO nanoleaves. The EDAX characterization was done to investigate each element present in the nanocomposites (Figure 6.2e-h), which shows the presence of Au, Ag, Pt, Cu and O elements present in the resulting hybrid nanostructure. As a layer of gold was sputtered on it to measure its FE-SEM image, the peaks of gold were also observed in the spectrum. The results indicate that the entire hybrid composites are mainly composed of Au, Ag, Pt, Pd, Cu and O elements. The results reprove that metal nanoparticles are successfully incorporated with leaf like CuO nanoplatelets through the proposed simple co-precipitation method.
6.2.2. Optical properties of metal (Au, Ag, Pt and Pd) decorated CuO nanoleaves

Figure 6.3 UV-vis absorption spectra of Au-CuO (a), Ag-CuO (b), Pt-CuO (c) and Pd-CuO (d); Inset shows the calculated plots of the $(\alpha h\nu)^2$-hv for metal decorated CuO nanostructures

UV-vis spectrum is an effective method to monitor the formation of composites. The optical plasmon resonance of single metal nanoparticles is confined to relatively narrow the wavelength ranges. The optical properties toward metal particles in the composites would be different from that of individual metal particles. Moreover, the position of absorption peak depends on the dimension of the metal as well as the surroundings. The characteristic absorption spectrum of CuO shows a peak at about 355 nm (Figure 6.3a-d), due to surface plasmon resonance of CuO. Figure 6.3a-d presents UV-vis spectra of the as-prepared metal decorated CuO nanoleaves. All the samples (Au-CuO, Ag-CuO, Pt-CuO and Pd-CuO nanocomposites) exhibited a representative absorption with intense transition in UV region of the spectra due to the band gap transition of CuO semiconductor. The direct band gap energy of about 2.54 eV for the as-prepared leaf-like CuO nanomaterials and metal-CuO composites can be estimated from Figure 6.3 insets. From insets of Figure 6.3, a typical absorption of the metals surface plasmon band can be easily observed in the UV-region between 200
and 300 nm. This not only confirms that metal NPs have been successfully supported on the surface of CuO nanocrystals, but also confirms that metal based CuO nanocomposites have much stronger absorption than that of CuO NPs, this obviously implies that the composites possess higher electrocatalytic activity for target electrocatalytic reaction than that of bare CuO nanoleaves. The increase in the band gap of the CuO nanocomposites is indicative of quantum size effects (Yang et al., 2015). This band is ascribed to a collective oscillation of conduction electrons in response to optical excitation and is affected by the dispersed metal particle size, the shape of the particle, and the electronic properties of the medium surrounding the particles (Tu et al., 2009).

FT-IR was also applied to examine the synthesized metal based CuO nanocomposites in the range from 400 to 4000 cm\(^{-1}\) at room temperature (Figure 6.4).

![FT-IR spectra of (a) Au-CuO, (b) Ag-CuO, (c) Pt-CuO and (d) Pd-CuO nanohybrids](image)

The bands at 480, 533.2 and 608.3 cm\(^{-1}\) correlated to metal oxide bond (CuO) (Zhang et al., 2006; Shin et al., 2008). Bands around 900-1500 cm\(^{-1}\) are due to the oxygen stretching and bending frequency (Vijayakumar et al., 2013). It is believed that the absorption peak at 3441 cm\(^{-1}\) is attributed to the O-H stretching vibration and its corresponding O-H bending vibration occurs at 1636 cm\(^{-1}\) due to the chemically adsorbed water molecules (Rahulan et al., 2011). The transformation of the initial carboxylic acid (COOH 1691 cm\(^{-1}\)) to a carboxyl ion (COO\(^{-}\) 1582 cm\(^{-1}\) and 1706 cm\(^{-1}\)
The IR spectrum exhibits clear peaks at around 1710 cm\(^{-1}\) for the stretching of C=O in the free COOH and at around 1390 cm\(^{-1}\) for the symmetric stretching of COO\(^{-}\), suggesting a stable carboxylic group-carrying species (partially dissociated) on the surface of the gold particles, suggesting a very stable carboxylic group-carrying species with bonding occurred to stabilize the gold nanoparticles. In figure 6.4b, the band at 723.96 cm\(^{-1}\) clearly shows the presence of Ag ions approximately equal with the reported literature (Vijayakumar et al., 2013). The band at 1035 and 1080 cm\(^{-1}\) in Ag-CuO corresponds to the C-N bending modes and also the resonance peak of C=O at 1649 cm\(^{-1}\) was observed for silver nanoparticles. In Figure 6.4c, the peak in the region of 1387 cm\(^{-1}\) is a complex band from the residual C-H groups and from hexachloroplatinic acid. The H-O-H in-plane deformation is observed at 1639 cm\(^{-1}\). A broad band at 3400 cm\(^{-1}\) is attributed to the O-H stretching vibrations from residual alcohol, water, and CuO-H bonds. In addition, the surface hydroxyl groups in CuO increase with increasing metal loading, which is confirmed by increasing intensity of the corresponding peaks. The decrease in intensity could be due to the modification of functional groups (C = O, C-OH and C-O) by Pd nanoparticles. In the FT-IR spectra of the as-prepared Pd NPs (Figure 6.4d), the peak located at about 1387 cm\(^{-1}\) is assigned to C-N stretching, indicating the presence of organic amine. The peak located at about 3451 cm\(^{-1}\) is assigned to N-H stretching, and 1639.3 cm\(^{-1}\) to N-H rocking vibrations of the organic amines (Zhang et al., 2012). The peak, which shifted to 3451 cm\(^{-1}\), revealed the covalent bonding of the N-H to the Pd surface.

6.2.3. Determination of the electrochemical active surface area

In our experiment, the electrochemical active surface areas (A) of different metal based CuO nanostructures modified electrodes were estimated by cyclic voltammetry using ferricyanide as probe. As shown in Figure 6.5 a-d (insets), the peak current increases linearly with increasing the square root of the scan rate for all four samples. This result suggests that the reaction occurring due to the activity redox of the metal-CuO nanocomposites modified electrode was nearly reversible, and the mass transfer process in the double layer region of the glassy carbon electrodes was mainly controlled by diffusion. The dependence of peak currents on different scan rates can be described according to Randles-Sevcik equation under semi-infinite linear diffusion conditions and room temperature (25°C)
Figure 6.5 Cyclic voltammograms of (a) Au-CuO, (B) Ag-CuO, (C) Pt-CuO and (d) Pd-CuO modified GCEs in 2 mM K$_3$[Fe(CN)$_6$] + 0.1 M KCl.

For each metal (Au, Ag, Pt and Pd) decorated CuO nanostructures modified electrode, a series of cyclic voltammograms were recorded as a function of different scan rates in 2 mM K$_3$Fe(CN)$_6$ solutions with 0.1 M KCl as supporting electrolyte for all the four samples. The two pairs of redox peaks (I/IV and III/II) are observed, resulting from the reversible transition between CuO(OH)$_2$ and CuOOH (I/IV) and the transition between CuOOH and CuO(OH)$_2$ (Hou et al., 2012). In agreement with earlier reports (Wang et al., 2014; Yang et al., 2010), two pairs of redox peaks (I/IV and III/II) are observed, which related from the redox reaction of Fe(CN)$_6^{3-}$, found between +0.2 and +0.3 V. Another pair of anodic and cathodic peaks, which is believed to be due to the redox reactions of CuO, was found between +0.7 and +0.8 V matching well with the theoretical standard potential of CuO at +0.747 V due to transition between Cu(OH)$_2$ and CuOOH (I/IV) and the transition between CuOOH and Cu(OH)$_2$. This result suggests that the reaction occurred on the metal based CuO modified electrodes were nearly reversible, and the mass transfer process in the double layer region of the glassy carbon electrodes was mainly controlled by diffusion. The cyclic voltammogram of the modified electrodes in 2 mM K$_3$Fe(CN)$_6$ containing 0.1 M KCl showed a slightly small peak separation and larger peak current (Figure 6.5a-d) than that of CuO/Nf/GCE, demonstrating the faster electron transfer and the larger electroactive surface area for M (Au, Ag, Pt and Pd)-CuO/Nf/GCE.
It can be seen that the electrode redox peak current rises with an increase of the square root of scan rates indicating a diffusion controlled process. The plot of the oxidation and reduction peak currents against the square root of scan rates ranging from 20-500 mV/s, (inset in Figure 6.5) shows an excellent linear direct relationship, which suggests that the electrocatalytic process is controlled by diffusion to the modified electrode/solution interface (Wang et al., 2014). According to Ma et al., 2014, to the Randles equation electro active surface area of the modified electrodes was calculated to be 4.376 cm$^2$.

6.2.4. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) can reveal the impedance changes of the electrode surface during the modification process. Figure 6.6 shows the EIS of different modified electrodes in 5 mM Fe(CN)$_6^{3-/4-}$ containing 0.5 M KCl as supporting electrolyte in the frequency range of 10$^5$-0.1 Hz. In general, the EIS spectra have semicircular sections at higher frequencies corresponding to the electron transfer limiting process, and the linear sections at lower frequencies relative to the diffusion limiting process.

![Electrochemical impedance spectra (EIS) of GCE modified with metal composites like Au-CuO (a), Ag-CuO (b), Pt-CuO (c) and Pd-CuO in 0.5 M KCl aqueous solution containing 5.0 mM [Fe(CN)$_6^{3-/4-}$]. The frequency range is from 0.1 Hz to 100 kHz at a potential of 0.2 V. The inset A represents the Randles equivalent circuit model for the impedance of the electrochemical sensing system.](image)
The impedance plot for the bare electrode is characterized by a semicircle at high frequency and a low frequency Warburg impedance (Rct 344 Ω). For Au-CuO/Nf/GCE, the plot is nearly a straight line (Figure. 6.6 inset), which represents Warburg resistance and the diffusion limiting step in the electrochemical process. Typically, an almost straight line in the plot implies low electron transfer resistance, indicating good conductivity of the redox probe. The Au-CuO/Nf/GCE shows a drastic change in the Rct value (Rct-271 Ω), which indicates the good conductivity of the modified electrode when compared to that of the other modified electrodes (Ag, Pt and Pd/Nf/CuO). Furthermore, the Au-CuO/Nf/GC modified electrode shows a straight line due to the heterojunction effect and exhibits lower transfer resistance. These results showed that the Au-CuO nanocomposites can act as a better electron transfer interface between the electrode surface and electrolyte solution.

6.2.5. Cyclic voltammetry studies of different M-CuO modified electrodes towards glucose

The electrocatalytic behaviour of different metal based CuO nanostructures modified electrodes towards the oxidation of glucose in alkaline medium was investigated in 0.1 M NaOH aqueous solution from 0.0 to +0.8 V at a scanning rate of 50 mV s\(^{-1}\) using cyclic voltammetry (shown in Figure 6.7). As shown in Figure 6.7, there are no obvious redox peaks on Au-CuO/Nf/GCE (Figure 6.7a), Ag-CuO/Nf/GCE (Figure 6.7b), Pt-CuO/Nf/GCE (Figure 6.7c) and Pd-CuO/Nf/GCE (Figure 6.7d) in 0.1 M NaOH solution without glucose (dot line). However, in the presence of glucose (1 mM or 1000 µM), the electrode modified with metal based CuO nanocomposites show higher back ground currents, indicating the increased active surface areas and enhanced electrocatalytic activity of the noble metals (Au, Ag, Pt and Pd). With the injection of glucose (1000 µM) into NaOH solution, the intensity of glucose oxidation peak increases but the corresponding reduction peak current intensity decreases indicating that metal based CuO nanomaterials can electrochemically catalyze the oxidation of glucose. As could be seen from Figure 6.7a-d (solid line), the oxidation peak of Cu(II)/Cu(III) cannot be observed clearly in the range 0.4 V to 0.8 V. This might be due to the overlay by the oxidation peak of water breakdown, which was consistent with the previous reports (Wang et al., 2014; Luo et al., 2011). Hence, anodic oxidation peak at +0.6 V indicates the strong catalytic effect of the Au-CuO on direct oxidation of glucose, which is similar to the
previously reported results on sensing of glucose based on CuO based materials (Luo et al., 2011; Xu et al., 2014; Kong et al., 2014).

The anodic peak potential got shifted to higher potential, which might due to the diffusion limitation of glucose at the electrode surface. From this observation, it is obvious that though CuO is responsible for electrocatalytic oxidation of glucose, metals are necessary to increase the sensitivity. Hence, a notable enhancement of the anodic current could be observed with all the modified electrodes viz. Au-CuO/Ni/GCE, Ag-CuO/Ni/GCE, Pt-CuO/Ni/GCE and Pd-CuO/Ni/GCE. The excellent electrocatalytic performance for the oxidation of glucose, suggest that the combination of metals (Au, Ag, Pt and Pd) and CuO nanoleaves leads to the high catalytic efficiency toward glucose oxidation. At the same time, the existence of a small quantity of metals can significantly enhance the catalytic effect of CuO.

6.2.6. Amperometric responses of different M-CuO modified electrodes towards glucose

For the electrochemical sensing applications, the sensing performance of the catalysts is usually evaluated by measuring the current response at fixed potentials versus time after the addition of analytes. Under the optimized experimental conditions, the current-time performance of the modified M-CuO/Ni/GCE was
investigated by chronoamperometric analysis (Figure 6.8). With the successive addition of glucose to a continuously stirring NaOH solution, the sensor had a rapid response to the change of fructose concentration and obtains a steady-state level within 5 s.

![Figure 6.8 Current-time responses for glucose oxidation at various modified electrodes (a) Au-CuO, (b) Ag-CuO, (c) Pt-CuO and Pd-CuO with successive addition of glucose into 0.1 M NaOH solution. Insets shows calibration curves for all the electrodes with current against glucose concentration](image)

Figure 6.8a-d depicts a typical amperometric response of different metal based CuO nanocomposites modified GCEs with successive additions of glucose (100 µM) to a vigorously stirred electrolyte solution at 0.6 V and their corresponding calibration curves are shown in Figure 6.8 inset. As can be seen from these diagrams, the rapid increase in the current density after each addition of glucose is noticed in all cases, indicating that all the sensors possessed a short response time. Au-CuO/Ni/GCE, Ag-CuO/Ni/GCE and Pt-CuO/Ni/GCE responded more quickly and sensitively to each addition of glucose than Pd-CuO/Ni/GCE. As expected, the detection current density, response time, and sensitivity got at +0.6 V obey the order Au-CuO/Ni/GCE > Ag-CuO/Ni/GCE > Pt-CuO/Ni/modified GCE, which is exactly consistent with the CV test result. Further, Figure 6.8a-d shows the dynamic amperometric responses at +0.6 V with the successive increments of glucose concentration. From the corresponding calibration curves of these modified GCEs (shown in the insets), a linear response with a sensitivity of 2628.6 µA mM⁻¹ cm⁻² glucose (R = 0.9998), a linear range of 5-
950 µM, and a detection limit of 13 µM (S/N = 3) were obtained for Au-CuO/Nf/GCE. It is clear that these detection parameters are much better than those of Ag-CuO/Nf/GCE (2528.6 µA mM⁻¹cm⁻², 5-1000 µM, 15 µM and 4 s; R = 0.9945), Pt-CuO/Nf/GCE (1705.7 µA mM⁻¹cm⁻², 2-1000 µM, 11 µM and 4 s; R = 0.9986) and Pd-CuO/Nf/GCE (761.4 µA mM⁻¹cm⁻², 100-500 µM, 49 µM and 4 s; R = 0.9971). In order to further compare the electrochemical properties of the different M-CuO towards glucose oxidation, its electrochemical data corresponding to different metals, have been summarized Table 6.1. The superior performance of Au-CuO/Nf/GCE towards glucose detection is ascribed to the well-distribution of Au on the CuO nanoleaves, large specific surface area and the synergistic property derived from CuO and Au. The wide linear range is due to the high surface to volume ratio with more electroactive species and large surface area for glucose molecules to adsorb and react, while the fast and sensitive catalytic performance is due to the promoted electron transfer, large aspect ratio, high active surface area and superb catalytic activity provided by the nanocomposite structure of CuO and Au. Meanwhile, its sensitivity is better than those of most reported noble metal glucose sensors (Table 6.2). Above all, when compared with some enzyme-based glucose sensors, Au-CuO shows larger sensitivity, shorter response time, lower detection limit, and wider linear range.

Table 6.1 The analytical performance of the Au-CuO/Nf/GCE glucose sensor compared with other reported nonenzymatic CuO-based glucose sensors

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Medium</th>
<th>Linear range</th>
<th>Sensitivity (µAmM⁻¹cm⁻²)</th>
<th>Detection limit (µM)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPG/CuO</td>
<td>0.1 M NaOH</td>
<td>12 mM</td>
<td>374.0</td>
<td>2.8</td>
<td>(Xiao et al., 2014)</td>
</tr>
<tr>
<td>Cu₂O-Au nanocomposites</td>
<td>0.1 M NaOH</td>
<td>2-100 µM</td>
<td>-</td>
<td>0.5</td>
<td>(Hu et al., 2012)</td>
</tr>
<tr>
<td>Au/CuO NSs b</td>
<td>0.1 M PBS</td>
<td>-</td>
<td>164.2523</td>
<td>39</td>
<td>(Lei et al., 2015)</td>
</tr>
<tr>
<td>Au-CuO/Nf/GCE</td>
<td>0.10 M NaOH</td>
<td>5 µM-950 µM</td>
<td>2628.6</td>
<td>15</td>
<td>This work</td>
</tr>
</tbody>
</table>

a nanoporous gold

b NSs-Nano sheet
6.2.7. Selectivity and stability

A challenge in glucose detection is the avoidance of interfering reagents. In human blood, a number of easily oxidizable interfering species such as AA, UA, DA and other carbohydrates co-exist along with glucose. The physiological level of glucose in human body is 3-8 mM, which is much higher than other oxidizable interferents (around 30:1). Hence, 0.1 mM glucose was selected to carry out the interference test with the addition of 0.01 mM interferents in 0.1 M NaOH solution and their current response shown in Figure 6.9a.

It is obvious that the as-prepared samples exhibited negligible response to the interfering species. This was probably due to the relatively less working potential, as well as the use of nafion, which is negatively charged and have repelled the

### Table 6.2 Analytical performance of metal (Au, Ag, Pt and Pd) based CuO nanocomposites

<table>
<thead>
<tr>
<th>Fabricated electrode</th>
<th>Electrolyte</th>
<th>Linear range (µM)</th>
<th>Sensitivity (µA mM⁻¹ cm⁻²)</th>
<th>Detection limit (µM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au-CuO/Nf/GCE</td>
<td>0.1 M NaOH</td>
<td>5-950</td>
<td>2628.6</td>
<td>13</td>
</tr>
<tr>
<td>Ag-CuO/Nf/GCE</td>
<td>0.1 M NaOH</td>
<td>5-1000</td>
<td>2528.6</td>
<td>15</td>
</tr>
<tr>
<td>Pt-CuO/Nf/GCE</td>
<td>0.1 M NaOH</td>
<td>2-1000</td>
<td>1705.7</td>
<td>11</td>
</tr>
<tr>
<td>Pd-CuO/Nf/GCE</td>
<td>0.1 M NaOH</td>
<td>100-500</td>
<td>761.4</td>
<td>49</td>
</tr>
</tbody>
</table>

![Figure 6.9](image_url)

**Figure 6.9** (a) Current-time response of Au-CuO/Nf/GCE upon the successive addition of sucrose (50 µM), fructose (50 µM), UA (100 µM), DA (100 µM) and AA (100 µM). (b) Standard addition of glucose in 0.1 M NaOH solution contained human urine sample (80 µL).
interfering substances such as ascorbic acid and uric acid easily (Li et al., 2013; Mahshid et al., 2013). Therefore, as-prepared Au based CuO nanocomposites modified GCE in our experiment exhibited high selectivity towards glucose. We also investigated the long-term storage stability of a proposed different metal based CuO biosensor was evaluated at +0.6 V using chronoamperometry techniques. The electrode was stored in air under ambient condition and the current response was tested every 2 days in 100 µM addition of glucose within 14 days period. The current response approximately shows 92 %, 92.3 %, 91.6 % and 90.1 % of the initial counterparts were retained for all metal based CuO modified GCE respectively. Due to the chemically stable Au-CuO phase in basic solution, the proposed sensor exhibits good stability. We have determined the repeatability of all modified electrodes sensor, a set of seven repetitive measurements was carried out in addition of glucose (200 µM) in 0.1 M NaOH solution and yield a R.S.D of 2.4%, for Au-CuO, Ag-CuO, Pt-CuO and Pd-CuO, respectively, indicating the highest repeatability of Au-CuO. Above all, when compared with some non-enzyme based glucose sensors, Au-CuO/Nf/GCE-shows larger sensitivity, shorter response time, lower detection limit and wider linear range.

6.2.8. Real sample analysis

Glucose concentrations in human urine samples were detected by the developed nonenzymatic glucose biosensor at +0.6 V (Figure 6.9 b). As shown in Table 6.3, the results are satisfying and the detection results all agree with those obtained by the glucose bio sensor in local hospital, which implies that the sensing ability of our Au-CuO/Nf/GCE is not only limited to the standard glucose samples but also it can be used to test on real human urine samples with a good reliability. Table 6.3 summarizes the glucose determination by the proposed sensor, which illustrates that our proposed glucose sensor offers an excellent and precise method for the determination of glucose in real samples.
Table 6.3 The detection of glucose in human urine samples with our proposed Au-CuO/Ni/GCE

<table>
<thead>
<tr>
<th>Samples</th>
<th>Conc. (µM)</th>
<th>Spiked Amount (µM)</th>
<th>Found amount (µM)</th>
<th>Biochemical analyser (µM)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>187.6</td>
<td>50</td>
<td>48.45</td>
<td>49.32</td>
<td>97.9</td>
</tr>
<tr>
<td>2</td>
<td>258.5</td>
<td>80</td>
<td>82.42</td>
<td>82.58</td>
<td>102.6</td>
</tr>
</tbody>
</table>

6.3. CONCLUSIONS

In summary, different noble metals (Au, Ag, Pt and Pd) were decorated on the leaf-like CuO nanostructures, which can be prepared through simple co-precipitation method with the use of different reducing agent and their electrochemical properties were investigated systematically. Non-enzymatic glucose detection was performed by employing different metal-CuO nanostructures modified GCE. It was found that all the metal based CuO nanostructures modified GCE exhibited excellent catalytic performance towards glucose, including high sensitivity for leaf-like CuO, respectively), fast response (< 3 s), relatively low detection limit, good stability and favorable selectivity. At the same time, for the comparison, Au-CuO, Ag-CuO, Pt-CuO and Pd-CuO were also prepared by the same M-CuO (1:2) ratios. The results reveal that Au-CuO shows the superiorities of fast response, good high sensitivity, good selectivity, and resistance toward electrode fouling to glucose detection. This performance is also attainable even for glucose detection in the human urine samples, and this may be attributed to the structure (which provides a large surface area and abundant active sites) and the synergistic effect of the Cu(II)/Cu(III) redox couples in alkaline environment. Due to the presence of metals, direct electron transfer between CuO and GCE is enhanced, leading to the improvement of the electrochemical and electrocatalytic performance of the resulting non-enzymatic glucose sensor.