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FABRICATION OF A pH SENSOR BASED ON METAL OXIDE NANO-PARTICLE AND ION EXCHANGING SURFACES

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ABSTRACT

In this paper, an electrochemical pH sensor has been reported using copper (ii) oxide nanoparticle, along with Nafion and chitosan modified glassy carbon electrode (CuO/GCE). The difference in peak potential shift while using CuO/GCE as pH sensor was found to be linear over the range of pH 3-9, with a sensitivity of 60 $mVpH^{1}$, measured by using square wave voltammetry (SWV). After three hours of continuous use, sensor shows a potential drift of 1.97 – 3.33%; and could retain 95% of its initial sensitivity after 1 week of use. It has been found that the fabricated pH sensor shows response both in the absence and presence of oxygen, which expands the sensors potential application into de-oxygenated environment. The CuO nanoparticle based sensor exhibit good sensitivity and long term stability that may show the way to develop a low cost pH sensor for a wider range of applications.

Keywords: *pH, metal oxide, nanoparticle, electrochemistry, sensor*

1. INTRODUCTION

In electrochemical sensor, pH sensor is a necessary analytical tool in laboratories, clinics and industries that provide a logarithmic measure of H^+ ion concentration. pH monitoring is crucial, as majority of chemical and biological reactions are pH dependent (Qin *et al*., 2015). Therefore, pH monitoring needs to be fast, accurate and reliable in various applications. However, a considerable amount of time involves for several calibration steps, as well as handling delicate pH sensors during the measurement processes (Fog *et al*., 1984). Natural abundant metal oxide as solid state sensing system is always researchers are looking for. Various metal oxide based potentiometric pH sensors have drawn much attention in past decades due to their stability against dissolutions, and independence from cationic interferences (Bezbaruah *et al*., 2002). Among the oxide materials being studied, CuO is one of the widely used metal oxide that is being used as catalyst for various applications (Kuo *et al*., 2007). Owing to its exceptional electrochemical activity and the possibility of promoting electron transfer at a lower potential, as well as it's availability, stability, good morphological and structural control of the synthesized CuO nanostructures; it is a good candidate for pH sensing applications (Li *et al*., 2011). In 2011, S. Zaman (Zaman *et al*., 2011) reported CuO nano flower as an electrochemical pH sensing materials, and showed the effect of the pH on the growth morphology of nanoflowers.

In this work, a facile, stable and sensitive pH sensor is fabricated by synthesizing CuO nanoparticle using hydrothermal method, followed by the drop cast of the nanoparticle along with chitosan and ion exchange resin Nafion on the surface of GC electrode. In oxygenated and deoxygenated environment the sensing abilities of the electrode were investigated in terms of static and dynamic properties, such as calibration, sensitivity, response time and stability. This method allowed the fabrication suitable for mass production and cost effective; and will open up the door to fabricate a miniaturized carbon based sensing platform, which would be suitable, both in clinical, industrial and environmental applications.

2. METHODOLOGY

2.1 Reagents

Cupper nitrate Cu $(NO_3)_2.3H_2O$, hexamethylenetetramine (HMT), $NH_3.H_2O$, were purchased from E.Merck, Germany. Disodium hydrogen phosphate (Na_2HPO_4), sodium dihydrogen phosphate ($NaH_2PO_4.2H_2O$), sodium bicarbonate ($NaHCO_3$), sodium carbonates (Na_2CO_3), NaOH pellets, Nafion and chitosan were purchased from Sigma-Aldrich, India. All chemicals were of analytical grade with high purity. Different pH solutions were prepared using phosphate buffer, sodium hydrogen carbonate, sodium hydroxide, sodium acetate and acetic acid.

2.2 Synthesis of CuO

For the hydrothermal synthesis of CuO nanoparticle, a mixture of hexamethylenetetramine (HMT) and $Cu(NO_3)_2.3H_2O$ were dissolved in 30 mL distilled water under continuous stirring, followed by introducing 5 ml of NH_4OH (5%). Once the solution became clear, 40 ml of this solution has been transferred into a teflon-lined

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stainless steel autoclave and heated at 160°C for 6 h. Once the autoclave cooled down naturally at room temperature, the black precipitated from autoclave collected, washed few times with distilled water and ethanol in order to remove the impurities. Precipitates obtained were dried at 50ºC for 6 h in air, to get CuO nanoparticle (Zhang *et al.*, 2011).

$$NH_4OH \rightarrow NH_4^+ + OH^-$$

$$2\left[Cu\left(NH_3\right)_4\right]^{2+} + 2OH^- \rightarrow CuO + NH_3 + H_2O$$

$$Cu^{2+} + 2OH^- \rightarrow CuO + H_2O$$

2.3 Fabrication of CuO/GCE

A simple casting method has been used for the fabrication of CuO/GCE (Liu *et al.*, 2013). At first, GCE was polished with 1.0 and 0.3 µm alumina powder, followed by washing with water and sonication in ethanol and water respectively. A mixture of 0.2g CuO nanoparticle, 0.1g chitosan and 0.1 ml Nafion was dropped on to the clean surface of GCE, and dried at room temperature for overnight.

2.4 Measurements

SWV and zero current potentiometric (OCP) measurements were performed using a potentiostat/galvanostat (model: µStat 8400, DropSens (Spain). Here three electrode cells has been used, where CuO/GCE were in use as a working electrode with buffer solutions as supporting electrolyte and Ag/AgCl and Pt wire acts as reference and counter electrodes, respectively. SWV measurements were conducted using a frequency of 50 Hz, pulse width of 20 mV and step height of 10 mV. The pH of the buffer solutions were perfectly determined using an Orion 2 Star commercial pH meter. Micro-nanostructure of particles has been investigated by scanning electron microscope-EDS (JEOL JSM-7600F, Tokyo, Japan).

3. RESULTS AND DISCUSSION

3.1 CuO Nanoparticle Characterizations

The morphology of the hydrothermally synthesized CuO nanoparticles was observed by SEM with a magnification of (5000X to 50,000X) (Figure 1 a-d). A flower shape CuO nanostructure can be seen that the particle sizes are less than 100 nm width of each rod. According to the EDS (Figure 2), the average content of copper (Cu) and oxygen (O) is 8.09% (atomic percentage) and 7.17% (atomic percentage) respectively, which confirm the copper oxide (Cu: O=1:1) component. However, C peak appeared, possibly from sample holder. Due to the higher in density of nanostructure, flower like CuO has a huge potential, as high surface area would improve the sensitivity of the current response.

3.2 Response of Modified Electrode to pH Changes

To demonstrate the sensing application of CuO/GCE, it was constructed by deposition of the aqueous dispersion of nanoparticle on GCE surface in the presence of chitosan and Nafion (Figure 3). Nafion is an anionic ion exchange resin, which facilitate holding CuO on the surface of the electrode, as well as block anionic interferences; and chitosan that has been used as an immobilization matrix. To investigate the properties of modified electrode, cyclic voltammograms (CVs) with different scan rate has been conducted with scan rates of 60-160 mVs^{-1}. On the increases of both anodic and cathodic current linearly with the scan rates, indicating that the electrochemical reaction is surface controlled. The current increases with scan rate for the sensor shows no significant resistance on the electrode surface (Table 1).

Since the primary focus of this paper is to fabricate and characterize the CuO/GCE as pH sensor, the SWV response in a series of aqueous buffer solutions ranging from pH 3 to 11 has been conducted. SWV is the fast, accurate and sensitive in compare to other relevant voltammograms (Harris *et al.,* 2010). A defined peak has been obtained in every buffer solution using CuO/GCE as electrode. This sharp peak at around 0.04V at pH 7 belongs to the reduction of Cu^{2+} to Cu. However, as the pH changes from 3 to 11, the peak potential shifts from higher potential to lower potential (Figure 4a) up to pH 9. Afterwards, the electrode shows non linear response. Therefore, in Figure 4a, an only pH change has been shown from pH 3 to 9. This linear response with different pH solution may attributes to fewer protons available while pH increases, that speeds up the reduction of Cu^{2+} to Cu; resulted lowering the peak potential. However, we also can see the reduction of peak current, which could be due to the limiting of species that can be reduced. Possible sensing mechanism has shown in equation 1 (Kurzweil *et al.*, 2009).

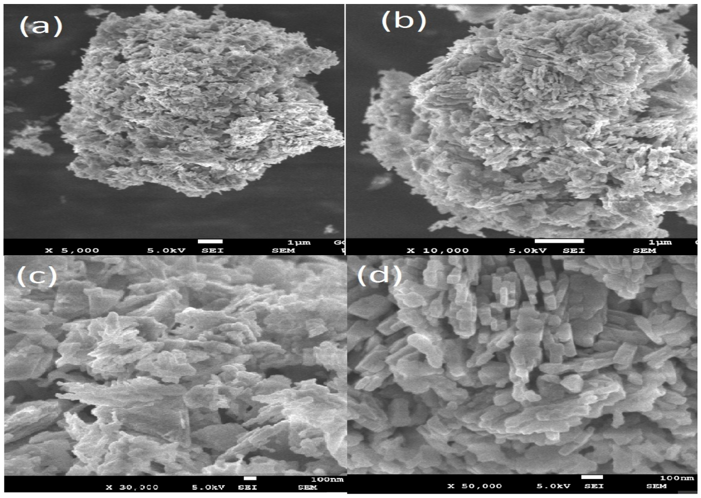

Figure 1: (a-d) Scanning electron microscopy (SEM) images of CuO nanoparticles at different magnifications (5000 to 50000X)

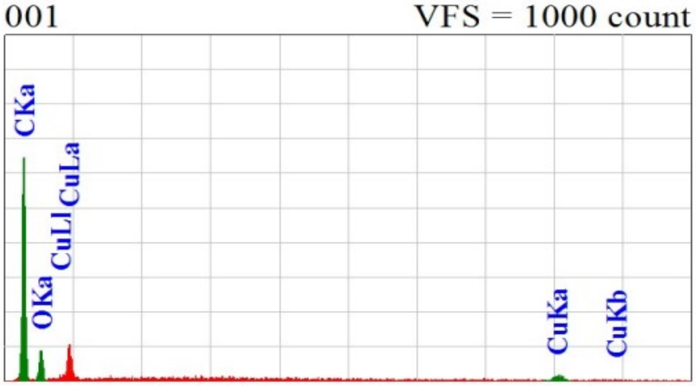

Figure 2: Energy Dispersive X-ray spectroscopy (EDX) images of CuO nanoparticles

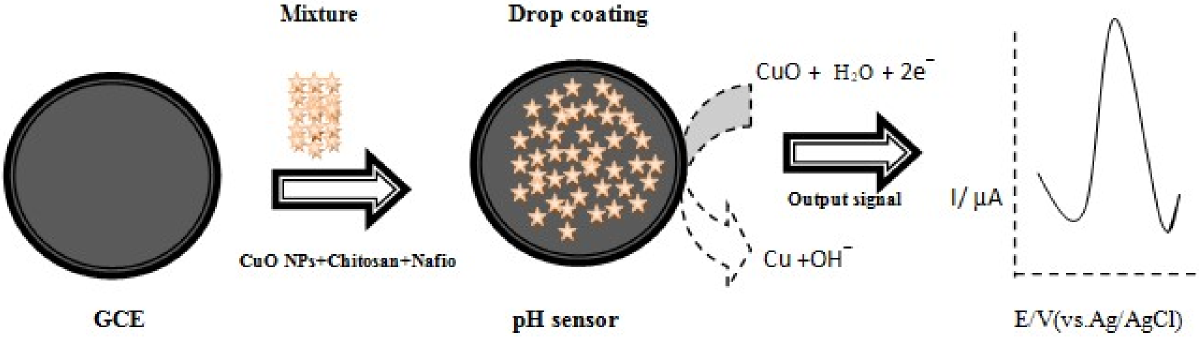

Figure 3: Schematic diagram fabrication of pH sensor

Table 1: Electrochemical parameters obtained from voltammograms

Scan rate Vs^{-1}	Anodic peak potential (E_{pa})	Cathodic peak potential (E_{pc})	Anodic peak current (i_{pa})	Cathodic peak current (i_{pc})	i_{pa}/i_{pc}
0.06	0.014	0.002	0.07754	-0.07321	1.05
0.08	0.014	0.002	0.08546	-0.08208	1.04
0.01	0.014	0.002	0.10383	-0.10054	1.03
0.12	0.014	0.002	0.11796	-0.11129	1.05
0.14	0.014	0.002	0.17837	-0.16937	1.05
0.16	0.014	0.002	0.22100	-0.21500	1.02

$$CuO + H_2O + 2e^- \rightarrow Cu + OH^- \qquad (1)$$

The measured potential is thus dependent on the pH and a linear relation from pH 3 – 9 has been obtained. Also due to each pH changes, potential shift around 60 mV that attributes to Nernstian behavior (Figure 4b). According to the equation 2, the sensitivity of the sensor can in that case be obtained by the slope of the linear regression (Flavia *et al.*, 2015).

$$E = E^0 - (2.303RT/F)\,pH = E^0 - 0.05916pH \qquad (2)$$

Where E^0 considered as the standard electrode potential, R is considered as the gas constant, T is considered as the temperature, and F is considered as the faradays constant. In this situation, owing to the redox reaction, all space charges are formed, that indicating a good performance of the sensor. In this work (Figure 4b), the pH sensor formed that demonstrated a mean sensitivity value of 60 ± 0.01 mV/pH which is close to the theoretical value. The correlation coefficient of R^2 values of about 0.97. This confirms the good sensitivity of the CuO/GCE to the variation of proton concentration in solution due to the redox reaction involved in the process.

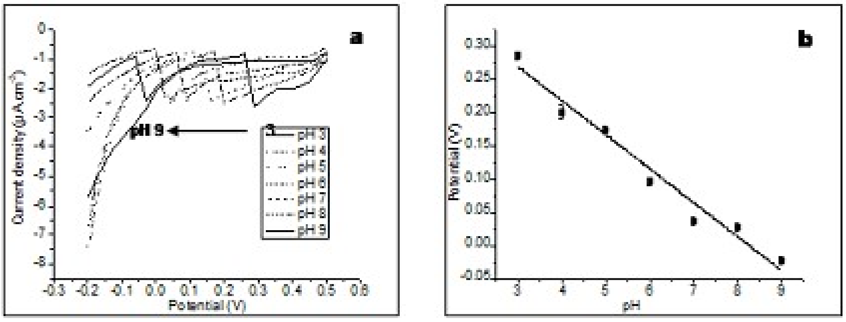

Figure 4: (a) SWV of 0.1 M buffers with different pH values (pH 3-9) on CuO/GCE (scan rate 0.05 V/s), (b) corresponding calibration curve.

The pH sensitivity obtained using SWV has been verified using OCP. In addition, investigation of pH response has been done in both directions (pH 3 to 9 and pH 9 to 3), just to make sure electrode provides reversible behavior and independent against pH value or direction of pH changes. It's concluded that, the potential response of the organized electrode demonstrates pH sensitivity of 60 mV/pH. As well as, it has also been found that CuO/GCE can successfully sense the pH ranging from 3 – 9 by measuring both SWV and OCP. It is needed to mention that all the experiment for pH measurement has been investigated with blank GC electrode, and no linear relation has been obtained.

Moreover, the drift of this sensor has been tested, along with oxygenated and deoxygenated environment. Sensitivity in this work compares favourably with recent reports tabulated in Table 2. To the best of our knowledge, no articles have demonstrated the use of CuO nanoparticle based GCE as sensing platform for detecting pH. We also have demonstrated stability, drift study on this system for H^+ detection. To determine the output response and the repeatability, the pH electrode was tested three to four times in a PBS buffer solution with pH ranging from 3 to 9. It was observed that the CuO/GCE showed excellent reproducibility, stable potentiometric response and good sensor stability. Similar tests have been obtained by Lidia *et al.* (2014), where author have modified gold electrode using WO_3 nanoparticle.

Table 2: A comparison of different pH sensors

Electrode	Sensitivity mV/pH	Drift %	pH range	Reference
GCE/CuO	60	1.9 – 3.3	3 - 9	This work
Gold /CuO NF	28	-	2 - 11	(Zaman, 2011)
Gold /WO_3 NPs	−57	-	5 - 9	(Lidia, 2014)
GCE/WO_3 NPs	60	2.4 – 5.0	3 - 11	(Irani, 2016)
AQ–Fc/AuNAE	70	1.0-3.0	2 - 11	(Jamal, 2013)
AQ–Fc/GCE	52	< 5.0	3 - 8	(Lafitpe, 2008)
AQ–CNT/GCE	51	1.4	3 - 10	(kumar, 2011)
AQ Sulfonate/GCE	38	2.0 – 3.0	2 - 10	(Shiu, 1996)
Thick Film/RuO_2	30	-	4 - 10	(Glance, 2012)

3.3 Electrochemical Characterization with and without Oxygen

In this work, we have evaluated the possibility of the CuO/GCE to be used in both an oxygenated and deoxygenated atmosphere. Figure 5a shows the voltammetric response of CuO/GCE that placed in buffer solution both in the absence and presence of oxygen. As oxygen is always present in the atmosphere, therefore, it is crucial that pH electrode should be performed equally in both environments. From the comparative results, it clearly can be seen that the reductive current differences slightly increases in the presence of oxygen. However, peak potential is unaltered; that concluded that this sensor can be used to measure the pH of solutions, irrespective of the O_2 concentration.

3.4 Drift and Stability Measurement

Fabricated electrode has been examined for the drift study and three buffer solutions with pH 5, 7 and 9 were chosen to determine the contribution the signal drift played. Figure 5b shows that pH signal needed 0 – 90 minutes to stabilize, depending on the pH values. However, a good accuracy has been obtained thereafter. The drift of the potential reading in a neutral pH buffer was 0.83 mV within 3 hours. In the same way a potential drift of 1.97 mV was recorded in an acidic solution and 3.33 mV for a basic media. Largest drift has been obtained for pH 9 buffer, however, it was less than 4%. Stability of the electrode has been investigated, and found 95% of its initial activity after 7 days of continuous uses. The method described herein demonstrates how the CuO/GCE could be utilized as a pH sensor over a large pH range, with good stability and excellent sensitivity.

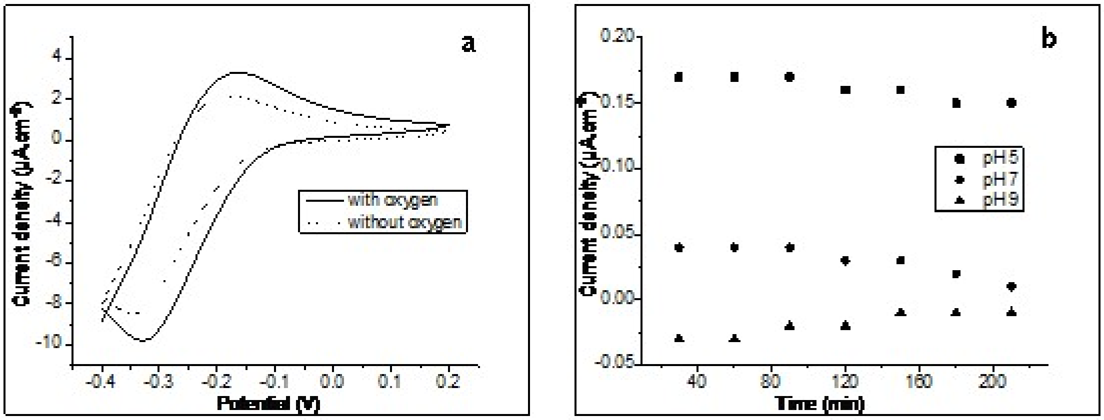

Figure 5: (a) CVs showing the response of the CuO immobilized layer to the presence and absence of oxygen in pH 6 buffer; (b) Electrode drift of CuO immobilized on the GCE.

3.4 Real Sample Test

It is evident from different research works that new electrode which are proposed as pH sensor usually avoid applying them for the sensing pH in real unbuffered samples. However, in this work, we have validated our sensor against the laboratory standard glass pH electrode in the real sample: malt vinegar and antacid. Electro-analytical SWV signals gained are visible in Figure (6a, 6b) and comparable values of pH was obtained in antacid at the pH value of 9.00 and malt vinegar at the pH value 4.00 using CuO/GCE as pH sensor. These results demonstrated that CuO/GCE showed same potential value for antacid as measured by the commercial pH sensor. Thereby, it can be concluded that our proposed pH sensor has a huge potential to be developed a solid state, cost effective, portable as commercial pH electrode and reliable pH sensor.

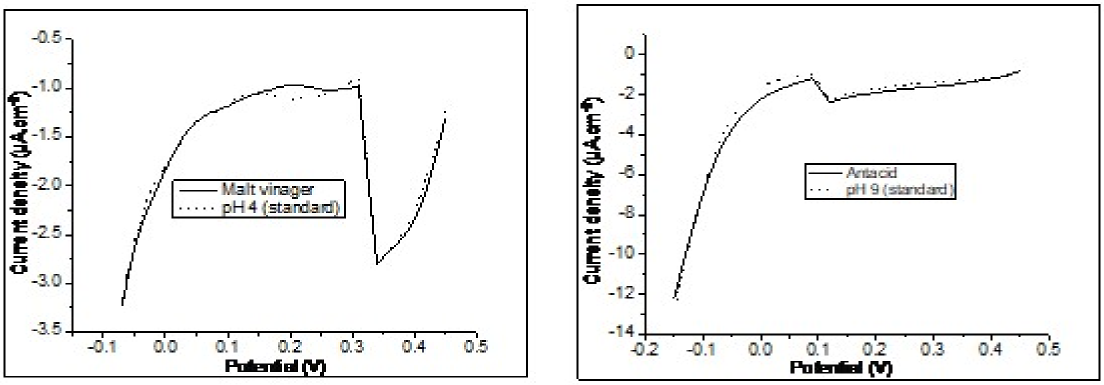

Figure 6: Electrochemical signal (SWV) obtained in “real” unbuffered samples for (a) malt vinegar; and (b) antacid using CuO/GCE.

4 CONCLUSIONS

In this study, we have developed a sensitive, selective and cost effective pH sensor using CuO nanoparticle modified GC electrode. Excellent linearity of potential for sensing pH has been obtained using CuO/GCE. The sensitivity of CuO/GCE has been found to be 60 ±0.01 $\mathrm{mVpH^{-1}}$ and a potential drift of 1.97-3.33% after three hours of continuous use. The sensor showed linearity range of pH 3 -9 and could retain 95% of its initial sensitivity after 1 week of use. The electrode was found to respond both in the presence and absence of oxygen, further expanding the potential applications to include de-oxygenated environments. In conclusion, the result shows that, the CuO nanoparticle is a very promising material for a stable pH sensor. The fabrication method is very cheap and easy applicable compared to the previously reported different sensing platforms. Further work is needed to improve the pH sensor, such as enhancing the stability and sensitivity, directly growth of CuO nanoparticle on different surfaces. Moreover, extensive fundamental electrochemical properties need to be investigated.

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