Activated Carbon -ZnO Nanocomposite for Electrochemical Sensing of Acetaminophen

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In this work, we reported the preparation of AC-ZnO by using simple chemical co-precipitation and ultrasonication techniques and investigated the electrocatalytic behaviour of acetaminophen (ACP) at AC-ZnO modified glassy carbon electrode. Then, the as prepared AC-ZnO was analyzed by using spectroscopy and electrochemical techniques such as Scanning Electron Microscopy (SEM), Cyclic Voltammetry (CV), Linear Sweep Voltammetry (LSV) and Amperometry method. Fortunately, AC-ZnO modified glassy carbon electrode shows the better electrocatalytic behaviour towards ACP than ZnO-GCE and AC-GCE. Finally, from the amperometric i-t curve the electrochemical parameters were calculated by varying the resultant linear response current with the concentration of ACP over the range from 0.05 to 1380 µM. In addition, the corresponding sensitivity and limit of detection (LOD) were calculated of about 8.33 µA µM⁻¹ cm⁻² and 0.83 µM respectively. Eventually, the proposed AC-ZnO/GCE was found as the suitable materials with unique stability, repetability and reproducibility towards ACP sensor.

Keywords: ZnO-AC, acetaminophen, electrochemical sensor.

1. INTRODUCTION

The recent research is motivated to explore the multidimensional metal oxides with proficient activities. For the two decades, many novel metal oxides such as NiO₂, CuO₂, SnO₂ MnO₂, ZnO₂, CO₃O₄ etc., have been found and used in various applications [1-6]. Fortunately, ZnO₂ is considered as a one of the competent metal oxide owing to it’s an exclusive electrocatalytic, conductivity and stability. ZnO and its nanocomposites have been prepared with different nanostructure such as nanofilm [7], nanorod [8], nanoflake [9], nanonails [10] by using chemical co-precipitation, hydrothermal, and electrochemical deposition. Among these all techniques the chemical co-
precipitation method is the suitable method to prepare the metal oxides with high purity and good homogeneity. In addition, ZnO has been prepared with different dimensional structure such as one dimensional (1D), two dimensional (2D) and three dimensional (3D). Here, 1D ZnO has been found with bulky nanorod like structure [11-13], 2D ZnO with nanosheets and 3D ZnO with dandelion and flower like structures [14]. Furthermore, ZnO and its nanocomposites have been used in different applications such as solar cell, supercapacitor [15], batteries [16], light emitting diode and sensor [17-21]. Particularly, ZnO is the hopeful materials for the electrochemical sensor application because of their suitable properties such as non-toxicity, high electron transfer feature, sensitivity and selectivity towards the sensing of different biomolecules, drug and organic pollutants [22-27]. To expand the electrochemical properties of ZnO, this has been prepared with carbon allotropes such as CNT, graphene, etc., [28-31]. According to the new innovation the biomass derived activated carbon (AC) is considered as the promising alternative for carbon allotropes owing to its small budget and its simple and ecologically approachable preparation procedure [32-37]. Hence, we can expect that the integration of AC can improve the electrochemical properties of ZnO.

Acetaminophen (C₈H₉NO₂) is used as analgesic and fever reducer drug and used to treat minor to moderate pain [38-41]. In the case of overdose, this causes many harmful side effects to human such as craving, queasiness, vomiting, stomach pain, panicking, dark urine, and yellowing of skin or white eyes [42-44]. Therefore, the instant determination of ACP is considered as important case in health care. Generally, ACP is detected by using different methods, such as chromatography (HPLC) [45], spectro-fluorimetry [46], flow-injection method [47], liquid chromatography [48], electrochemical sensor [49-53]. Among these all techniques, the electrochemical method is the low cost, quick response and simple method for detecting ACP.

In this report, an efficient flower-like ZnO-Activated Carbon nanocomposite was prepared and used to detect ACP. The intercalation of AC with ZnO shows the prompt response and exhibit an efficient electrochemical activity towards the detection of ACP with high sensitivity and exclusive selectivity.

2. EXPERIMENTAL SECTION

2.1. Reagents and materials

Zn(NO₃)₂, and acetaminophen were purchased from Wako pure chemical industries and Sigma-Aldrich. NaNO₃ were purchased from Katayama Chemicals. The supporting electrolytes were prepared by using 0.05 M Na₂HPO₄ and NaH₂PO₄. The PH of the electrolytes solution was adjusted by addition of NaOH or H₂SO₄. All the solutions were prepared using doubly distilled water and all chemicals are analytical grade and used without any further purifications.

2.2. Synthesis of ZnO nanoflake and AC-ZnO composite

In the synthesis of ZnO nanoflake, 0.25 g of Zn(NO₃)₂ was dissolved in 15 ml DD water and 15 ml ethanol. After the 10 min vigorous stirring, 0.6 g of NaNO₃ was added to the above Zn(NO₃)₂
solution and the stirring continue for moreover 30 min. Subsequently, 1M of NaOH solution was drop wise added to the above mixture and then the mixture was continuously stirred for 13 hr at 120°C. Finally, the well dried white color precipitate was collected and centrifuged using ethanol and water. The resultant ZnO powder dried in oven at 60°C for 12 hr. In the end, the ZnO powder treated to the calcination at 350°C for 3hr. To prepare ZnO-AC composite, mango leaves derived [54] AC and ZnO powders were mixed in 10 ml of water in the ratio of (1:2) and the as prepared mixture subjected to ultra-sonication for 3hr.

2.3. Characterization of ZnO nanoflake and AC-ZnO composite

The varieties of techniques were used to study the as prepared AC-ZnO. The surface characterization of AC-ZnO was obtained using Hitachi S-3000 H Scanning Electron Microscopy (SEM). CHI627A electrochemical analyzer was used to probe the electrochemical activity of AC-ZnO towards the proposed analyte in CV, LSV and amperometric i-t. For the electrochemical experiments, GCE was used as a working electrode, a saturated Ag/AgCl electrode used as a reference electrode and a platinum electrode used as the counter electrode.

2.4. Fabrication of AC-ZnO modified Glassy carbon electrode (GCE)

Beforehand to the electrochemical experiments, the GC electrode was polished with alumina on polishing cloth followed by ultra-sonication in DD water and ethanol. The defined amount of as-synthesized AC-ZnO was dispersed in ethanol under ultra-sonication for 2hr to get homogeneous suspension. After that, the optimum amount of prepared AC-ZnO was casted on the well-polished GCE surface and dried at 40°C in an air oven. Finally, the modified AC-ZnO/GCE was rinsed with DD water for removing the unbound active material for all experiments.

3. RESULTS AND DISCUSSION

3.1. Surface characterization of ZnO nanoflake and AC-ZnO

The as prepared ZnO nanoflake and AC-ZnO were characterized by using SEM. Fig. 1(a, b) show the surface morphologies of ZnO nanoflake at different magnifications. It can be found that the each ZnO nanoflake microsphere is made by the interconnected ultrathin nanosheets. Fig. 1(c, d) have shown the successful decoration of ZnO nanoflake on AC. The superior performance was obtained due to the effective intercalation of AC into the ZnO nanoflakes. Herein, the AC has played an vital role with high surface area and electrochemical activity for sensor application.
Figure 1. SEM images of ZnO (a, b) and AC-ZnO (c,d) at different magnification.

3.2. Electrocatalytic behavior of ACP at AC-ZnO/GCE electrode

![Scheme 1](image)

**Scheme 1.** Schematic illustration for electrochemical detection of ACP at AC-ZnO.

Fig. 2 shows the electrochemical oxidation of ACP at different modified electrodes such as (a’) bare GCE, (b’) ZnO-GCE, (d’) AC-GCE, (e’) AC-ZnO/GCE with presents of ACP and (c’) AC-ZnO/GCE with absence of ACP (338µM) in PBS (pH 7.2) at scan rate of 50 mV/s. In Fig. 2a, the CV...
curve of (e’) AC-ZnO/GCE shows the higher oxidation peak current at lower oxidation potential than modified electrodes. Herein, the integration of AC with ZnO nanoflake was observed with enhanced electrocatalytic activity towards the ACP is shown in scheme 1.

![Figure 2](image)

**Figure 2.** (a) CV curves of film comparison for (a’) bare GCE, (b’) ZnO-GCE, (d’) AC-GCE, (e’) AC-ZnO/GCE with presents of ACP (338 µM) and (c’) AC-ZnO/GCE with absence of ACP in pH 7.2 (0.05) PBS at scan rate of 50 mV s⁻¹. (b) CV curves of different scan rate of 10 to 100 mV S⁻¹ with presents of ACP(338 µM) in (0.05) PBS pH 7.2.

3.3. Effect of the different scan rate and pH towards the detection of ACP

![Figure 3a](image) and ![Figure 3b](image)

Fig.2b show the CV curve of AC-ZnO/GCE with scan rate in N₂ saturated PBS with presence of ACP (338µM). It was clearly revealed that the oxidation current increased with increasing scan rate, when the oxidation potential shifted positively. Moreover, the oxidation current values clearly shown the linear dependance with sqrt of scan rate (10 to 100 mV/s). From the linear equation plot (inset) determined the correlation coefficient of about 0.9853 is shown in Fig. 2b. Eventually, the result proposed that the kinetic of the overall process were controlled by the diffusion process. Fig. 3a shows the CV curve of AC-ZnO/GCE with various concentration of ACP (49µM to 909µM) in N₂ saturated
PBS at scan rate of about 50 mV/s. It displays the linear increment in oxidation current with increasing the concentration of ACP. The linear equation plot (inset) with correlation coefficient ($R^2$) of about 0.988 is shown in Fig. 3a. Finally, AC-ZnO/GCE is found as the unique active material with linear and efficient electrocatalytic response towards the ACP.

**Figure 3.** (a) CV curves of different concentration of ACP for linear range for 49 µM to 909 µM in PBS (0.05) pH 7.2 at scan rate of 50 mV s$^{-1}$ (inset: the linear calibration plot of different concentration vs current). (b) CV curves of different pH 1 to 11 with presents of ACP (338 µM) in PBS (0.05) pH 7.2 at scan rate of 50 mV s$^{-1}$.

To understand the effect of pH at AC-ZnO/GCE, the CV curve were recorded containing ACP (338 µM) in N$_2$ saturated PBS at scan rate of 50 mV s$^{-1}$ as shown in Fig. 3b. In this experiment, the pH of the electrolyte were varied from 1 to 11, when the oxidation potentials were shifted to the negative direction. On other hand, positively shifted oxidation peak potentials were observed with decreasing the pH from 11 to 1. The inset in Fig.3b shows the relationship curve for pH vs Ipa and pH vs $E_{pa}$. From the calibration curve the maximum oxidation peak current of ACP was obtained at pH 7.2. Furthermore, the slope value is calculated of about -33.63 from the linear equation plot of pH vs $E_{pa}$. Fortunately, the slope value is equal to the theoretical value of 59 mV pH$^{-1}$ at 25ºC, which was
calculated from Nernst equation that exhibits an equal number of proton (H\(^+\)) and electron (e\(^-\)) transfer process. Thus, the oxidation of ACP at the modified electrode was concluded as the equal number of proton (H\(^+\)) and electron (e\(^-\)) transfer process.

3.4. Determination of ACP at AC-ZnO/GCE using different electrochemical techniques

The various electrochemical techniques such as CV, LSV and amperometric are considered as the promising techniques to study and compare the analytical performance of the proposed ACP sensor. Fig. 4 shows the typical LSV curve for electrocatalytic oxidation of ACP at AC-ZnO/GCE modified Electrode with the presence of different concentrations of ACP in N\(_2\) saturated PBS at 50 mV/s where the linearly increased oxidation peak current was observed with increasing ACP concentration. The linear equation plot was drawn for the relationship of ACP concentrations (5 to 933 µM) vs oxidation peak current (I\(_{pa}\)) with correlation coefficients of 0.989 (inset) is displayed in Fig. 4. The lower limit of detection and sensitivity were measured to be 2.5 µM and 2.1 µA µM\(^{-1}\) cm\(^{-2}\). Better sensitivity and selectivity can obtain by using an amperometric i–t experiments compared than CV and LSV study. Fig. 5a shows the appropriate amperometric response curve of AC-ZnO/GCE electrode for the step wise additions of ACP with different concentrations in PBS. The rotation speed of the AC-ZnO/GCE was fixed to 1200 RPM and the applied potential fixed to 0.55 V. The linear equation plot was observed for I\(_{pa}\) vs concentration ACP with correlation coefficient of about 0.9953. The calculated LOD and sensitivity are 0.83 µM and 8.3 µA µM\(^{-1}\) cm\(^{-2}\). In this work, we achieved a very low LOD and high sensitivity toward the detection of ACP, which is more comparable than the other related modified electrodes available in literature (see Table 1). Hence, the AC-ZnO/GCE modified electrode is more suitable for the highly sensitive determination of ACP sensor.

**Figure 4.** LSV cueves of different concentration of ACP linear range for 3 µM to 933 µM in pH 7.2 (0.05) PBS at scan rate of 50 mV s\(^{-1}\) and inset; the linear plot of different concentration vs current.
3.5. Selective detection of ACP in the presence of different interferences

From Fig. 5b, we determined the selectivity of AC-ZnO/GCE electrode toward determination of ACP in the presence of potential interferences such as biologically co-active species. The AC-ZnO/GCE demonstrated a well stipulated response toward the each addition of ACP whereas no notable responses were observed for (a) ascorbic acid (b) dopamine (c) uric acid (d) sulfide (e) nitride (f) EtOH (g) MeOH (h) glucose. The result confirmed that the AC-ZnO/GCE modified electrode possess high selectivity toward the detection of ACP.

3.6. Stability, repeatability and reproducibility studies

The stability of the proposed ACP sensor was proped in N2 saturated PBS (pH 7), and its oxidation peak current response was monitored sporadically. The 94.27 % of the initial oxidation peak current response remain withstand even after 1 week in air at ambient temperature. It implies the unique stability of the reported ACP sensor. To estimate the reproducibility and repeatability of the ACP sensor, chose three individual as prepared modified electrodes and measured the corresponding
oxidation peak currents in the presence of ACP. In this experiment, relative standard deviation (RSD) was measured of about 2.14%, which indicates the better reproducibility and reatability of AC-ZnO/GCE towards ACP sensing.

Table 1. Comparison of different electrochemical sensors with the proposed sensor for determination of ACP

<table>
<thead>
<tr>
<th>Modified electrodes</th>
<th>Techniques</th>
<th>Linear ranges (µmol L⁻¹)</th>
<th>Sensitivity (µA/µmol L⁻¹)</th>
<th>LOD (µmol L⁻¹)</th>
<th>Ref</th>
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<tbody>
<tr>
<td>(ERGO)/ Neodymium Hexacyanoferrate Carbon-coated nickel nanoparticles/GCE</td>
<td>LSV</td>
<td>-</td>
<td>0.531</td>
<td>14.22</td>
<td>[55]</td>
</tr>
<tr>
<td>Boron-doped diamond electrode/GCE</td>
<td>DPV</td>
<td>7.8-110</td>
<td>-</td>
<td>2.3</td>
<td>[56]</td>
</tr>
<tr>
<td>IL/CNTPE</td>
<td>DPV</td>
<td>-</td>
<td>-</td>
<td>0.5</td>
<td>[57]</td>
</tr>
<tr>
<td>f-MWCNTs – GCE</td>
<td>DPV</td>
<td>3-300</td>
<td>-</td>
<td>0.6</td>
<td>[59]</td>
</tr>
<tr>
<td>MWCNTs/ CTS–Cu</td>
<td>DPV</td>
<td>0.1-200</td>
<td>0.603</td>
<td>0.024</td>
<td>[60]</td>
</tr>
<tr>
<td>PAY/nano-TiO2/GC</td>
<td>DPV</td>
<td>12-120</td>
<td>-</td>
<td>2.0</td>
<td>[61]</td>
</tr>
<tr>
<td>ERG/Ni₂O₃–NiO</td>
<td>DPV</td>
<td>0.04-100</td>
<td>-</td>
<td>0.02</td>
<td>[62]</td>
</tr>
<tr>
<td>Naftion/TiO2–GR</td>
<td>DPV</td>
<td>1-100</td>
<td>-</td>
<td>0.21</td>
<td>[63]</td>
</tr>
<tr>
<td>Cu²⁺Y/ZMCPE</td>
<td>DPV</td>
<td>0.25-900</td>
<td>-</td>
<td>0.1</td>
<td>[64]</td>
</tr>
<tr>
<td>LNT–CFO/GCE</td>
<td>Amperometric i-t</td>
<td>0.5-901</td>
<td>-</td>
<td>0.19</td>
<td>[65]</td>
</tr>
<tr>
<td>GNPs/PNFCTs/GCE</td>
<td>DPV</td>
<td>0.3-575</td>
<td>-</td>
<td>0.1</td>
<td>[66]</td>
</tr>
<tr>
<td>AC-ZnO</td>
<td>Amperometric i-t</td>
<td>0.05-1380</td>
<td>8.3</td>
<td>0.02</td>
<td>This work</td>
</tr>
</tbody>
</table>

4. CONCLUSION

In this work, the preparation and the characterization of ZnO and AC-ZnO were described. Then the various electrochemical studies such as CV, LSV and amperometric i-t were carried out to predict the electrocatalytic performance of AC-ZnO modified GCE towards the ACP sensor. From these electrochemical studies, we probed that the AC-ZnO modified glassy carbon electrode exhibit the considerable lower limit of detection and sensitivity. In addition, the AC-ZnO modified GCE found with good storage stability, reproducibility and repeatability.

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