Two-dimensional ZIF-L nanosheets as high performance non-enzymatic glucose sensor

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Abstract:
An effective biosensor based on two-dimensional (2D) Co-ZIF-L nanosheets for sensitive electrochemical non-enzymatic glucose detection is developed, which exhibits high electrocatalytic activities towards glucose due to the ordered porous structure as well as ultrahigh specific surface area. The fabricated Co-ZIF-L nanosheets electrodes present an outstanding performance with higher sensitivity of 769.5 µA mM⁻¹ cm⁻² and lower detection limit of 90.4 nM, while the constructed 3D ZIF-67 nanoparticles electrodes show a weaker sensitivity of 697.4 µA mM⁻¹ cm⁻² and a limited detection range from 2 µM to 414 µM. Furthermore, the Co-ZIF-L based non-enzymatic glucose biosensors possess an acceptable selectivity, long-term stability as well as reproducibility. This work may offer a new approach to develop 2D ZIF nanosheets as a potential candidate in electrochemical biosensors.
1. Introduction:

Diabetes mellitus (DM) is increasing rapidly to be a worldwide epidemic with no effective cure [1, 2]. However, the sensitive and quantitative detection of blood glucose level can monitor and prevent the occurrence of DM timely. Therefore, various approaches have been developed for glucose detection [3-7]. Electrochemical detection, which owns relatively high sensitivity, selectively, and feasibility, has been recognized as the most promising and efficient methodology towards glucose oxidation [8-10]. The oxidation of glucose to glucolectone is generally accompanied with the reduction of electrocatalyst, resulting in amperometric response which scales linearly with glucose concentration. The conventional electrochemical glucose sensors can be classified into two categories: enzyme-based biosensors and non-enzymatic biosensors. The enzyme-based biosensors have been applied earlier and been widely explored with high sensitivity and good selectivity for glucose detection [2, 11]. However, their stability is limited by vulnerability of the enzymes in the detecting environment, which limits their practical application [12, 13]. On the contrary, the non-enzymatic glucose sensors possess high stability, sensitivity, and selectivity [14-16]. Therefore, intensive attention have been paid to developing the non-enzymatic glucose sensors, especially the noble metals (Au, Pd, etc.) [13, 17-19] and transition metal oxides (Co$_3$O$_4$, CuO, etc.) [20-25] based materials.

Though, noble metals based materials exhibit high activity towards glucose oxidation in the non-enzymatic environment, the scarcity and high price hinder their widespread application [26, 27]. Recently, transition metal oxides, which are earth-abundant and economical, are considered as a substitution of noble metals for glucose detection. Unfortunately, their poor
conductivity and small active sites result in low activity and sensitivity in the electro-oxidation process of glucose [28].

In view of the requirement of both the price and the surface area of the potential electrocatalyst, metal organic framework (MOFs), which process large surface area, relative high crystallization, tunable pore size, and economical efficiency, are increasing to be promising candidate as non-enzymatic glucose sensors and much work has been done recently. [29-36] Zeolitic imidazolate frameworks (ZIFs), which is a subfamily of MOFs, shares similar structure with zeolites, therefore ZIFs owns the virtues of both MOFs and Zeolites such as various porous structures, large surface area, low price, and high chemical and thermal stability [37]. The ultrahigh porous structures enable the superior mass diffusion both at their external surface and within the interior surface, which could enlarge the faradaic currents greatly [38]. In this regard, ZIFs nanoparticles have been explored as potential detecting materials in the construction of glucose sensor, however, the random stack of those three dimensional nanoparticles could reduce the exposed surface area and further limit the mass diffusion of glucose molecule [39, 40]. Very recently, a novel two-dimensional (2D) zeolitic imidazolate framework with leaf-shaped morphology (ZIF-L) has been facilely synthesized, which could maximize the efficient diffusivity and selectivity [41-43]. 2D ZIF-L nanosheets have demonstrated high aspect ratio, extremely large specific surface area, and abundance of active sites in compare to their corresponding three-dimensional ZIFs. The electrocatalytic properties of nanosheets biosensors is, therefore, expected to enhance greatly since catalytic reaction always prefer to occur on the surface of the catalysts [44, 45].

In this work, we synthesized 2D Co-based ZIFs nanosheets (Co-ZIF-L) as electrocatalytic sensor for glucose detection. The glucose detection evaluation has been done through cyclic voltammetry (CV) and chronoamperometry in alkaline solution. The results reveal that Co-ZIF-L exhibits high electrocatalytic performance with sensitivity of 769.5 µA mM⁻¹ cm⁻², low
detect limit of 90.4 nM, an acceptable selectivity, and long-term stability and reproducibility toward glucose oxidation. This work offers a new strategy to develop 2D ZIF based highly sensitive non-enzymatic glucose sensors.

2. Experimental section

2.1 Materials and reagents

Cobalt nitrate hexahydrate (Co(NO$_3$)$_2$·6H$_2$O, 99%), 2-methylimidazole (MIM, 99%), nafion, potassium hydroxide (KOH, 99%), potassium chloride (KCl, 99%), sucrose, and glucose were bought from Sigma-Aldrich. Ascorbic acid (AA), uric acid (UA), and fructose were purchased from Lanyi Chemical Products Company of Limited Liability. Deionized water was used throughout the experiment. All the regents in this paper were used as received without further purification.

2.2 Preparation of Co-ZIF-L and ZIF-67

For the preparation of Co-ZIF-L, 0.0582 g (0.2 mmol) Co(NO$_3$)$_2$·6H$_2$O was dissolved in 4 ml of deionised water to form solution A, at the meantime, 0.13 g MIM was also dissolved in 4 ml of deionised water to form solution B. Then solution A was poured into solution B quickly and the mixture reacted without stirring for 2 h at room temperature. The purple product was obtained by centrifugation (7800 rpm for 10 min) and washed with water for three times and then dried in an oven at 70°C overnight. Similarly, the pure ZIF-67 was synthesized by simply changing the mass of MIM from 0.13 g to 0.7874 g.

2.3 Characterization

The morphologies, structures, and composition of the prepared samples were obtained by using scanning electron microscopy (SEM, FESEM JEOL-7500), energy dispersive spectroscopy (EDS) coupled with the SEM GBC MMA X-ray powder diffractometer with Cu
Kα radiation (40 kV, 25 Ma, λ = 0.15418 nm), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR), and Raman spectroscopy.

2.4 Electrochemical measurements

The glassy carbon electrode (GCE, 3 mm diameter, 0.07 cm²) was polished by 1.0, 0.3 and 0.05 μm alumina slurries sequentially, and then ultrasonic cleaned with ethanol and deionised water, separately. The homogeneous ink was prepared by dispersing 1 mg Co-ZIF-L or ZIF-67 in the mixture solution of 1 mL deionised water and 5 μL nafion solution (5 wt%). The working electrode (loading mass: 0.085 mg cm⁻²) was prepared by dropping 6 μL the prepared ink on cleaned GCE and then dried in air at room temperature.

All electrochemical measurements were carried out on an electrochemical station (Bio-logic VSP-300) using the conventional three-electrode cell under stirring at room temperature. The modified GCE was served as the working electrode, while Ag/AgCl electrode (3 M KCl electrolyte) and carbon electrode were served as reference electrode and counter electrode, respectively. In the paper, all potentials were referred to the Ag/AgCl reference electrode while all the current densities were calculated using the geometric surface area (0.07 cm²). The electrolytes used throughout the experiments were 0.1 M KOH solution.

3. Result and discussion

3.1 Characterizations

As shown in Fig. 1, the leaf-like nanosheets with approximately 10 μm in length and 300 nm in thickness, and nanoparticles with dodecahedron structure of around 3 μm in thickness were synthesized, separately. The corresponded elemental mapping images using EDS (Fig. S1)
revealed that Co, N, and C were uniformly distributed in the nanosheets and nanoparticles, respectively. The XRD patterns in Fig. 2a confirmed that the nanosheets were Co-ZIF-L while the nanoparticles were ZIF-67 [21, 46]. It should be noted that Co-ZIF-L presents remarkable increases of the diffraction peaks at 20 of 15-20° especially, which demonstrate the increase of specific crystal face came from Co-ZIF-L crystal network [47]. The FT-IR spectra were then used to confirm the structure of the synthesized Co-ZIF-L and ZIF-67, as presented in the Fig. 2b. The results reveal that Co-ZIF-L had the similar curve with that of ZIF-67 because of the same building blocks, suggesting these synthesized products shared the same chemical bonding [48]. Moreover, the peaks in the range of 500-1500 cm\(^{-1}\) could be assigned to the bending and stretching modes of the imidazole. The peaks at 990 and 1142 cm\(^{-1}\) could be attributed to the C-N stretching modes and the bands observed at 1574 cm\(^{-1}\) are the result of C=N stretching vibration in MIM [49]. Raman spectra of ZIF-67 and Co-ZIF-L at room temperature were also similar (Fig. 2c). The \(\nu\) (Co-N), imidazole ring puckering, \(\nu\) (C5-N), \(\nu\) (C-N), C-H wagging, \(\nu\) (C4-C5), \(\nu_{\text{asym}}\) (C-H methyl), \(\nu\) (C-H\text{arom}) are clearly observed at peaks of 425, 675, 1141, 1172, 1456, 1493, 2927, 3112 cm\(^{-1}\), respectively [50, 51]. TGA curves of the heated ZIF-67 and Co-ZIF-L under Ar flow were shown in Fig. 2d. Co-ZIF-L presents a gradual weight loss initially, and then exhibits a sudden weight loss at around 270°C which results from the evaporation of the guest water molecule and the removal of the weakly linked MIM [41]. After that, Co-ZIF-L provides a continuous mass loss with the increase of the temperature mainly due to the thermal decomposition and carbonation of organic linkers [52, 53]. In contract, there is a moisture loss at the temperature below 200°C and a long plateau from 200°C to 570°C of ZIF-67 curve.

3.2 Electrochemical behaviour of the sensor
The two-dimensional Co-ZIF-L nanosheets process the abundant exposed active sites and the efficient charge transfer within the small diffusion path, indicating an exciting catalytic activity [54]. For comparison, Co-ZIF-L and ZIF-67 were synthesized and used as working electrodes directly for cyclic voltammetry measurements to investigate their electrocatalytic activity towards glucose oxidation. As shown in Fig. 3a, the CV curves of the synthesized products exhibited that the electrochemical activity of Co-ZIF-L was higher than that of ZIF-67 both in the absence and presence of glucose. In the glucose-free alkaline solution, there are two pairs of redox peaks in the CV of Co-ZIF-L with apparently appeared pair of redox peaks at around 0.17 V and another poorly defined one at round 0.52 V. Moreover, the redox peaks are attributed to the reversible transition between [Co (II)(MIM)$_2$]$_n$ and [Co (III)(MIM)$_2$(OH)]$_n$ via [Co (II)(MIM)$_2$]$_n$ + n OH$^-$ $\leftrightarrow$ [Co (III)(MIM)$_2$(OH)]$_n$ + ne$^-$ and the further conversion between [Co (III)(MIM)$_2$(OH)]$_n$ and [Co (IV)(MIM)$_2$(OH)$_2$]$_n$ via [Co (III)(MIM)$_2$(OH)]$_n$ + n OH$^-$ $\leftrightarrow$ [Co (IV)(MIM)$_2$(OH)$_2$]$_n$ + ne$^-$. After the addition of glucose, the potential of the apparent oxidation peak (0.17 V) shifts positively with a mild movement, which can be ascribed to the concentration polarization during the electrocatalytic process. In the beginning, there is a short dynamic balance at the anodic peak potential between the ions Co$^{2+}$, Co$^{3+}$ and OH$^-$. Then the glucose participates in the reaction and consumed some Co$^{3+}$. In order to reach a new balance, Co$^{2+}$ would react with OH$^-$ at the surface of electrode, which leads to the concentration polarization of OH$^-$ and the potential should shift to a more positive value to form the Co$^{3+}$ [55]. In addition, the oxidation of glucose on Co-ZIF-L mainly occurs at the consumption of [Co (IV)(MIM)$_2$(OH)$_2$]$_n$, and it can be seen clearly that the current density changed a lot in the presence and absence of 10 mM glucose in the range of 0.4 V to 0.7 V. For comparison, the CVs of corresponding ZIF-67 in the presence and absence of 10 mM glucose displayed a slight negative trend, suggesting rather low electrocatalytic activities towards glucose oxidation. With the increase of scan rate, the CVs and redox peaks of Co$^{2+}$,
Co$^{3+}$ would be further explored (Fig. 3b), the current densities of the redox (I， II) were proportional to the square root of the scan rate, which indicated the electrochemical reaction on the electrode interface was a diffusion-controlled process and further implied the redox reactions of the Co-ZIF-L were rapid [56]. Considering the reaction current density of [Co(III)(MIM)$_2$(OH)$_n$] → [Co(IV)(MIM)$_2$(OH)$_2$]$_n$ increase obviously near the oxidation potential of peak -after the addition of glucose, the amperometric responses of Co-ZIF-L (Fig. 3c and Fig. 3d) and ZIF-67 (Fig. S2) were investigated with an optimal potential of 0.55 V in 0.1 mol L$^{-1}$ KOH solution. As shown in Fig. 3c, the Co-ZIF-L electrode exhibits a high performance with good sensitivity, and it presented that the oxidation current density increased obviously with the addition of 0.5 nM glucose. The corresponding current density verse glucose concentration in alkaline solution was displayed in Fig. 3d, and a linear relationship of the corresponding calibration curve ranges from 2 µM to 614 µM, with a lower detection limit of 90.4 nM (S/N = 3) and a high sensitivity of 769.5 µA mM$^{-1}$ cm$^{-2}$. By contrast, ZIF-67 exhibits a less sensitive performance with unconspicuous rise after adding 0.5 nM glucose and the linear range is from 2 µM to 414 µM with a sensitivity of 697.4 µA mM$^{-1}$ cm$^{-2}$ (Fig. S2). The high sensitivity and low detection limit of Co-ZIF-L could be attributed to the ordered porosity and 2D structure of the electrocatalyst, which provide ultrahigh specific area and enable the facile access of glucose to the exterior and interior surface of catalytic sites with minimal diffusion resistance. When the oxidation reaction processed, the current density baseline happened to decrease slightly (Fig. 3c), which may be attributed to the faster consumption than the diffusion of glucose, the change value of pH, or the absorbed reaction intermediates on surface electroactive sites [55]. Table 1 lists the electrocatalytic performance of this biosensor and other non-enzymatic glucose sensor. It demonstrates that the Co-ZIF-L biosensor processed rather low detection limit and a higher
sensitivity, indicating the 2D MOFs exhibited a promising prospect in the construction of non-enzymatic glucose sensor.

3.3 Selectivity, stability, reproducibility and repeatability of the sensor

To further investigate the performance of the Co-ZIF-L glucose sensor, selectivity, stability, reproducibility and repeatability tests were carried out. Selectivity is one of the most essential parameter to evaluate the performance of glucose sensor, which needs to compare the oxidation currents caused by glucose and other interfering species. As shown in Fig. 4a, considering the normal physiological level of glucose exceed thirty times as compared with interfering species, 0.1 mM glucose, 0.05 mM UA, 0.05 mM KCl, 0.05 mM AA, 0.05 mM sucrose, 0.05 mM fructose and 1.0 mM glucose were successively added into 0.1 M KOH solution. There are remarkable increased amperometric responses of the addition of glucose and the negligible current densities caused by these interferents, suggesting a good selectivity of Co-ZIF-L electrode. To further investigate the performance of the Co-ZIF-L glucose sensor, stability, reproducibility and repeatability tests were also carried out. The amperometric signal of Co-ZIF-L showed almost no change after 5150 s, implying that the sensor achieved good stability (Fig. 4b). Furthermore, after chronoamperometry test for 4500s, the electrocatalytic activity of Co-ZIF-L seemed no difference with its initial response in the CVs (Fig. S3). Reproducibility and repeatability also occupy very important position in practical detection process, which were displayed in Fig. 4c and Fig. 4d, respectively. As for the electrode-to-electrode reproducibility, five newly fabricated sensors were measured towards 10 mM glucose in the 0.1 mM KOH with a relative standard deviation (RSD) of 4.9%. In addition, the same sensor was tested for parallel five times to evaluate the repeatability in the alkaline solution with a RSD of 5.8%. These two results suggest the good reproducibility and repeatability of Co-ZIF-L sensor.
4. Conclusion

In summary, two dimensional Co-ZIF-L nanosheets and three dimensional ZIF-67 nanoparticles were successfully synthesized and applied as enzymeless sensors towards glucose. The obtained Co-ZIF-L electrode exhibited an outstanding performance as a non-enzymatic glucose sensor with higher sensitivity (769.5 µA mM$^{-1}$ cm$^{-2}$) and lower detect limit (90.4 nM) than that of three dimensional ZIF-67 nanoparticles (a sensitivity of 697.4 µA mM$^{-1}$ cm$^{-2}$ and the detect limit range from 2 µM to 414 µM). The high electrocatalytic activities mainly attributed to the ordered porous structure and ultrahigh specific surface area of the Co-ZIF-L electrode. The results illustrate the superiority of two dimensional Co-ZIF-L nanosheets over three dimensional ZIF-67 nanoparticles for glucose oxidation, which could extend the further exploration of ZIF-L as glucose sensor due to their high sensitivity.
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Figure 1. (a) Low and (b) High magnification SEM images of Co-ZIF-L, (c) Low and (d) High magnification SEM images of ZIF-67.
Figure 2. (a) XRD patterns, (b) FT-IR spectra, (c) Raman spectra and (d) TGA data of the ZIF-67 and Co-ZIF-L.
Figure 3. (a) The CVs of the ZIF-67 and Co-ZIF-L in the absence and presence of 10 mM glucose at scan of 30 mV s\(^{-1}\); (b) The CVs of the Co-ZIF-L in 0.1 M KOH solution at various scan rate of 20, 40, 60, 80, 100, 120, 140, 160 mV s\(^{-1}\), the inset curve is the plots of peak currents against the square root of the scan rate for the Co-ZIF-L sample; (c) The amperometric response of Co-ZIF-L to the continuous addition of glucose at 0.55 V in 0.1 M KOH; (d) the corresponding calibration curve for (c).
Table 1. Comparison of the electrocatalytic performances of Co-ZIF-L with other reported non-enzymatic glucose sensors

| Electrode                        | Detect limit (µM) | Sensitivity (µA·mM⁻¹·cm⁻²) | Linear range (µM) | Reference  |
|----------------------------------|-------------------|-----------------------------|-------------------|------------|
| Ag-0.5%@ZIF-67/GCE               | 0.66              | 379                         | 2 - 1000          | [39]       |
| Co₂P/NPCNT-modified electrode    | 0.88              | 338.8                       | up to 7 000       | [57]       |
| NPC-Co₃O₄                        | 2 × 10⁻⁶          | 140000                      | 5 × 10⁻⁶ - 2.05 × 10⁻³ | [20]       |
| Ni-MIL-77                        | 0.25              | 1.542                       | 1 - 500           | [58]       |
| Fe₃O⁴/MIL-101(Fe)               | 0.0049            | -                           | 0.005 - 0.100     | [35]       |
| NiO nanosheets modified GCE      | 0.18              | 1138                        | 1 - 4 00          | [59]       |
| Ni-MOF/Ni/NiO/C nanocomposite    | 0.8               | 367.45                      | 4 - 5664          | [60]       |
| 3D graphene frameworks/Co₃O₄     | 0.157             | 122.2                       | up to 80          | [22]       |
| Co₂N₀.6₇ nanosheets              | 0.1               | 921.2                       | 10 - 8000         | [61]       |
| CuO/GCE                          | 0.070             | -                           | 0.5 - 5 000       | [62]       |
| Au-Ni                            | 0.1               | 2133.5                      | 0.4 - 900         | [9]        |
| ZIF-L-Co/GCE                     | 0.0904            | 769.5                       | 2 - 614           | This work  |
Figure 4. (a) The amperometric response of Co-ZIF-L towards the addition of 1.0 mM GL, 0.05 mM UA, 0.05 mM KCl, 0.05 mM AA, 0.05 mM sucrose, 0.05 mM fructose and 1.0 mM GL in 0.1 M KOH at +0.45 V; (b) Long term stability of Co-ZIF-L at +0.55 V for 3000 s; (c) The reproducibility of five fresh Co-ZIF-L carbon glass electrodes for 10 mM glucose in 0.1 M KOH; (d) Changes of the catalytic activity of the same Co-ZIF-L over 5 times of recycling detection in 0.1 M KOH.
