Zinc ferrite nanoparticles: simple synthesis via lyophilisation and electrochemical application as glucose biosensor

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Abstract

With increasing diabetes patients in the near future, development of non-enzymatic glucose biosensor is highly demanded due to their greater sensitivity and resistance to external stimuli compared to enzymatic biosensors. Zinc ferrite (ZnFe$_2$O$_4$, ZFO) nanoparticles (NPs) were fabricated using a simple solution combustion method together with freeze drying. The NPs have high crystallinity, large aspect ratios and narrow size distributions. Plenty of defects have been induced during lyophilisation and greatly improves the glucose biosensing performance during electrochemistry test. The freeze-dried ZFO NPs are highly crystalline and agglomeration-free, these assures the sample with high sensitivity, superior selectivity, low detection limit and outstanding stability for electrochemical glucose biosensing.

1. Introduction

Diabetes mellitus is a chronic illness that is highly responsible for death and disability in the world; however, the figure of diabetes patients is expected to double in the next two decades [1]. There is an increasingly high demand for glucose detection and monitoring in diversified samples, ranging from human blood to food and pharmaceuticals. Apparently, glucose biosensors constitute ~ 85% in the industry [2], but only enzymatic glucose biosensors are commercially available due to their superior selectivity, non-toxicity, simplicity and relative low cost [3–5]. Under comparison to enzyme-based glucose detection, non-enzymatic glucose sensors could show greater sensitivity and produce higher oxidation current signals [6]. Moreover, enzymes are sensitive to external stimuli, such as changes in chemical environment and temperature/pH values, which make enzymatic glucose sensors only suitable in human bodies [7]. Hence, there is greater potential in non-enzymatic glucose biosensors as they are not easily affected by environmental factors, thus making them versatile and suitable for more applications like food testing and fuel cells [6].

It is reported that many transition metals and transition metal oxides (TMOs) display considerable electro-activity towards carbohydrates and especially glucose. They can thus be incorporated onto the electrode surface in the electro-catalysis of glucose oxidation [8], because the nanostructures possess high activity for surface reactions, high catalytic efficiency and superb adsorption ability [9]. Nanostructured glucose biosensors may be more promising than enzyme-based glucose biosensors, as they can be operated at relatively low applied potential with improved rate of mass transport and electron transfer [10–12]. Previous research shows that electrochemical biosensors based on magnetic nanoparticles (NPs) could achieve better performance than non-magnetic NPs-based ones, such as lower detection limit, superior sensitivity, greater signal-to-noise ratio, and shorter response time [13, 14].

The technology for glucose biosensing has been emerging in a fast pace, and the current trend is chip-based testing or wearable sensors [15]. This means nanomaterial-based catalyst has to be developed with strong sensing ability and excellent stability. In this work, solution combustion method is used together with lyophilisation to fabricate zinc ferrite (ZnFe$_2$O$_4$, ZFO) NPs; the low-risk synthesis could produce NPs of high purity and
crystallinity with small sizes and narrow distributions, which display high sensitivity, high selectivity, low detection limit and outstanding stability for electrochemical glucose biosensing. In contrast to other detection methods [16, 17], the approach used in this work is simple, portable and noble metal-free, and might be potentially scalable in its application for glucose biosensing.

2. Experimental section

The chemicals used in this work included iron (III) nitrate nonahydrate (Fe(NO₃)₃·9H₂O, 99%, Acros Organics), zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O, 98%, Sigma-Aldrich), urea (NH₂CONH₂, 99%, Sigma-Aldrich) and hydrogen peroxide (H₂O₂, 30%, VWR), which were used as received without any further purification. The deionised water used is generated from Milli-Q system with ρ = 18.2 MΩ·cm. D- (+)-glucose (C₆H₁₂O₆, ≥99.5%), D- (-)-fructose (C₆H₁₂O₆, ≥99%), sucrose (C₁₂H₂₂O₁₁, ≥99.5%), L-ascorbic acid (C₆H₈O₆, 99%) and uric acid (C₅H₄N₄O₃, ≥99%) powders, as well as sodium hydroxide (NaOH, ≥99%) pellets were purchased from Sigma-Aldrich and separately dissolved in deionised water to form aqueous solutions of suitable concentrations, which would be used later for electrochemical biosensing tests. Commercial ZFO NPs were purchased from Sigma-Aldrich for comparison only.

2.1. Synthesis of samples

Different combinations of masses of raw powders (as listed in table S1) were weighed and each combination was added into a 50 ml beaker containing 15 ml deionised water. The solutions were mixed by stirring at 500 rpm on a magnetic stirring plate followed by ultrasonication for 30 min. The resultant solutions were then separately transferred into 20 ml glass bottles, capped and heated in an oven at 100 °C for 60 h.

After precipitation reaction completed, the as-prepared precursors were separately transferred into 50 ml centrifuge tubes (Corning Inc.), which were each tightly covered with a piece of filter paper. They were frozen in liquid nitrogen for 5 min, quickly placed in a 300 ml freeze drying flask (Fisher Scientific) and immediately loaded onto a FreeZone 2.5 Plus lyophiliser (Labconco, USA) for 180 h of freeze drying to completely drive off the liquid phases in the raw precursors. The lyophiliser collector was set at the temperature of −80 °C and the pressure of 0.01 mbar.

After freeze drying, the precursor powders were immediately removed from the centrifuge tubes, separately transferred and evenly distributed into high purity alumina combustion boats (99.7% Al₂O₃, Morgan Advanced Materials). They were placed into a box furnace (Carbolite, UK), heated at 1.0 °C min⁻¹ to 500 °C and annealed isothermally for 4 h in air. After naturally cooling down to room temperature, the final samples were collected and separately stored.

2.2. Characterisation and testing techniques

The crystalline phases of the samples were determined by a D8 Advance powder X-ray diffractometer (XRD, Bruker, Germany); the Cu-Kα radiation was produced at 40 kV and 40 mA with λ ≈ 1.54059 Å. All samples were scanned under locked coupled θ–θ mode with a step size of 0.02° at the speed of 1 s/step.

The morphologies of the samples were characterised in a JSM-7600F field emission gun scanning electron microscope (FEG-SEM, JEOL, Japan), which was operated at an accelerating voltage of 10 kV under secondary electron imaging (SEI) mode. The crystal structure of ZFO NPs and EDX elemental mapping were analysed using a JEM-2100F field emission gun transmission electron microscope (FEG-TEM, JEOL, Japan) operated at the accelerating voltage of 200 kV, which was equipped with DigiScan II scanning TEM (STEM, Gatan, USA) and EDX (EDAX, USA) modules.

The catalytic activities of the samples on glucose oxidation were tested via an electrochemical approach using a PGSTAT302N potentiostat/galvanostat three-electrode workstation (Metrohm Autolab, Netherlands), which was equipped with an electrochemical chip cell interface. The cyclic voltammetry (CV) tests were performed on DropSens DRP-110 electrochemical chips (Asturias, Spain), of which the working electrode (WE) and counter electrode (CE) are carbon-based and the reference electrode (RE) is silver solid pseudo-reference electrode. 10 mg of ZFO NPs was uniformly dispersed in 400 µl of ethanol (CH₃CH₂OH, 95%, Aik Moh) in an ultrasonic bath for 30 min 20 µl of the homogeneous mixture was transferred dropwise onto a new electrochemical chip, so that the NPs could stay intact with the carbon electrode upon drying. The electrolyte solutions (NaOH and NaOH/glucose) were prepared to have 0.1 M NaOH; 60 µl of each electrolyte solution was separately added to the samples on the chips. The scanning range for cyclic voltammetry (CV) tests was set from 0 V to 0.80 V (versus Ag/AgCl) with the step size being 2.44 mV; all tests were performed for 5 cycles and only the third cycle was used for analysis. In order to investigate the effect of glucose concentration and existence of other species, as well as the long-term stability, the sample was coated onto a glassy carbon electrode and loaded onto the three-electrode workstation as the WE, with Pt foil and Ag/AgCl being the CE and RE respectively.
3. Results and discussion

3.1. XRD and phase formation

The entire synthesis process of the TMO NPs can be separated into two steps, namely precipitation of precursor powders, as well as heat treatment for phase formation and crystallisation. The overall reaction mechanism during the entire procedure can be split into two steps: firstly, the individual nitrate salts react with urea to form the respective hydroxides (Equation 1a–1b), which are then subjected to dehydration and/or chemical reactions at the later stage of thermal annealing (Equation 2a–2e).

**Equation 1:** Reaction mechanism during precipitation of precursor powders

\[
14\text{Fe(NO}_3\text{)}_3 \cdot 9\text{H}_2\text{O} + 3\text{NH}_2\text{CONH}_2 & \xrightarrow{100\, ^\circ \text{C}} 14\text{Fe(OH)}_3 \downarrow + 3\text{CO}_2 \uparrow + 48\text{NO}_2 \uparrow + 111\text{H}_2 \\
7\text{Zn(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O} + \text{NH}_2\text{CONH}_2 & \xrightarrow{100\, ^\circ \text{C}} 7\text{Zn(OH)}_2 \downarrow + \text{CO}_2 \uparrow + 16\text{NO}_2 \uparrow + 37\text{H}_2\text{O}
\] (1a–1b)

**Equation 2:** Reaction mechanism during thermal annealing

In Sample A: Zn(OH)$_2$ $\xrightarrow{\Delta} \text{ZnO} + \text{H}_2\text{O}$ $\uparrow$ (2a)

In Sample B: 8Zn(OH)$_2$ + 2Fe(OH)$_3$ $\xrightarrow{\Delta} 7\text{ZnO} + \text{ZnFe}_2\text{O}_4 + 11\text{H}_2\text{O}$ $\uparrow$ (2b)

In Sample C: 4Zn(OH)$_2$ + 4Fe(OH)$_3$ $\xrightarrow{\Delta} 3\text{ZnO} + \text{ZnFe}_2\text{O}_4 + \text{Fe}_2\text{O}_3 + 10\text{H}_2\text{O}$ $\uparrow$ (2c)

In Sample D: 2Zn(OH)$_2$ + 8Fe(OH)$_3$ $\xrightarrow{\Delta} 2\text{ZnFe}_2\text{O}_4 + 2\text{Fe}_2\text{O}_3 + 14\text{H}_2\text{O}$ $\uparrow$ (2d)

In Sample E: 2Fe(OH)$_3$ $\xrightarrow{\Delta} \text{Fe}_2\text{O}_3 + 3\text{H}_2\text{O}$ $\uparrow$ (2e)

Formation of ZnFe$_2$O$_4$: Zn(OH)$_2$ + 2Fe(OH)$_3$ $\xrightarrow{\Delta} \text{ZnFe}_2\text{O}_4 + 4\text{H}_2\text{O}$ $\uparrow$ (2f)

Figure 1(a) shows the XRD patterns of the synthesised TMO NPs samples A–E after heat treatment. Sample A is ascribed to pure ZnO (JCPDS #36–1451, space group: P6$_3$mc), which has a hexagonal lattice with wurtzite crystal structure with; sample E is ascribed to pure α-Fe$_2$O$_3$ (JCPDS #33–0664, space group: R-3c), which has a rhombohedral lattice with corundum crystal structure. As shown in e a/e, full dehydration of the respective hydroxides forms ZnO and Fe$_2$O$_3$. It is obvious that pure ZnO has much higher peaks compared to pure Fe$_2$O$_3$; at the fixed annealing temperature of 500°C, ZnO has been well crystallised, but the thermal energy supplied seems to be insufficient for full crystallisation in Fe$_2$O$_3$.

In samples B–D, the amount of Zn reduces whereas the amount of Fe increases, therefore the intensities of the peaks corresponding to ZnO sharply decrease and finally diminish, while the peaks corresponding to Fe$_2$O$_3$ start to appear and intensify. When annealed at 500°C in air, since Zn(OH)$_2$ and Fe(OH)$_3$ co-exist in various ratios, not only dehydration of the individual hydroxides would occur, but they can also react with each other according to e b–d to form ZFO (JCPDS #22–1012, space group: Fd-3m) [18], which has a cubic lattice with spinel crystal structure.

Formation of ZFO as the new phase, of which the chemical reaction is given in e f, is thermodynamically favourable, as the lattice transformation and crystallisation processes could release extra energy built up during thermal annealing. As the reactants are in large amount, according to Le Chatelier’s Principle, the process...
favours forward reaction until one of the reactants is fully consumed, or it stops when equilibrium is reached. This explains the co-existence of mixed phases in samples B–D.

From figure 1(a) and equation 2(b), it could be spotted that sample B is comprised of ZnO and ZFO. The sample was then subjected to dilute nitric acid, followed by washing several times with deionised water and ethanol. Subsequently, the mixture underwent another round of freeze drying and heat treatment. The final product was labelled as sample F, which could be purely ascribed to ZFO. The XRD pattern shown in figure 1(b) shows that the ZFO NPs are polycrystalline and of much higher crystallinity compared to the commercial product.

3.2. Morphology and particle size distribution

In sol-gel/solution-based synthesis, liquids form the majority phase in precursors. The traditional ways to remove the liquid phases would include drying in ambient conditions and/or heating; when the liquids evaporate, the capillary force leads to collapse of the overall structures [19]. In colloidal systems where solid phases are dispersed within the liquid phase, solid phases should be kept in their original positions during removal of liquid phase, so as to prevent agglomeration. This approach is termed as lyophilisation and commonly known as freeze drying [20].

In this work, when the hydroxide colloidal precursors are frozen at low temperature and then subjected to low pressure, the liquid phase will sublime and get removed by vacuum in the stage of primary drying; as the materials being lyophilised longer, more residual liquid phase will be further desorbed in the stage of secondary drying, thus producing the final dry samples [21]. During freeze drying, as there is no liquid-to-gas phase transformation, NPs are not subjected to capillary force, and thus left intact in the suspension [22, 23]. Figure S1 (available online at stacks.iop.org/NANOX/2/024001/mmedia) shows that the NPs have small average sizes ranging from 27.18 nm to 57.44 nm; little agglomeration is observed in the samples and the size distributions are relatively narrow, the uniformity should mainly credit to the lyophilisation process employed before heat treatment [24].

The as-synthesised ZFO NPs (sample F) was compared with the commercial product and the FEG-SEM images are displayed in figure 2. It can be observed that before electrochemistry testing, the particle sizes of both are similar and averaged around 30–40 nm (figures 2(a)/(c)). The histograms and particle size distributions curves (figure S2) are established based on random measurement of 300 particles from each of the FEG-SEM images, and the average particle sizes are also calculated from these data; sample F has a smaller average size and

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**Figure 2.** FEG-SEM images of the as-synthesised NPs and commercial product compared before and after stability test.
narrower distribution compared to the commercial product, this means freeze drying is an excellent technique that could help in the control of particle size distribution.

The high crystallinity and narrow size distribution of the NPs could be confirmed by TEM. Figure 3(a) is the low magnification TEM image of sample F which shows a number of synthesised NPs after heat treatment. One of the particles is magnified and the high resolution TEM (HRTEM) image is displayed in figure 3(b). Two individual regions in the same particle are marked by the red and blue squares, and their respective fast Fourier transform (FFT) patterns are overlapped as displayed in figure 3(b’). Strong diffractions that contains the first five diffraction peaks in XRD (figure 1) are observed in small areas (10 x 10 nm2), and this indicates that the NP is highly crystalline with a zone axis of [1 0 1]. In comparison with sample C (figure S3), which only has a strong diffraction in (3 1 1) plane and a weak diffraction in (4 2 2) plane, there could be two factors that lead to the much higher crystallinity of sample F: the first is the removal of residual phases that might hinder the crystallisation of ZFO, and the second is the extra heat treatment carried out.

The freeze drying process has also induced some defects on the synthesised NPs (possibly in large amount). Figure 3(c) is the HRTEM image of the white square region in figure 3(b) with much better phase contrast, and crystal twinning is observed at the edge of the particle. The lattice of ZFO is distorted to form mirror images (marked by the red zig-zag lines) along the twinning planes (which are (−1 1 1) plane), as represented by the yellow lines in figure 3(c) [25–27]. The lattice is also strained as illustrated in figure 3(d); the RGB mapping was performed by the overlapping of the inverse FFT (IFFT) images of figure 3(c) along < 1 1 1 > and < 2 0 0 > directions, and the dark spots correspond to the sites with the largest strain energy. Moiré fringes are another commonly observed feature in sample F (figure 3(e)); this is caused by the partial lattice rotation possibly occurred during the freezing process, and the coupling of diffraction spots in the FFT pattern (figure 3(c) inset) is a good illustration of the phenomenon [28]. These defects accumulate large amount of surface energy and would be beneficial to the biosensing of glucose, as proved by the electrochemistry tests.

3.3. Electrochemical biosensing of glucose
The synthesised ZFO NPs (sample F) and commercial product were separately mounted onto the electrochemical chips. An initial comparative test on the glucose biosensing abilities was carried out and the CV profiles are shown in figure S4(a). A distinct oxidation peak could be observed at ~0.4 V (versus Ag/AgCl) for both samples, which signifies the formation of enediol-ZFO complex structure [29]. The peak current of sample
F is much higher than the commercial product, and this is credited by the large surface energy stored in the various forms of defects.

Following that, detailed testing for sample F was performed and the results are summarised in figure 4. The sample was first subjected to electrolytes with various glucose concentrations and the CV profiles are displayed in figure 4(a). It is clear that as the glucose concentration increases, the oxidation peak at ~0.4 V gives stronger signal. A calibration curve is established based on the peak current as shown in figure S4(b). It seems that the change of peak current against glucose concentration is split into three sections; each is showing excellent linear relationship with different gradient. Over the entire range, it generally follows a linear increase but the linearity of the fit is slightly lower. To further determine the effects of scanning rates on the electrochemical performance, the electrolyte was fixed at the glucose concentration of 10 mM at pH = 13. Figure 4(b) shows that as the scanning rate increases, the signal of the oxidation peak becomes more and more obvious. A calibration curve is also established (figure S4(d)) and it shows that the peak current density has an exponential relationship with the scanning rate.

To exclude the effects of possible interferences, the ZFO NPs were dispersed and coated onto a glassy carbon electrode, which was loaded as the WE immersing in the electrolyte contained in a quartz cell. The CE and RE are Pt foil and Ag/AgCl respectively. Chronoamperometry (CA) tests were performed by sequentially adding various chemicals at fixed intervals and the i–t curves are given in figure 4(c). With a starting electrolyte of 0.1 M NaOH, 0.1 mM glucose solution was injected and a sharp increase of signal is detected (blue profile in figure 4(c)). Following that, 0.1 mM solutions of other species (fructose, ascorbic acid, sucrose, uric acid and H2O2) were sequentially added at an interval of 2 min, and the change in signal appears negligible compared to that brought by the addition of glucose. Another injection of 0.1 mM glucose leads to the second obvious increase in the signal and this shows the high selectivity of ZFO in the electro-oxidation of glucose, and that the glucose biosensing would be accurate without having the interference of other substances possibly existing in the samples in the actual application scenarios. Next, 0.1 mM glucose solution was sequentially injected into the starting electrolyte (0.1 M NaOH) at the interval of 1 min. The red profile in figure 4(c) shows an increasing signal of the oxidation reaction and the calibration curve (Figure S4(c)) shows a quadratic relationship between the peak current and glucose concentration. This is quite different from figure S4(b) (which covers a larger range), and it reflects the dynamic change in the sensitivity of glucose.

**Figure 4.** Electrochemical performance of the as-synthesised ZFO NPs. Cyclic voltammograms with variation of (a) glucose concentrations and (b) scan rates; (c) chronoamperometric i–t curves with sequential addition of various chemicals; (d) 15-day stability test.
The stability of the ZFO NPs was monitored over time and figure 4(d) shows that the performance of the as-synthesised ZFO NPs remains at 90% at the end of 15 d. In comparison, the stability of the commercial ZFO NPs is not as good and drops to below 50% after 15 d. The excellent stability of the as-synthesised ZFO NPs originates from the agglomeration-free property brought by the freeze drying fabrication process as illustrated in figures 2(b)/(d) and figure S2.

4. Conclusions

In this work, zinc ferrite (ZnFe$_2$O$_4$) NPs were successfully synthesised by a simple solution combustion method followed by heat treatment. Electrochemistry tests have shown that the as-synthesised ZFO NPs have outstanding biosensing ability on glucose, as illustrated by the large oxidation peak current density at ~ 0.4 V (versus Ag/AgCl) and high selectivity without inference by other species. Apart from those, the sample has a good sensitivity of 0.1 mM, which is beyond the detection limit of most of the enzymatic glucose biosensors, and this value falls far below the physiological glucose levels in human blood. The outstanding performance is believed to originate from the small particle size and homogeneous distribution, large electrochemical surface area contributed by the active sites, as well as the high surface energy caused by the defects. The use of lyophilisation technique during the fabrication process endows the ZFO NPs with an agglomeration-free property, which brings about excellent performance stability (> 90%) over 15 d. These properties make ZFO NPs potentially applicable in non-enzymatic glucose biosensors development.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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