Mesoporous MnFe$_2$O$_4$ magnetic nanoparticles as a peroxidase mimic for the colorimetric detection of urine glucose†

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Mesoporous MnFe$_2$O$_4$ magnetic nanoparticles (mMnFe$_2$O$_4$ MNPs) were prepared with a one-step synthesis method and characterized to possess intrinsic peroxidase-like activity, and had obvious advantages over other peroxidase nanozymes in terms of high catalytic affinity, high stability, mono-dispersion, easy preparation, and quick separation. The mMnFe$_2$O$_4$ MNPs were used as a colorimetric sensor for indirect sensing of urine glucose based on the sensing principle that H$_2$O$_2$ can be produced from glucose oxidation catalyzed by glucose oxidase (GOx), and under the catalysis of the mMnFe$_2$O$_4$ MNPs nanozyme, H$_2$O$_2$ can oxidize 3,3',5,5'-tetramethylbenzidine (TMB) to produce a blue color in a few minutes. This sensor is simple, cheap, sensitive, and specific to glucose detection with a detection limit of 0.7 µM, suggesting its potential for on-site glucose detection.

1. Introduction

Glucose, an important energy source in the human body, participates in many physiological and pathological functions. Irregular glucose metabolism in urine is an early warning of health problems,¹ such as diabetes, a metabolic disease characterized by high glucose in blood and urine, resulting in serious damage to the human body,² suggesting the importance of early and accurate detection of urine glucose for health monitoring. For this purpose, various biosensors have been invented for glucose detection, including electrochemical³–⁷ and fluorescence⁸–¹⁰ techniques. However, most of these biosensors are complicated in construction and sophisticated in equipment, indicating the necessity to develop a simple, low cost and easy-to-detect method for on-site monitoring of the glucose level.

Another indirect method for evaluating glucose level is to detect H$_2$O$_2$ generated from glucose oxidase catalyzed by glucose oxidase (GOx).¹¹ Horseradish peroxidase (HRP), a natural enzyme catalyzing the oxidation of 3,3',5,5'-tetramethylbenzidine (TMB) or other substrates by H$_2$O$_2$, is the enzyme most commonly used as a diagnostic kit for H$_2$O$_2$ sensing.¹² However, the activity of HRP is not stable in a harsh environment (such as in extreme pH medium, organic solvents, and high temperature), and preparing pure HRP is time-consuming and expensive,¹³ thereby limiting the practical application of HRP as a natural enzyme. To solve these problems, an increasing number of scientists have turned their attention to the construction of efficient enzyme mimics. Since Yan et al. first reported Fe$_3$O$_4$ magnetic nanoparticles (NPs) as peroxidase mimics (termed as “nanozyme”),¹⁴ many other nanozymes have been developed and applied for indirect glucose detection,¹⁵–¹⁸ such as ZnO NPs,¹⁹ V$_2$O$_5$ nanowires,²⁰ Au NPs,²¹ Pt NPs,²² and Pd NPs.²³ However, the enzyme-like activity of most nanozymes can be easily affected by additional coating or modification. Therefore, it is still necessary to develop new nanozymes with high performance.

In the past few years, spinel ferrites (MFe$_2$O$_4$, M = Zn, Co, Ni, Cd, Mn) have attracted increasing attention due to their wide application in the fields of magnetic materials, energy, environmental protection, biomedicine, and catalytic application.²⁴–²⁷ Their chemical and physical properties can be effectively regulated by tuning the shape, size, and morphology.²⁸ Thus, ferrite nanomaterials with different morphologies have been successfully prepared, such as homogeneous hollow microspheres of spinel ferrites,²⁹ porous “timber-like” ZnFe$_2$O$_4$ structures³⁰ and MnFe$_2$O$_4$ nanomaterials with nano-octahedron, nano-sheet or nano-wire morphologies.³¹ Interestingly, the MnFe$_2$O$_4$ nanomaterials showed high morphology-dependent oxidase-like activity, with a considerably higher oxidase-like activity for the MnFe$_2$O$_4$ nanomaterials with a nano-octahedron morphology than those with a nano-sheet or nano-wire morphology. Therefore, the tunable morphology-dependent enzyme-like property of the spinel ferrites has attracted the attention of an increasing number of researchers.
Here, we report the one-step green-synthesis of mesoporous MnFe₂O₄ magnetic nanoparticles (mMnFe₂O₄ MNPs) with high intrinsic peroxidase activity, uniform distribution, high stability, and rapid separation. As shown in Scheme 1, H₂O₂ can be generated from glucose oxidation catalyzed by GOx, and under the catalysis of the mMnFe₂O₄ MNPs nanozyme, TMB can be oxidized by H₂O₂ to produce a blue color observable with the naked eye in a few minutes. Based on this principle, we developed a colorimetric sensor for glucose detection, which showed great potential for point-of-care monitoring of urine glucose due to its easy preparation, low cost, and quick detection.

2. Experimental section

2.1 Materials
Sodium acetate (NaAc), ferric chloride (FeCl₃·6H₂O), manganous dichloride (MnCl₂·4H₂O), ethylene glycol (EG), hydrogen peroxide (H₂O₂), 3,3',5,5'-tetramethylbenzidine (TMB), fructose, lactose, and maltose were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China), glucose from Sigma-Aldrich, glucose oxidase (GOx, 10 KU) from Aladdin. All other chemicals were of analytical grade and used without further purification. Deionized water was used throughout the experiment.

2.2 Apparatus and characterization
A JEOL JEM-2010FEF transmission electron microscope (TEM) and a JSM-7900F scanning electron microscope (SEM) were used for measuring the morphology and size of mMnFe₂O₄ MNPs. The X-ray diffraction (XRD) pattern of mMnFe₂O₄ MNPs was obtained with a Shimadzu XRD-7000 diffractometer with Cu Kα radiation (λ = 0.154056). The zeta potential and size of mMnFe₂O₄ MNPs were measured with a Malvern Nano-ZS90 apparatus. Energy dispersive X-ray spectroscopy (EDS) was performed on an Oxford X-max 80 T. X-ray photoelectron spectra (XPS) were acquired using an ESCALAB 250Xi electron spectrometer. The spectra were measured using Al Kα radiation (12.5 kV, 400 W) in a chamber with a base pressure of 8 × 10⁻¹⁰ Pa. UV-Vis spectra were collected using a Shimadzu UV-2450 spectrophotometer.

2.3 Synthesis of mMnFe₂O₄ MNPs
The mMnFe₂O₄ MNPs were synthesized with a solvothermal method as previously reported with small modifications. Briefly, NaAc (2.7 g) was first completely dissolved in EG (30 mL) under ultrasonication for 10 min, followed by adding MnCl₂·4H₂O and FeCl₃·6H₂O at a molar ratio of 1:2. Next, the mixture was transferred into a Teflon autoclave and sealed to heat overnight at 180 °C. After cooling to room temperature naturally, the mMnFe₂O₄ MNPs were obtained with magnet, followed by three washes with water and ethanol and drying at 30 °C. Finally, the dried mMnFe₂O₄ MNPs were stored at room temperature for further use.

2.4 Peroxidase activity, reaction-rate factors and steady-state kinetics
The peroxidase activity of mMnFe₂O₄ MNPs was studied using TMB as the substrate. Briefly, mMnFe₂O₄ MNPs (10 mg L⁻¹) were quickly mixed with 2.0 mL solution of TMB (400 μM) and H₂O₂ (20 mM) in citric buffer (25 mM, pH 4.0), the absorbance at 652 nm was recorded. Similarly, the factors affecting the rate of catalytic reaction, such as pH, temperature, reaction time, salt concentration, H₂O₂ concentration, and steady-state kinetics, were investigated using TMB as the substrate. Finally, the initial rates were calculated from the plot of absorbance versus time.

2.5 Glucose sensing
For glucose sensing, 20 μL of GOx (10 mg mL⁻¹, pH = 7) was first mixed separately with 180 μL of glucose solution at different concentrations (0.0, 0.5, 2.5, 5.0, 10.0, 16.0, 50.0, 100.0, 500.0, 1000.0 μM) (pH = 7), and incubated at 37 °C for 30 min. Then, the mixture was supplemented with 1770 μL of citric

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Scheme 1 Schematic illustration of glucose detection with glucose oxidase (GOx) and mMnFe₂O₄ MNPs-catalyzed system.
buffer (25 mM, pH 4.0), 10 µL of mMnFe₂O₄ MNPs (2 mg mL⁻¹) and 20 µL TMB solution (40 mM). After incubation at 37 °C for 30 min, the absorbance of the resulting solution was measured at 652 nm. Meanwhile, the control experiments were performed using maltose, lactose, and fructose to replace glucose in a similar way.

3. Results and discussion

3.1 Characterization of mMnFe₂O₄ MNPs

Fig. 1 shows the SEM and TEM images of mMnFe₂O₄ MNPs. In the SEM and TEM images, mMnFe₂O₄ MNPs were seen to present uniform nanocrystals with a size of nearly 180 nm and a well-defined meso-structure. Fig. S1,† shows the dynamic light scattering (DLS) size distribution of mMnFe₂O₄ MNPs. In Fig. S2,† the EDS result showed the existence of Mn, Fe and O elements. The nanoparticles were further characterized by X-ray photoelectron spectroscopy (XPS) (Fig. S3†), and the XPS results are consistent with the previous reports. The above results confirmed that successful synthesis of mMnFe₂O₄ nanoparticles.

The structure of mMnFe₂O₄ nanoparticles was investigated by FT-IR (Fig. S4†) and XRD (Fig. S5†). All the diffraction peaks are consistent with the FCC structure of mMnFe₂O₄ with high crystallinity (JCPDS card no. 74-2403).† The porous structure of the nanocrystals was investigated by N₂ adsorption–desorption analysis (Fig. S6a†). The mesopore size was shown to be about 7.6 nm from the HK pore size distribution curve (Fig. S6b†), and the surface area was calculated to be 53.4 m² g⁻¹. The magnetic property of mMnFe₂O₄ MNPs was characterized by field dependent magnetization (Fig. S7†), and mMnFe₂O₄ MNPs were shown to possess superparamagnetic property with 70 emu g⁻¹ of maximum saturation magnetization (Mₛ) value, which is almost comparable to the Mₛ value of Fe₂O₃ nanoparticles.‡

3.2 Peroxidase-like activity of mMnFe₂O₄ MNPs

After treatment with mMnFe₂O₄ MNPs and H₂O₂, the colorless TMB solution rapidly turned blue, with the blue color from the oxidized TMB product (oxTMB). In, Fig. 2a, the UV-vis absorbance of oxTMB at 652 nm was seen to be obviously enhanced in the mixture of mMnFe₂O₄ MNPs + TMB + H₂O₂. However, neither H₂O₂ nor mMnFe₂O₄ MNPs alone can efficiently oxidize TMB to produce a blue color. Therefore, TMB can be oxidized by H₂O₂ under the catalysis of mMnFe₂O₄ MNPs, which is also the case for horseradish peroxidase (HRP). These results indicated that mMnFe₂O₄ MNPs may possess an intrinsic peroxidase-like activity, which was further characterized by using other peroxidase substrates, such as 2,2-azino-bis (3-ethylbenzthiazoline-6-sulfonic acid) (ABTS) and o-phenylenediamine (OPD), to replace TMB (Fig. 2b), and mMnFe₂O₄ MNPs were shown to possess a broad peroxidase-like activity. Moreover, in Fig. S8,† the peroxidase-like activity was observed to be caused by mMnFe₂O₄ MNPs rather than ions leached from mMnFe₂O₄ MNPs in acidic solution.

The kinetic mechanism of the peroxidase-like activity of mMnFe₂O₄ MNPs was investigated by analyzing apparent steady-state kinetic parameters at varying TMB concentrations (50–800 µM). The typical Michaelis–Menten curves were obtained by measuring the absorbance of TMB at 652 nm for 300 s (Fig. 3a). Michaelis–Menten constant (Kₘ) and maximum initial velocity (Vₘₐₓ) were calculated through Lineweaver–Burk plots (Fig. 3b and c). It was reported the smaller the Kₘ value, the stronger the affinity between enzyme and substrate. The apparent Kₘ value for the mMnFe₂O₄ MNPs with TMB as the substrate is 0.07 mM, which is significantly lower than that of the other catalysts (Table S1†), suggesting higher affinity of mMnFe₂O₄ MNPs for TMB. This could be due to the mesoporous structure of mMnFe₂O₄ MNPs, which can enhance the uptake of TMB by mMnFe₂O₄ MNPs and strengthen the catalytic activity. In Fig. 3d, mMnFe₂O₄ MNPs were shown to decompose H₂O₂ to produce ·OH radical, which is consistent with previous report that the catalytic mechanism of nanozymes is to bind and react with H₂O₂ and then release hydroxyl radical (OH) to react with TMB.

3.3 Optimization of experimental conditions

Like natural enzyme HRP, the peroxidase-like activity of mMnFe₂O₄ MNPs is dependent on reaction conditions. The
The catalytic activity of mMnFe$_2$O$_4$ MNPs is much higher in acidic solutions (Fig. S9a†). In Fig. S10,† the SEM result showed that the morphology of mMnFe$_2$O$_4$ MNPs remained almost intact at pH 4.0 for 2 h. Considering the stability and catalytic efficiency of mMnFe$_2$O$_4$ MNPs, pH 4.0 was defined as the optimal pH value experiment. Meanwhile, the incubation temperature of mMnFe$_2$O$_4$ MNPs with TMB and H$_2$O$_2$ was also investigated and the results are shown in Fig. S9b,† with 37°C as the optimal temperature. Additionally, the optimal concentration of H$_2$O$_2$ was investigated in the range of 0 to 60 mM, and the absorbance at 652 nm obviously increased and reached a plateau at 20 mM (Fig. S9c†), so 20 mM was chosen as the optimal H$_2$O$_2$ concentration for further experiments. Similarly, 0.4 mM of TMB (Fig. S9d†) and 10 μg mL$^{-1}$ of mMnFe$_2$O$_4$ MNPs (Fig. S9e†) were found to be the optimal parameters for further experiments. Furthermore, the incubation time of mMnFe$_2$O$_4$ MNPs with TMB and H$_2$O$_2$ was also optimized to achieve the best catalytic activity of the nanozymes (Fig. S9f†), and 15 min was shown as the optimal incubation time. In this study, the optimized experimental conditions consisted of pH 4.0, 37°C, 20 mM of H$_2$O$_2$, 0.4 mM of TMB, 10 μg mL$^{-1}$ of mMnFe$_2$O$_4$ MNPs, and 15 min of incubation time.

Besides, the enzymatic-like reaction activity of mMnFe$_2$O$_4$ MNPs was shown not to be affected by adding NaCl (0–0.25 M) to the reaction media (Fig. S11†), confirming the high stability of our nanozymes in NaCl media.

### 3.4 Application to glucose detection

Since the catalytic activity of mMnFe$_2$O$_4$ MNPs depends on H$_2$O$_2$, H$_2$O$_2$ is the main product of glucose oxidation catalyzed by glucose oxidase (GOx). When combined with GOx, the mMnFe$_2$O$_4$ MNPs could be used for glucose detection instead of traditional HRP. Fig. 4a shows the glucose concentration-response curves to the absorbance of oxTMB. The linear range for glucose was from 0.5 to 16.0 μM with a detection limit of 0.7 μM (S/N ≥ 3) (Fig. 4b), which was lower than the detection limit of several previously reported nanozyme-based methods (Table S2†).

### 3.5 Specificity test

Specificity is important for the application of mMnFe$_2$O$_4$ MNPs probes. The specificity tests were performed in the presence of common ions (14 cations: Cd$^{2+}$, Pb$^{2+}$, Zn$^{2+}$, Cu$^{2+}$, Fe$^{3+}$, K$^+$, Na$^+$, As$^{3+}$, Cr$^{3+}$, Mn$^{2+}$, Ag$^+$, Ca$^{2+}$, Ba$^{2+}$, Mg$^{2+}$) and anions (8: none, Cl$^-$, Br$^-$, NO$_3^-$, SO$_4^{2-}$, CO$_3^{2-}$, F$^-$, OH$^-$). Inset: the corresponding photographs, determination of the specificity of glucose detection. (c) UV-vis spectra of TMB + mMnFe$_2$O$_4$ MNPs + GOx system in the absence (none) and presence of glucose (1 mM), maltose (10 mM), lactose (10 mM), and fructose (10 mM). Inset: the variation of colors with different solutions. (d) The absorbance ratio at 652 nm for (c). The error bars represent the standard deviation of three measurements.
As\(^{3+}\), Cr\(^{3+}\), Mn\(^{2+}\), Ag\(^{+}\), Ca\(^{2+}\), Ba\(^{2+}\), Mg\(^{2+}\); 7 anions: Cl\(^{-}\), Br\(^{-}\), NO\(_3\)^{−}, SO\(_4\)^{2−}, CO\(_3\)^{2−}, F\(^{−}\), OH\(^{−}\)), which did not interfere with H\(_2\)O\(_2\) determination (Fig. 5a and b), confirming that the mMnFe\(_2\)O\(_4\) MNPs probe is specific to H\(_2\)O\(_2\). The specificity of the mMnFe\(_2\)O\(_4\) MNPs nanozyme toward glucose detection was investigated by performing the control experiments using 10 mM of fructose, lactose, and maltose to replace glucose (1 mM). In Fig. 5c and d, the absorbance at 652 nm for glucose was seen to be obviously higher than that of glucose analogues, confirming that the mMnFe\(_2\)O\(_4\) MNPs nanozyme is highly specific to glucose, probably due to the high affinity of glucose oxidase for glucose.

### 3.6 Real sample test

The potential of the mMnFe\(_2\)O\(_4\) MNPs nanozyme for glucose detection was further evaluated by detecting glucose in urine samples from healthy people and a diabetic volunteer. The UV-vis spectra and the colorimetric differentiation are shown in Fig. S12.† According to the calibration curve, the concentration of glucose was 8.2 mM (147.6 mg dL\(^{-1}\)) in the diabetic urine, but could hardly be detected in healthy human’s urine. The obtained values were further analyzed by spiking different concentrations of glucose into the healthy human’s urine and recovering them (Table S3†). Based on the recovery rate and the relative standard deviation (RSD), there was no significant difference between the spiked value and the detected value, indicating the potential of this colorimetric probe for real sample testing.

### 4. Conclusion

In paper, we reported the synthesis and characterization of the mMnFe\(_2\)O\(_4\) MNPs with intrinsic peroxidase-like activity as well as their application in colorimetric detection of urine glucose. As a novel peroxidase nanozyme, the mMnFe\(_2\)O\(_4\) MNPs nanozyme shows several advantages over HRP and other peroxidase nanozymes, such as mesoporous nanostructure, high stability, good dispersibility, excellent separability, and high catalytic efficiency. Based on the reaction mechanism of Scheme 1, we developed a simple, low-cost, highly sensitive, and selective colorimetric method for glucose detection, which shows the practicability of glucose detection in the urine of healthy and diabetic people, suggesting its potential as a simple and useful probe for bioanalysis. The overall results indicate that the mMnFe\(_2\)O\(_4\) MNPs nanozyme may have broad application prospect as a powerful artificial peroxidase.

### Ethical statement

For the human urine experiments, informed consent was obtained from all human subjects. All experiments were performed in compliance with relevant laws or guidelines. All experiments followed institutional guidelines, and were approved by the institutional committee.

### Conflicts of interest

There are no conflicts of interest to declare.

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