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Mixed-solvent liquid exfoliated MoS₂ NPs as peroxidase mimetics for colorimetric detection of H₂O₂ and glucose†

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Ultra-small molybdenum disulfide nanoparticles (MoS₂ NPs) were prepared by a facile liquid exfoliation method with ethanol/water as the solvent. The produced MoS₂ NPs were of high purity due to the easily removable ethanol/water solution. The prepared MoS₂ NPs exhibited an intrinsic peroxidase-like activity in analogy to that of horseradish peroxidase (HRP). A custom-made spectrometer was employed to investigate the peroxidase-like activity of MoS₂ NPs in the presence of H₂O₂ and glucose. The change in absorption detected from MoS₂ NPs is proportional to the amount of target. The calibration curve of H₂O₂ and glucose shows a good relationship between the concentration of target and the change in the absorption of MoS₂ NPs. The limit of detection of H₂O₂ and glucose achieved by this method could approach 1.25 μ M and 7 μ M respectively. This method has been applied for the detection of glucose in serum from humans. Therefore, these produced MoS₂ NPs offer an alternative high-efficiency and economic way to detect diabetes.

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Introduction

The natural enzyme, horseradish peroxidase (HRP), is widely used for the detection of H₂O₂ due to its catalysis capability. The addition of a chromogenic substrate, such as 3,3',5,5'-tetramethylbenzidine (TMB), is able to produce a color change in the presence of H₂O₂.^{1,2} Furthermore, glucose in serum could be oxidized to produce H₂O₂ under the catalysis of glucose oxidase (GOx). This produced H₂O₂ then reacts with HRP, which could be used to diagnose diabetes.^{3–5} However, high costs of preparation, purification and easy inactivation of HRP motivate people to seek alternative mimic enzymes as complementary peroxidase enzyme to sense glucose for clinical diagnosis.^{6–8} Many nanomaterials exhibit good peroxidase properties, such as Fe₃O₄,⁹ Co₃O₄,¹⁰ and Au NPs,¹¹ Prussian blue,¹² carbon

nanodots,¹³ etc. Comparing to HRP, these peroxidase mimetics have advantages of lower cost, flexibility in design, and good chemical stability.

Molybdenum disulfide (MoS₂) is a typical layered transition metal dichalcogenides (TMDs) formed by a stack of S–Mo–S through weak van der Waals force.^{14,15} MoS₂ has been regarded as one of the most promising materials due to its unique structure and electronic properties.^{16,17} An intrinsic peroxidase-like activity possessed by MoS₂ nanomaterials has been densely studied in the past few years.^{18–23} However, most of these MoS₂ nanomaterials were synthesized by hydrothermal method,^{19–21} which required high temperature and pressure. A few MoS₂ nanomaterials were prepared by liquid exfoliation,^{18,22,23} but the organic solvent and surfactant were difficult to remove and the residual could affect the peroxidase performance. Zhou *et al.* reported that an alternative way to synthesis MoS₂ nanosheet,²⁴ which could avoid the drawbacks inherited from the above-mentioned methods. Jia *et al.* modified the method introduced by Zhou and successfully fabricated MoS₂ nanoplates.²⁵

Herein, a mixed-solvent liquid exfoliation method on the basis of Jia's has been introduced to synthesis MoS₂ NPs. A custom made spectrometer has been established to systematically investigate the catalysis performance of MoS₂ NPs to get the optimized parameters. The as-prepared MoS₂ NPs exhibits good catalysis capability and the detection limit of H₂O₂ and glucose performed by this method could approach 1.25 μ M and 7 μ M respectively. A test of serum has been conducted by using this method and the results are comparable to that from commercial glucometer. This indicates the practicality of this

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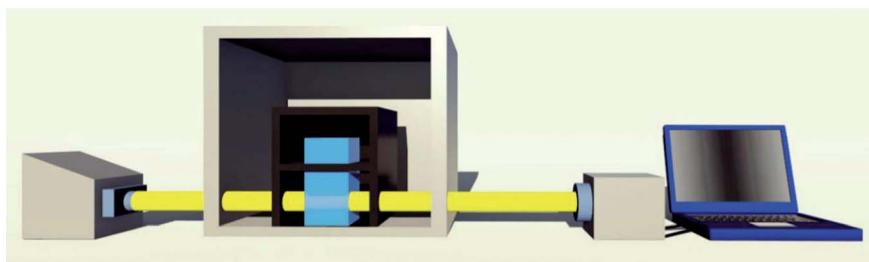


Fig. 1 Schematic diagram of this custom made thermal controlled spectrometer. From left to right: tungsten halogen lamp, drying oven, cuvette, spectrometer and computer.

prepared MoS_2 NPs and its relative test method could be used as an alternative way for the diagnosis of diabetes. However, there is still much room for improvement, compared with these using high-precision glucometer. More fundamental insights could be provided to improve this flexible and economic method for clinical diagnosis.

Experimental section

Chemicals and materials

H_2O_2 , sodium acetate and acetic acid were obtained from Chongqing Chemical Reagent Company (China). Horseradish peroxidase (HRP, $>150 \text{ U mg}^{-1}$), glucose, GOx, lactose, sucrose and fructose were obtained from Shanghai Sangon Biotech Co., Ltd (China). 3,3',5,5'-Tetramethylbenzidine (TMB) were purchased from Merck & Co., Inc (USA). MoS_2 powder ($\geq 98\%$, $2 \mu\text{m}$ in size) were purchased from Tianjin Chemical Reagent Factory Kaida chemical plant. All chemicals and reagents were of analytical grade and used as received without further purification, and ultrapure water was used throughout the work. Ultrapure water was prepared in the lab using a water treatment device. Serum was kindly donated from the Department of Clinical Laboratory at the University-Town Hospital of Chongqing Medical University (Shapingba District, Chongqing Municipality).

Apparatus

High-resolution transmission electron microscopy (HRTEM) images were carried out with an FEI Tecnai G2 F30 transmission electron microscope (USA). X-Ray photoelectron spectroscopy (XPS) data were recorded in a Thermo Fisher ESCALAB 250xi (England) using $\text{AlK}\alpha$ radiation (1486.6 eV). Binding energies were calculated with respect to C (1s) at 284.8 eV. Binding energies were measured with a precision of ± 0.05 eV. X-Ray diffraction (XRD) spectra were obtained through a X'-Pert3 Powder X-ray diffractometer (PANalytical, Netherlands). Zeta potential was measured by Zetasizer Nano-ZS (Malvern, UK). The atomic force microscopy (AFM) images were performed on a Multi-mode Nanoscope III3d scanning probe microscopy system (Burker, USA). The pH of the solutions was detected by a PHS-3D pH meter (Shanghai Precision Scientific Instruments Co., Ltd., China).

The custom made thermal controlled spectrometer is shown in Fig. 1. Drying oven is used to control the temperature of the

cuvette's surrounding environment. Unpolarized light from a tungsten halogen lamp (HL-2000-HP, Ocean Optics) illuminates the cuvette and the transmitted light is collected by spectrometer (HR4000, Ocean Optics). The illumination and absorption of cuvette is conducted through fibers, which dramatically enhance the flexibility of this setup. The spectral information was recorded and analyzed by a program written in C++ and Matlab.

Preparation of MoS_2 NPs

The MoS_2 NPs were prepared according to the mixed-solvent liquid exfoliation method reported previously.²⁵ Briefly, 300 mg MoS_2 powder was added into a 250 mL beaker, 100 mL of ethanol/water with ethanol volume fraction of 45% was added as dispersion solvent. The sealed beaker containing the above mixture was ultrasonicated for 24 h. In order to remove the aggregates, the obtained dark green suspension was centrifuged at 6000 rpm for 20 min three times. After that, collected supernatant was heated at 70 °C in a drying oven to remove the ethanol and water successively. Then the product was resolved in water and centrifuged for 20 min twice at 6000 rpm. At last, the supernatant was further purified by a 0.22 μm Millipore membrane filter. The final product was stored at 4 °C until required for further use.

Detection of H_2O_2 and glucose

The detection of H_2O_2 was performed as follows: 0.3 mL of TMB solution (0.8 mM in ethanol) performed as peroxidase substrate and 0.3 mL H_2O_2 with different concentrations were added into 2.1 mL of acetate buffer solution (0.2 M, pH = 3.5) in a 4 mL cuvette. Then, 0.3 mL of MoS_2 NPs solution (100 $\mu\text{g mL}^{-1}$) was injected to the above mixture immediately, and the mixture was incubated at 30 °C for 20 min. The absorption of the mixture was recorded at 656 nm, which is a typical absorption wavelength of oxidized TMB (oxTMB).

The detection of glucose was realized as follows: 0.03 mL of 5.0 mg mL^{-1} glucose oxidase (GOx) and 0.27 mL of glucose with different concentrations in 10 mM acetate buffer solution (pH 5.5) were incubated at 37 °C for 30 min to produce H_2O_2 . The other procedure of detection was the same as that of H_2O_2 .

In selectivity experiment, the target was replaced by sucrose (1.35 mM), lactose (1.35 mM) and fructose (1.35 mM) respectively during the experiment while the detection procedure was the same as that of glucose.



For the detection of glucose in human serum, the proteins in serum samples were separated by modified precipitation process according to the literature.¹⁸ Firstly, diluting 0.3 mL of serum with 0.2 mL water, then adding 0.5 mL Ba(OH)₂ (0.11 M) and 0.5 mL ZnSO₄ (0.0765 M) to above mixture. After centrifugation at speed of 4000 rpm for 15 min, 0.5 mL of the supernatant was extracted and diluted with 1.5 mL of acetate buffer solution (10 mM, pH 5.5). The other detection process was the same as the above mentioned glucose detection procedure.

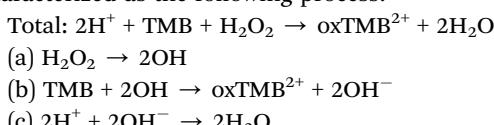
Results and discussion

Characterization of MoS₂ NPs

MoS₂ NPs were obtained from the bulk MoS₂ by the simple mixed-solvent liquid exfoliation method. The high resolution transmission electron microscopy (HRTEM) image of the resulting MoS₂ NPs shown in Fig. 2(a) indicates that these NPs are spherical and well-dispersed, with an average diameter of 3.7 nm (Fig. 2(b)). The XPS spectrum shown in Fig. 2(c) demonstrates the Mo and S elemental peaks. And the high-resolution XPS spectra were collected to analyze the chemical states of Mo and S in MoS₂ NPs. The peaks at 232.4 and 229.3 eV observed by the high-resolution spectrum of Mo (Fig. 2(d)) are attributed to Mo⁴⁺ 3d_{3/2} and Mo⁴⁺ 3d_{5/2}, respectively. In addition, the peaks at 163.3 and 162.1 eV shown in the high-resolution spectrum of S (Fig. 2(e)) are corresponding to the S 2p_{1/2} and S 2p_{3/2} orbits of divalent sulfide ions (S²⁻).^{22,26} XRD was used to further investigate the crystal structure of the prepared MoS₂ NPs and bulk MoS₂ crystals. As shown in Fig. 2(f), both bulk MoS₂ crystals and MoS₂ NPs are mainly identified as 2H-MoS₂, which has a dominant peak at 14.3°, representing the (002) plane (JCPDS 37-1492). In addition, the broadening (002) peak and the absence of most other peaks of MoS₂ NPs provide a direct evidence of a decrease in the particle size.^{22,23} The thickness of the MoS₂ NPs is around 1–2 nm, as shown in the atomic force microscopy (AFM) image and height profile of MoS₂ NPs (Fig. 2(g)–(i)). The zeta potential of the MoS₂ NPs was measured to be –28.2 mV (Fig. 2(j)). This indicates that MoS₂ NPs exhibit a great colloidal stability in aqueous media.

Peroxidase-like activities of MoS₂ NPs

The peroxidase-like activity of MoS₂ NPs was investigated in terms of the catalytic oxidation of the peroxidase substrate TMB in the presence of H₂O₂ under acidic conditions (pH = 4). According to previous literatures,^{18,20,26} the reaction could be characterized as the following process:



A series of absorption spectra for comparison is shown in Fig. 3. The absorption spectra of TMB and TMB–MoS₂ NPs systems have no significant difference in the range between 500 nm and 800 nm. Although TMB–H₂O₂ system exhibits a little absorption in 656 nm, it could be ignored compared to spectrum collected from TMB–H₂O₂–MoS₂ NPs system, which

displays a strong absorption peak at 656 nm. This is a typical peak of the oxidation products of TMB. The inset images represent different systems after 10 min of reaction. TMB and TMB–MoS₂ NPs systems remained colorless, which means no oxidation reaction occurred. TMB–H₂O₂ system shows a pale green color, which is due to the slow oxidation of TMB by the presence of H₂O₂. However, the TMB solution turns to be blue after the addition of MoS₂ NPs and H₂O₂. These results suggest that the prepared MoS₂ NPs have the peroxidase-like catalysis capability and could effectively catalyze the oxidation of TMB by H₂O₂. MoS₂ NPs could facilitate the electron transfer between TMB and H₂O₂ in the oxidation of TMB catalyzed by MoS₂ NPs. In this process, TMB molecules are absorbed on the surface of MoS₂ NPs, and donate lone-pair electrons from the amino groups to MoS₂ NPs, resulting in the increase in electron density and mobility in the MoS₂ NPs. This will accelerate the electron transfer from the MoS₂ NPs to H₂O₂, and promote the decomposition of H₂O₂ in acidic media into ·OH, which oxidizes TMB to form a blue product.^{18,20}

Optimization of experimental conditions

The optimization of detection parameters, including the concentration of MoS₂ NPs, temperature, pH and reaction time were investigated to enhance the catalysis capability of MoS₂ NPs. Fig. S1(a)† shows the time-dependent absorption changes against the different concentrations of MoS₂ NPs. The change in absorption approached the maximum when 10 µg mL⁻¹ MoS₂ NPs was utilized. The effect of temperatures on the catalytic activity was shown in Fig. S1(b).† It can be found that MoS₂ NPs show good activity over a wide temperature range from 25 °C to 45 °C, and 30 °C was chosen as the optimal temperature for the subsequent experiments. In addition, the catalytic activity was also pH-dependent (Fig. S1(c)†) and the buffer solution with pH of 3.5 was employed for the further experiments. Finally, the effect of reaction time on the catalytic activity of MoS₂ NPs was investigated, which was shown in Fig. S1(d).† Obviously, 20 min was the optimal reaction time because the maximum change in the spectra could be achieved and the absorption had little change from this time. Therefore, the optimal MoS₂ NPs concentration, temperature, pH, and reaction time were selected which are 10 µg mL⁻¹, 30 °C, 3.5, and 20 min, respectively, and they are used in the following experiments.

Kinetic assay of peroxidase-like activity of MoS₂ NPs

The peroxidase-like catalytic behavior of MoS₂ NPs was studied by employing the steady-state kinetics. The kinetic parameters were harvested through altering the concentration of H₂O₂ or TMB while holding the other one invariable. The adsorption of MoS₂ NPs monitored at the wavelength of 656 nm was recorded from 0–60 s during the peroxidase-like activity. The transient of adsorption can be fitted to the equation, $I = vt + b$, where v is the velocity characterized the adsorption change rate between the initial and final stage, b is the initial value of adsorption and t is the time. The maximum initial velocity (V_{\max}) and Michaelis–Menten constant (K_m) shown in Table S1† were calculated using the Lineweaver–Burk plot, $1/v = (K_m/V_{\max}) \times (1/S) + 1/V_{\max}$, where v is the initial



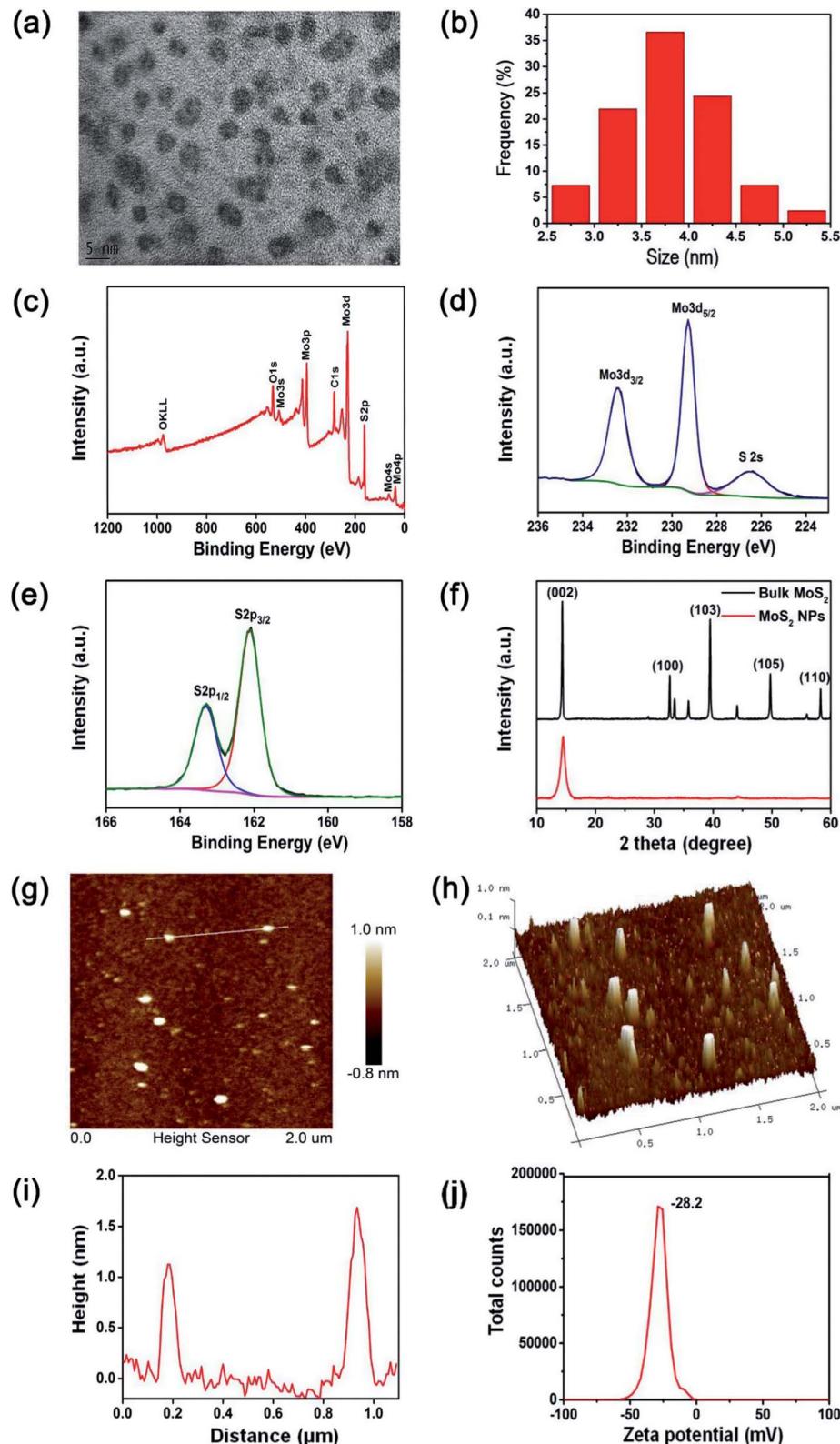


Fig. 2 (a) HRTEM image of MoS_2 NPs, (b) size distribution of MoS_2 NPs, (c) XPS spectrum of MoS_2 NPs, (d) high-resolution peak-fitting spectra of the Mo 3d, (e) high-resolution peak-fitting spectra of the S 2p, (f) XRD patterns of bulk MoS_2 crystals and MoS_2 NPs, (g) AFM image of MoS_2 NPs, (h) AFM 3D height profile of MoS_2 NPs, (i) height profile along the white line shown in the AFM image, (j) zeta potential distribution of MoS_2 NPs.

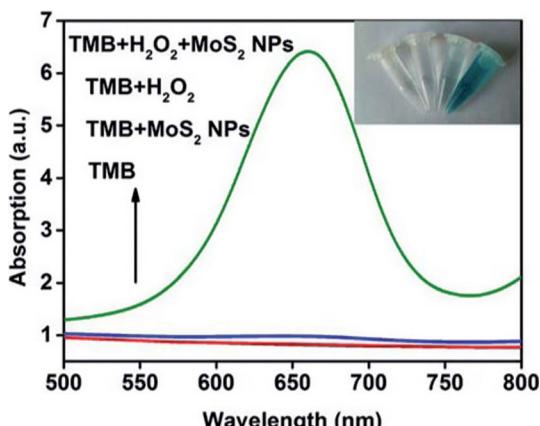


Fig. 3 Absorption spectra changes at 656 nm corresponding to (from bottom to top): TMB, TMB–MoS₂ NPs, TMB–H₂O₂ and TMB–H₂O₂–MoS₂ NPs in pH 4.0 acetate buffer (0.2 M) at 40 °C for 10 min. Inset: images of different systems (from left to right): TMB, TMB–MoS₂ NPs, TMB–H₂O₂ and TMB–H₂O₂–MoS₂ NPs. The concentration of MoS₂ NPs, TMB, and H₂O₂ are 10 µg mL⁻¹, 0.8 mM, 0.08 mM, respectively.

velocity and S is the concentration of the substrate.^{27–30} K_m usually indicates the affinity of the enzyme to the substrate. The smaller the K_m is, the stronger the affinity will be.^{20,31,32}

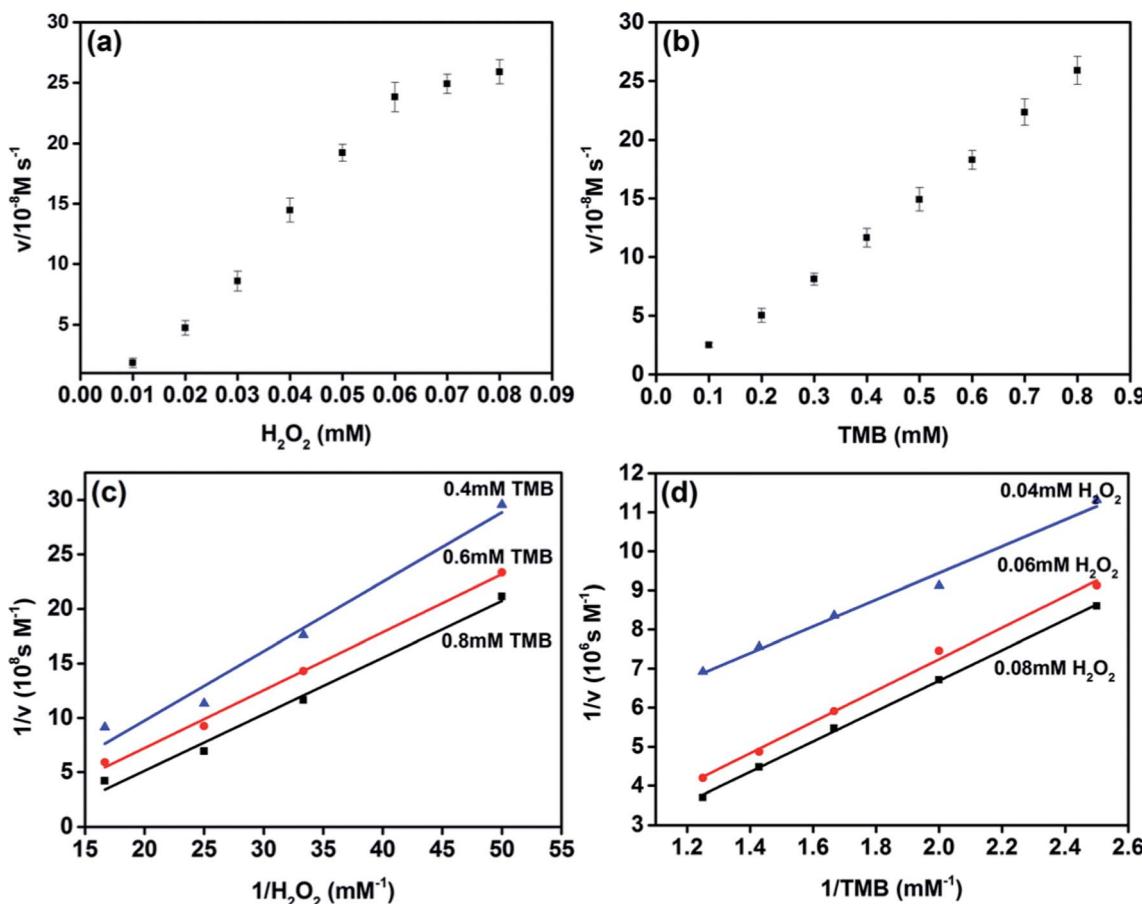


Fig. 4 Steady-state kinetic assay and catalytic mechanism of MoS₂ NPs (a–d). The concentration of MoS₂ NPs was fixed at 10 µg mL⁻¹ in 3 mL of acetate buffer solution (0.2 M, pH = 3.5) at 30 °C. (a) The concentration of TMB was 0.8 mM and the H₂O₂ concentration was varied. (b) The concentration of H₂O₂ was 0.08 mM and the TMB concentration was varied. (c) and (d) Double-reciprocal plots of activity of MoS₂ NPs at a fixed concentration of one substrate and the other varied. The error bars represent the standard error derived from three repeated measurements.

The apparent K_m value of MoS₂ NPs with H₂O₂ as substrate was obviously lower than that of HRP, which indicates that MoS₂ NPs exhibits higher affinity to H₂O₂ than that of HRP. The apparent K_m value of MoS₂ NPs with TMB as substrate was higher than that of HRP, is in accordance with the observation that a higher concentration of TMB was required to utilize to achieve the optimal activity of MoS₂ NPs. To further investigate the catalysis mechanism of MoS₂ NPs, the activity employing a wide range of TMB and H₂O₂ concentrations was carried out. The double-reciprocal plots of initial velocity *versus* different concentrations of one substrate were acquired while the concentration of this counterpart is set to be invariable (Fig. 4). The parallel slope of the lines reveals a ping-pong mechanism.^{18,20,33} In other words, the MoS₂ NPs bond and react with the first substrate, and then release the first product before reacting with the second substrate.

Detection of H₂O₂ and glucose

On the basis of the intrinsic peroxidase-like property of MoS₂ NPs, a colorimetric approach for the detection of H₂O₂ and glucose was utilized under the optimal experimental conditions. Fig. 5(a) shows the absorption spectra of MoS₂ NPs with different H₂O₂ concentration. It can be seen that the catalytic

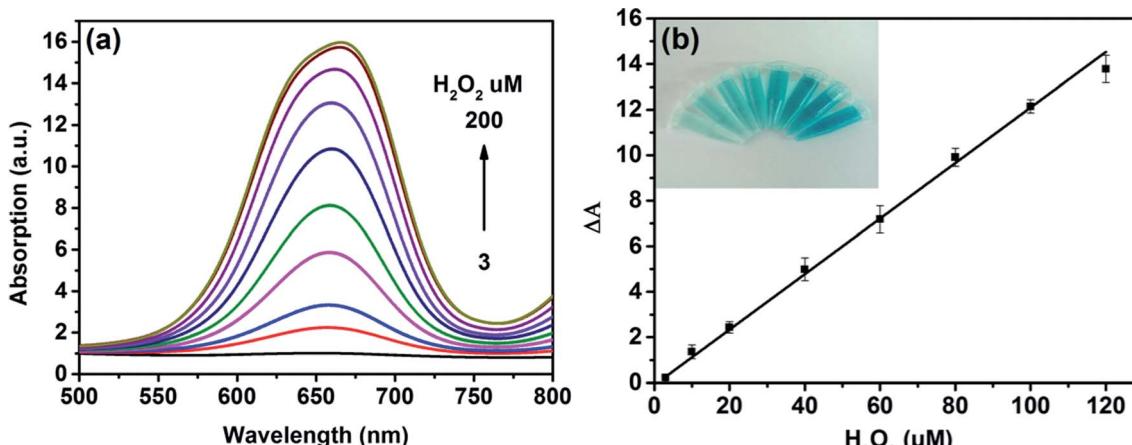


Fig. 5 (a) Absorption spectra changes in the presence of different H_2O_2 concentrations (intensity from weak to strong: 3, 10, 20, 40, 60, 80, 100, 120, 160, 200 μM). (b) The linear calibration plot for H_2O_2 (3, 10, 20, 40, 60, 80, 100, 120 μM). $\Delta A = \text{Abs}(20 \text{ min}, 656 \text{ nm}) - \text{Abs}(0 \text{ min}, 656 \text{ nm})$. The inset of (b) are the images of color changes for the corresponding concentrations of H_2O_2 .

activity of MoS_2 NPs is dependent on the concentration of H_2O_2 . Fig. 5(b) exhibits the calibration plot for H_2O_2 . It shows that the absorption of the mixture has a good linear relationship with the concentration of H_2O_2 ranging from 3 to 120 μM ($R^2 = 0.9983$) and the detection limit is calculated to be 1.25 μM . A comparison of this approach with other colorimetric methods for H_2O_2 detection is listed in Table S2.† It is shown that by employing MoS_2 NPs produced by this method, this sensing ability to H_2O_2 is comparable to other colorimetric methods.

Since H_2O_2 is the main product during the GOx-catalyzed reaction, this sensing strategy can be employed for the determination of glucose when MoS_2 NPs is combined with glucose oxidase (GOx). GOx can catalyze glucose oxidation to generate H_2O_2 and the following produced H_2O_2 can further oxidize TMB to bring a blue-color product through the catalysis of MoS_2 NPs. Fig. 6(a) illustrates the absorption spectra of different concentrations of glucose from 15 to 270 μM . Fig. 6(b) shows the

calibration curve for detecting glucose with a linear range from 15 to 135 μM . Moreover, the detection limit was found to be as low as 7 μM . Also, the LOD obtained by this method was much lower than the level of about 1 mM for glucose in human blood serum, indicating that the probe was suitable for detection of glucose in clinic.

The recovery was performed and the results are shown in Tables S4 and S5.† It can be seen that the recoveries are range from 95% to 99%. These results showed that this proposed method has a promising reliability for the detection of H_2O_2 and glucose.

Selectivity analysis for glucose detection

NaCl , KCl , NH_4Cl etc. are utilized to test the selectivity of the MoS_2 NPs-based sensing method towards H_2O_2 . Mixture of 40 μM H_2O_2 and various concentrations of these impurities were measured and the results are shown in Table S6.† The negligible

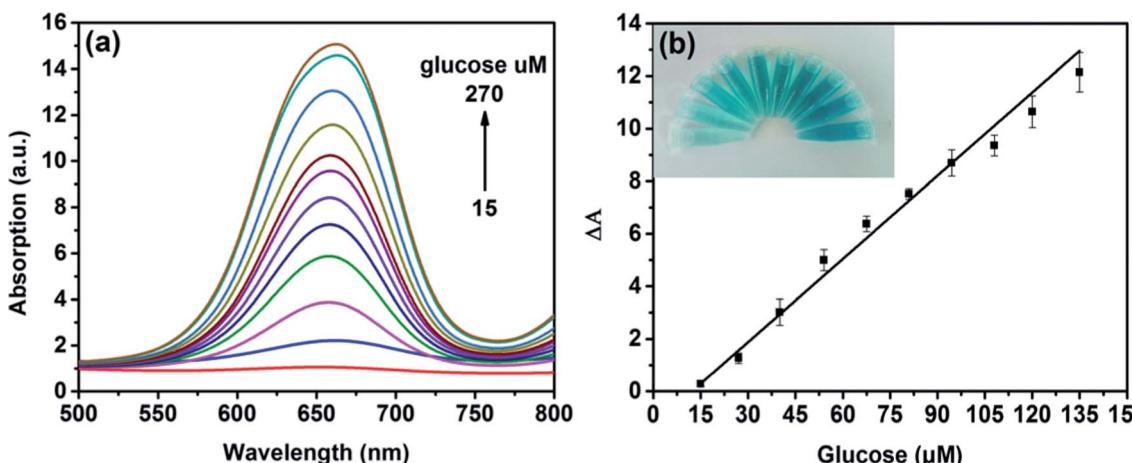


Fig. 6 (a) Absorption spectra changes in the presence of different glucose concentrations (intensity from weak to strong: 15, 27, 40.5, 54, 67.5, 81, 94.5, 108, 121.5, 135, 189, 270 μM). (b) The linear calibration plot for glucose detection (15, 27, 40.5, 54, 67.5, 81, 94.5, 108, 121.5, 135 μM). The inset of (b) are the images of color changes for the corresponding concentrations of glucose.



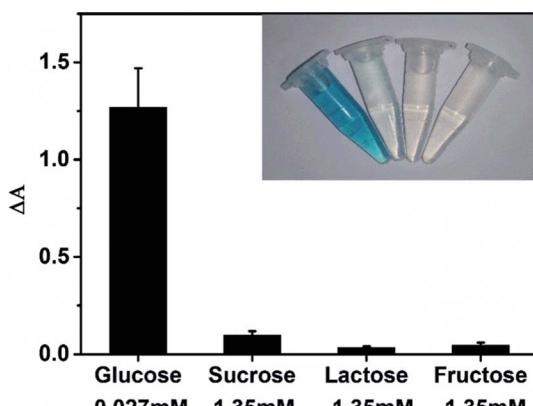


Fig. 7 Selectivity analysis for glucose detection using other sugars as control (the concentration was 0.027 mM for glucose, 1.35 mM for sucrose, 1.35 mM for lactose, 1.35 mM for fructose.). Inset of this figure were images of colored production corresponding to the above four solutions. The error bars represent the standard deviation of three measurements.

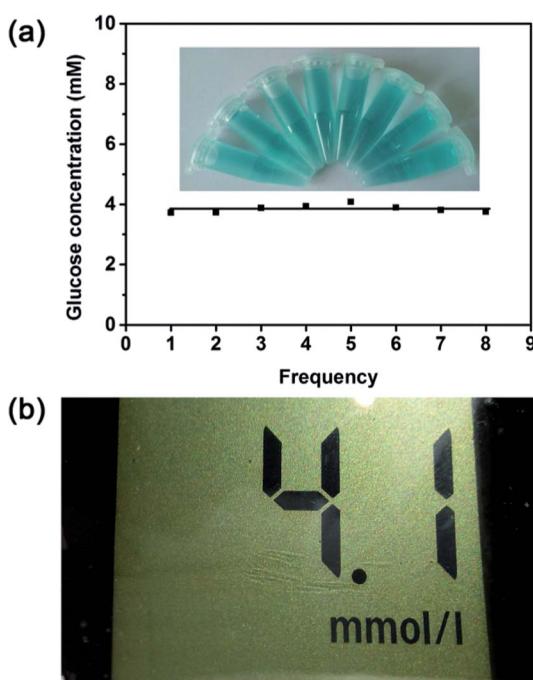


Fig. 8 (a) Reproducibility experiments of the colorimetric detection of glucose in serum samples. Inset of (a) are the corresponding color change of each independent experiment. (b) The glucose concentration in serum sample tested through a medical electronic glucometer.

change in absorption of these mixtures compared to that collected from pure H_2O_2 indicates the presence of these impurities has little effect on the detection of H_2O_2 .

The selectivity of MoS_2 NPs-based sensing method towards glucose was investigated in a series of control experiments. Some alternative sugars including sucrose, lactose and fructose were examined using the same detection procedure as that of glucose. Fig. 7 shows that no obvious interference is observed

even the concentrations of other sugars are 50 times higher than that of glucose. Therefore, this MoS_2 NPs produced here has a high selectivity for glucose detection because of the high specificity of GOx towards glucose.

Serum analysis

The glucose detection strategy reported here was then employed to detect the real samples to prove its practicability. Serums were selected as the detecting targets. On the basis of this method described in previous section, the glucose level in the human serum sample was tested. As shown in Fig. 8a, the glucose concentration of the serum sample is calculated to be 3.85 mM, which is not much different from the result obtained from the medical electronic glucometer (4.1 mM) (Fig. 8b). To confirm its suitability for real assay, another three different serum samples were used for comparison. As illustrated in Table S7,† the detection results of proposed method agree well with the detection results of glucometer. Therefore, this proves that this method initiated here is applicable for the glucose detection in human serum.

The serum used in this paper was kindly donated from the Department of Clinical Laboratory at the University Town Hospital of Chongqing Medical University (Shapingba District, Chongqing Municipality) with the permission of the patients.

This donation and experiment conducted in study was in compliance with the regulations issued by the Chongqing Medical University.

Conclusions

MoS_2 NPs in ultra-small size was synthesized by a simple facile liquid exfoliation method in the presence of ethanol/water mixture. This environmental friendly and economic fabrication method benefits from the utilization of ethanol/water mixture. A custom-made thermal controlled spectrometer has been established to analyze the intrinsic peroxidase-like activity of the prepared MoS_2 NPs. The detection of H_2O_2 and glucose with high sensitivity and good selectivity by using this MoS_2 NPs has been demonstrated and the MoS_2 NPs exhibits a good performance to sense the serum. The potential of MoS_2 NPs used as catalyst for other oxidation reactions could be carried out in the future research and this could create a new opportunity for this enzyme-mimicking MoS_2 NPs in various significant fields.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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