Electronic Supplementary Information for

Accelerating the peroxidase-like activity of $MoSe_2$ nanosheets at physiological pH by dextran modification

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Experimental Section

1. Chemicals and reagents

Molybdenum selenide ($MoSe_2$), polyethylene glycol (PEG, MW 6000) were purchased from Aladdin. 3,3′,5,5′-Tetramethylbenzidine (TMB) and dextran (Dex, MW 40000) were purchased from Sigma and stored in a refrigerator (4 ℃) for future use. Glucose oxidase (GOx) was purchased from Yuanye Biotechnology Co., Ltd. 1-Butyl-3-methylimidazolium hexafluorophosphate (BMIPF6) (≥97.0%), the ionic liquid (IL) used in this study, was purchased from Aladdin-Reagents Co., Ltd. Glucose, maltose, chitosan (CS) were purchased from Shanghai Biotech Engineering Co., Ltd. Sucrose, fructose, lactose, acetic acid, N, N-dimethylformamide, acetone, barium hydroxide ($Ba(OH)_2$), zinc sulfate heptahydrate ($ZnSO_4 \cdot 7H_2O$) were purchased from Xilong Chemical Co., Ltd. H_2O_2 (30%), hydrochloric acid (HCl, 36%), tris (hydroxymethyl) aminomethane (Tris) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Water is deionized water. All these chemical reagents are of analytical grade.

2. Preparation of dextran-functionalized $MoSe_2$ nanosheets (dex-$MoSe_2$ NS)

Dex-$MoSe_2$ NS was prepared according to the literature with some modification.[1] Typically, 1.0 g of bulk-$MoSe_2$ was added to 16 mL of dextran solution (2.0 g L^{-1}) and sonicated for 16 h in a sonicator with an ultrasonic power of 70% and a water level of 53%. The resulting solution centrifuge at 1977 (×g) for 90 min to remove unexfoliated $MoSe_2$. Then, the supernatant was collected and recentrifuged at 12210 (×g) for 90 min to obtain the precipitate. The collected precipitate was re−dispersed in water (9.0 mL)

and centrifuge at 3025 (×g) for 90 min. The supernatant liquid (3025-12,210 (×g)) was obtained for further experiments.

The dextran solution was replaced with a polyethylene glycol solution and other operating steps were the same as above to obtain PEG-$MoSe_2$.

The preparation method of CS-$MoSe_2$ was performed according to the previously method.[2] 1.0 g of bulk-$MoSe_2$ and 0.25 g of chitosan were ground with a pestle in an agate mortar for 10 min. Then add 20 μL of IL as a grinding aid. After being ground for 90 min, the mixture was collected and washed with acetone, dimethylformamide, and 0.5% acetic acid to remove IL and the excess chitosan. The washing process was repeated three times. Finally, the precipitate was dispersed in water and centrifuged at 5000 rpm for 15 min to remove the thick $MoSe_2$. The obtained CS-$MoSe_2$ nanosheet dispersion was diluted with water to 8.0 mL and stored at 4 ℃ before usage.

3. Apparatus

UV-2450 UV-Vis spectrophotometer (Shimadzu, Japan). Zetasizer Nano ZS90 potentiometer (Malvern, UK). HC-2064 high-speed centrifuge (Zhongke Zhongjia, China). JEOL 200 kV Field emission type transmission electron microscope (JEM-2100F, Japan). Thermo ESCALAB 250Xi electron (Thermo, USA). Atomic force microscopy (AFM) dimension icon (Bruker, Germany). PE Spectrum One spectrometer (Perkin-Elmer, USA). FLexar-NexION300X ICP-MS (Perkin-Elmer, USA). TECAN microplate reader SPARK (Tecan, Switzerland). Thermo Scientific ESCALAB 250Xi, monochrome Al Ka (hv = 1486.6 eV), power 150 W, 500 μm beam spot, the binding energy is calibrated at C1s 284.8 eV.

4. Evaluation of the peroxidase-like activity of dex-$MoSe_2$ NS in neutral media

To verify the peroxidase-like activity of dex-$MoSe_2$ NS under neutral conditions, 10 μL of dex-modified $MoSe_2$, 100 μL of 2.4 mol L^{-1} H_2O_2, and 80 μL of 5 mmol L^{-1} TMB (prepared with deionized water) were mixed in 210 μL tris-HCl (10 mmol L^{-1}, pH 7.4). The color changes upon time were immediately monitored by UV-Vis measurements. To uncover the peroxidase-like catalytic path of dex-$MoSe_2$ NS, hydroxyl radical capture experiments were performed. To highlight the robustness of dex-$MoSe_2$ NS, the nanozyme was first incubated in different pH values or different concentrations of TMB and different concentrations of H_2O_2 solution for 30 minutes, and then its activity was measured at room temperature.

5. Colorimetric detection of serum glucose

Glucose detection was carried out as follows: 20 μL GOx (10 mg mL^{-1}) was mixed with 180 μL glucose solution with different concentrations and the mixture was incubated at 37 ℃ for 30 min to produce H_2O_2. Then, 175 μL Tris-HCl buffer solution (10 mmol L^{-1}, pH 7.4), 25 μL dex-$MoSe_2$ NS and 100 μL TMB (5.0 mmol L^{-1}) were added to the mixed solution and further incubated at normal temperature for 30 min. The colorimetric signals (at 652 nm) were recorded using a TECAN microplate reader.

This analytical method was applied for the glucose detection in human serum samples which were provided by Guilin Integrated Traditional Chinese and Western Medicine Hospital in Guangxi Province. Before the detection of glucose in serum samples, the proteins in serum samples were removed by precipitation. 50 μL $Ba(OH)_2$

(0.080 mol L^{-1}) and 40 μL $ZnSO_4$ (0.076 mol L^{-1}) were added to 60 μL serum samples.[3] Then, H_2O was added until the total volume was 840 μL. The mixture was centrifuged at 3880 rpm for 10 min. A standard addition method was used for the detection of serum glucose. The other detection procedure was the same as that of glucose detection.

Supplementary Figures and Table

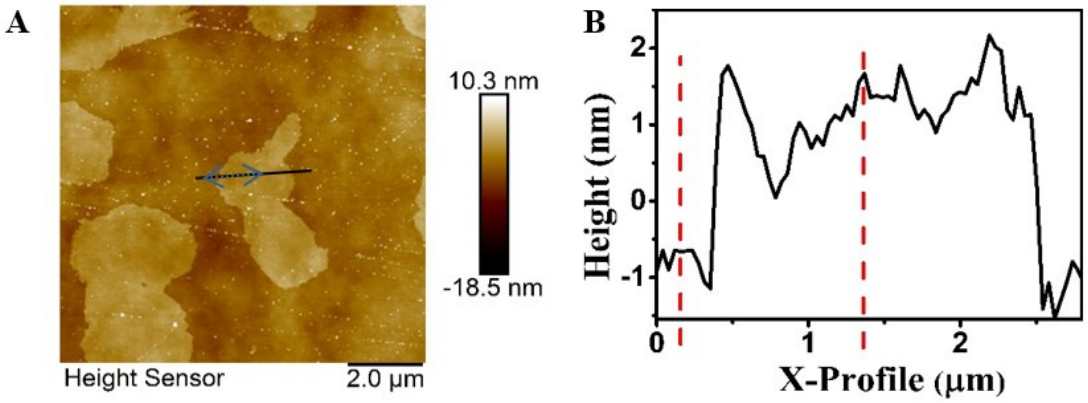


Fig. S1. Atomic force microscopy (AFM) images and height profiles of dex-$MoSe_2$. (A) AFM images of dex-$MoSe_2$ (scale bar, 2 μm). (B) Height profile of dex-$MoSe_2$.

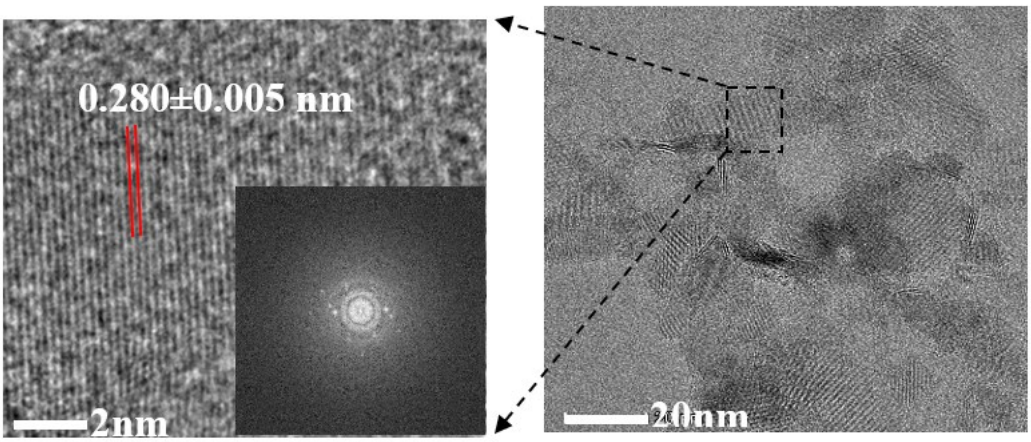


Fig. S2. TEM images and SAED pattern of dex-$MoSe_2$.

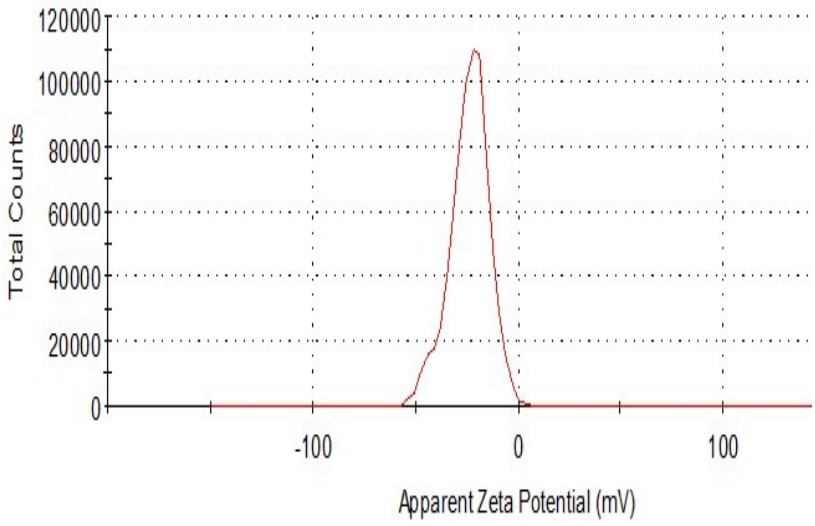


Fig. S3. Zeta potential distribution of dex-$MoSe_2$ NS (43.6 mg L^{-1}) in water.

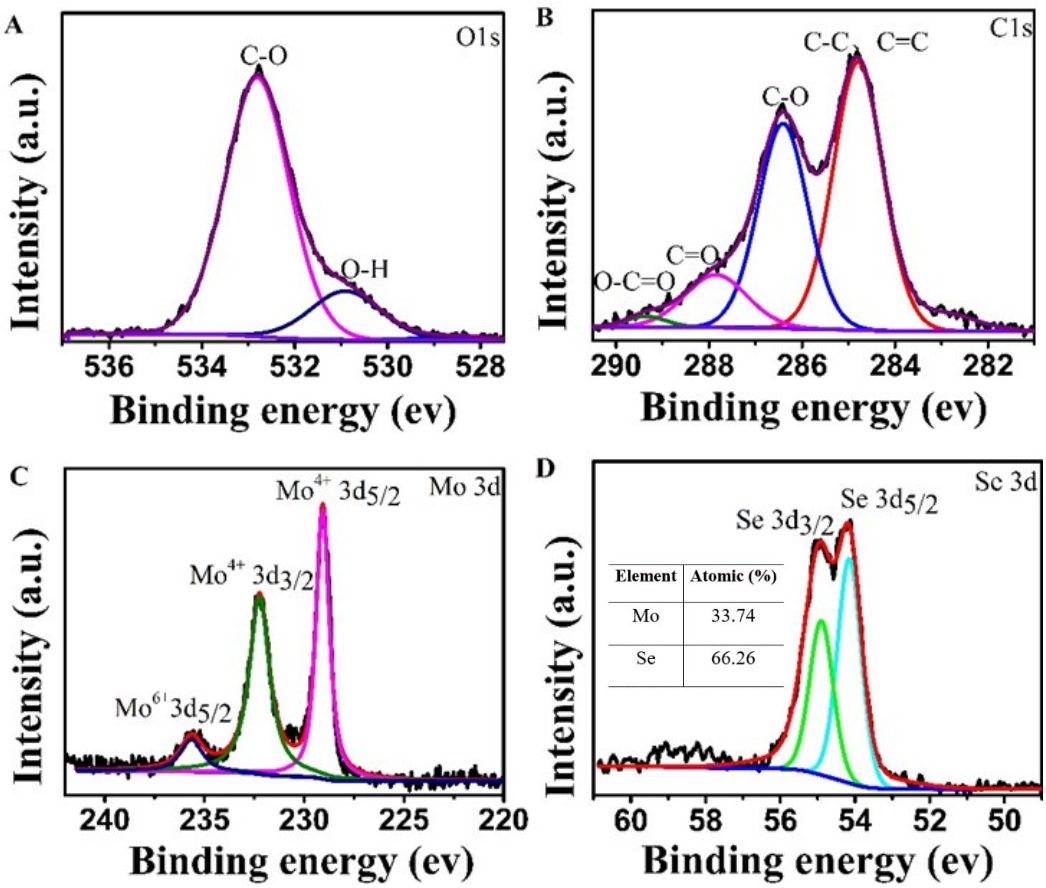


Fig. S4. XPS spectra of dex-$MoSe_2$ NS: (A) O1s; (B) C1s; (C) Mo 3d; (D) Se 3d. Inset of Fig. S4D is the atomic ratio of Mo to Se.

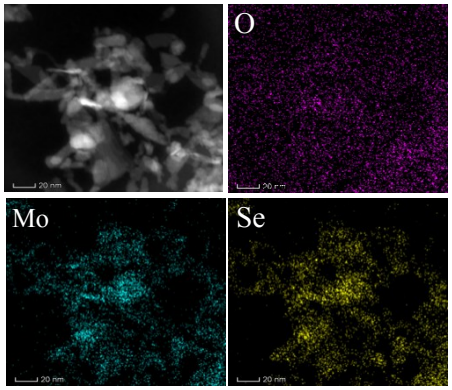


Fig. S5. EDS mapping of dex-$MoSe_2$ NS.

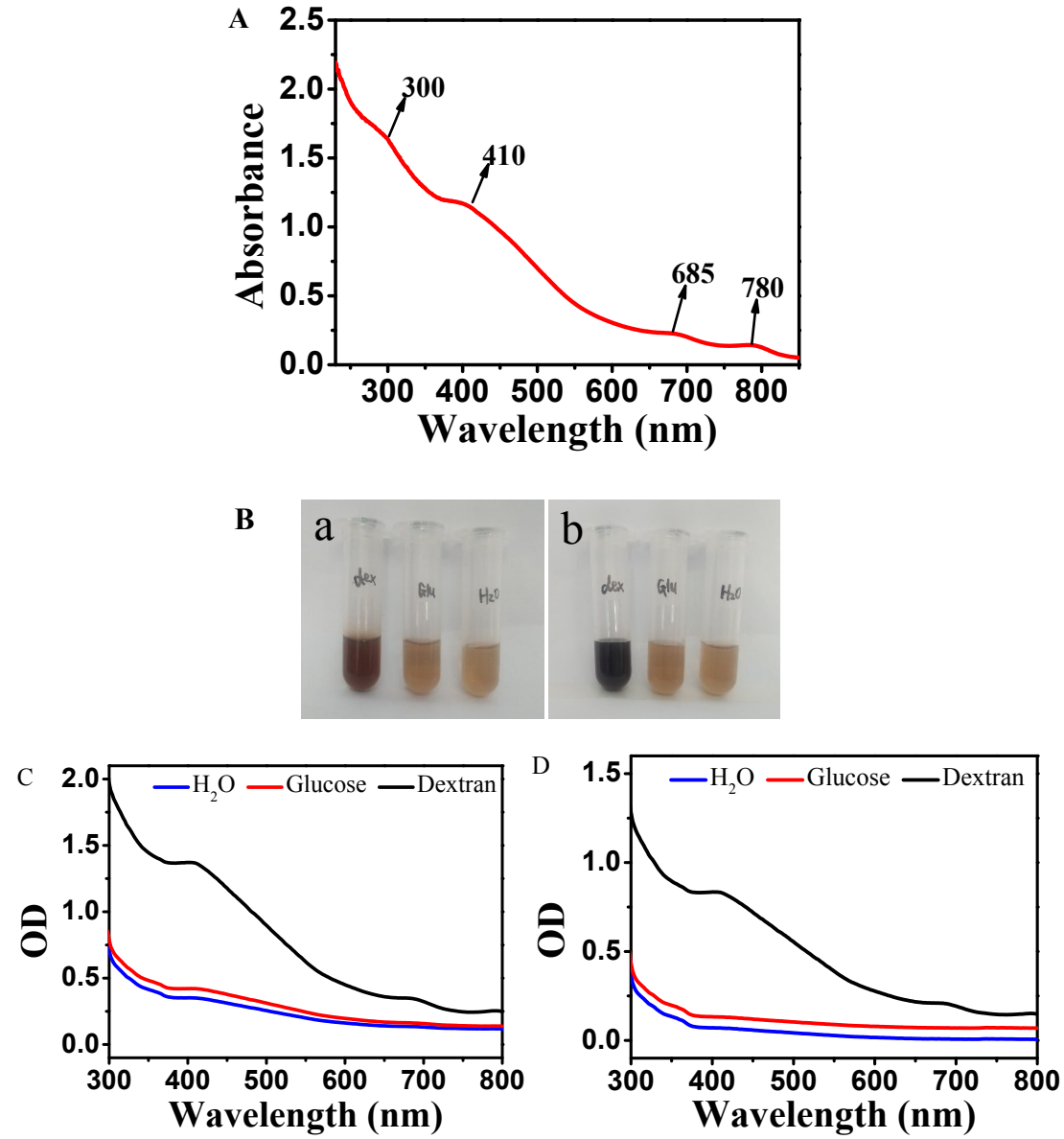
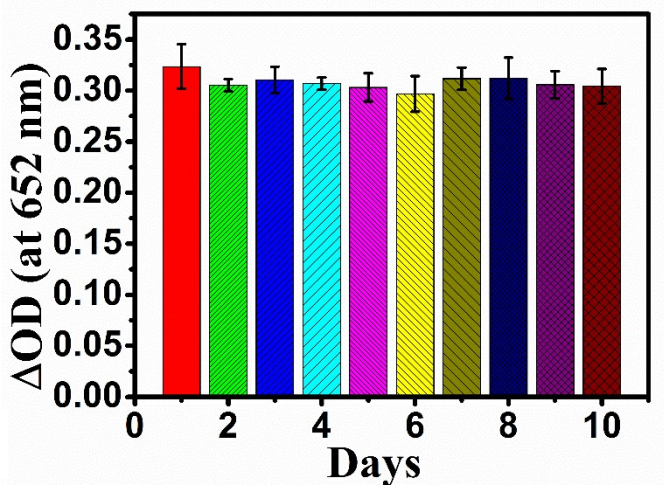


Fig. S6. (A) UV-Vis spectrum of dex-$MoSe_2$ NS solution (28.7 mg L^{-1}); (B) Photographs of the $MoSe_2$ NS solution after different ultrasonic times with dextran, glucose, and H_2O, respectively, (a) one hour, (b) two hours. (C) UV-Vis spectra of dex-$MoSe_2$ NS solution after ultrasound exfoliation for one hour. (D) UV-Vis spectra of dex-$MoSe_2$ NS solution (6 times dilution at the same ratio before the collection) after ultrasound exfoliation for two hours. Every one hour, the resulting solutions were centrifuged at 3025 (×g) for 10 min to discard unexfoliated $MoSe_2$ bulk materials. The supernatants were collected and compared.

A



B

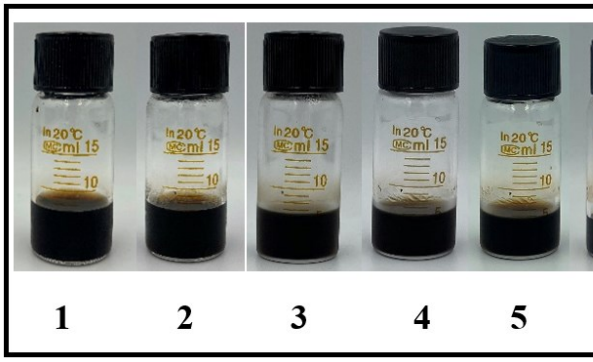


Fig. S7. The stability of the dex-$MoSe_2$ nanosheets solution in ten days. (A) The catalytic activity and (B) the appearance of $MoSe_2$ nanosheets solution in ten days. 200 μL of every $MoSe_2$ nanosheets solution in Fig. S7B was used for one test of the catalytic activity in Fig. S7A.

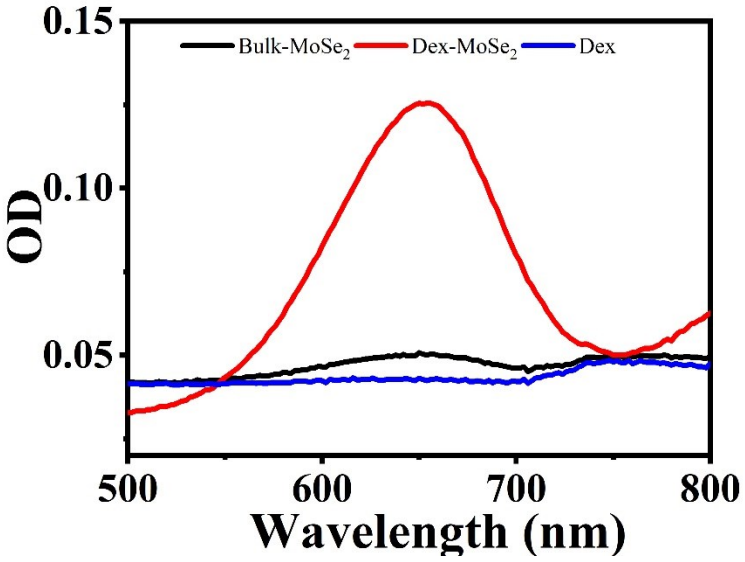


Fig. S8. The effect of ultrasound processing on the catalytic activity of $MoSe_2$. The mixture of bulk-$MoSe_2$ and dextran without ultrasound processing (Bulk-$MoSe_2$, Black line); The mixture of bulk-$MoSe_2$ and dextran with ultrasound processing (Dex-$MoSe_2$, Red line); Dextran (Blue line).

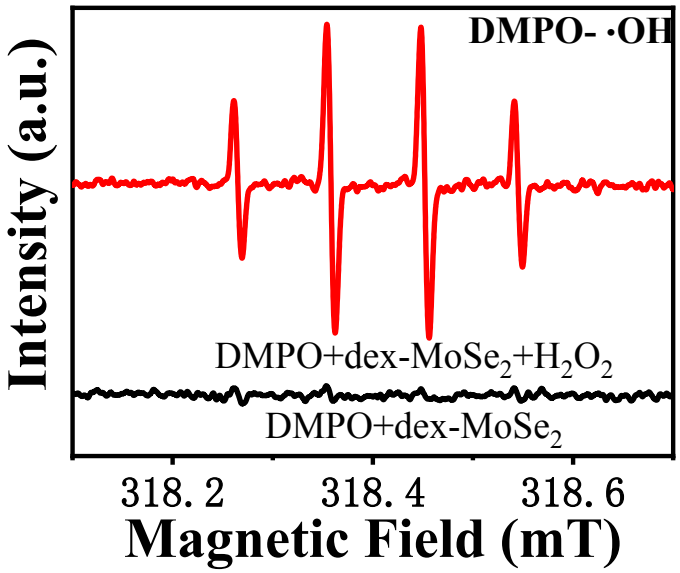


Fig. S9. Electron spin resonance (ESR) of dex-$MoSe_2$ NS for $^{\bullet}OH$.

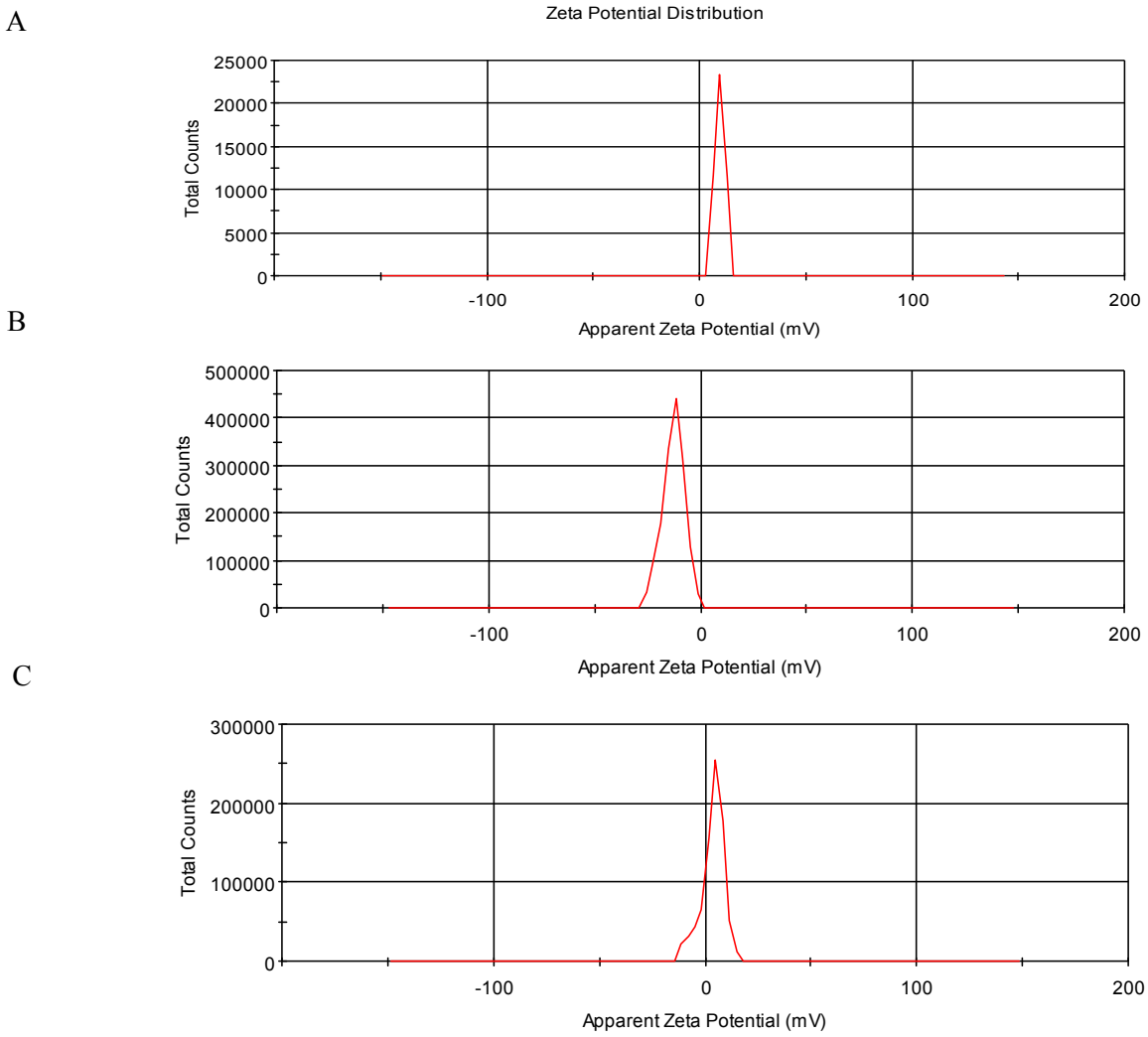


Fig. S10. Zeta potential changes of different solutions. (A) The Zeta potential of TMB (2 mmol L^{-1}) in water; (B) The Zeta potential of dex-$MoSe_2$ (9.60 mg L^{-1}, calculated by ICP-MS) in water; (C) The Zeta potential of the mixture with 500 μL dex-$MoSe_2$ (9.60 mg L^{-1}) and 100 μL TMB (2 mmol L^{-1})

Table S1. Reliability of our assay in sensing glucose in clinical serum samples.

Samples	Glucose meter method (mmol L^{-1})	added (mmol L^{-1})	Total found[n] (Mean ± SD) (mmol L^{-1})	Recovery (%)	RSD (%)
1[#]	3.80	0.247	0.262±0.007	106.1	2.97
2[#]	4.37	0.248	0.259±0.011	104.4	4.30
3[#]	5.51	0.250	0.252±0.019	101.6	7.53
4[#]	7.01	0.253	0.246±0.003	97.2	1.16
5[#]	6.81	0.252	0.250±0.014	100.4	5.77

n=3, Average from triplicate measurements.

References

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2. L. Huang, Q. Zhu, J. Zhu, L. Luo, S. Pu, W. Zhang, W. Zhu, J. Sun and J. Wang, *Inorganic Chemistry*, 2019, **58**, 1638-1646.
3. T. Lin, L. Zhong, L. Guo, F. Fu and G. Chen, *Nanoscale*, 2014, **6**, 11856-11862.