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Supporting information for

Preparation of enzyme functionalized carbon nanotubes and their application in glucose and Fe^{2+}detection through "turn on" and "turn off" approaches

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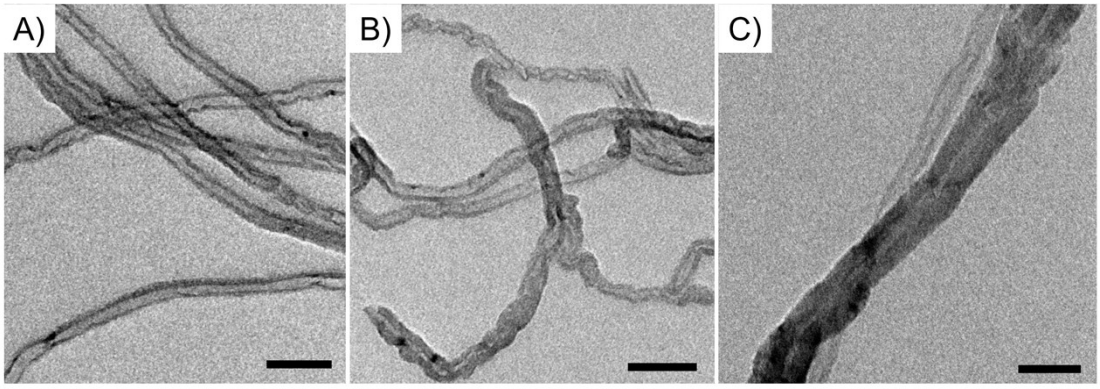

Fig. S1 The TEM measurement of CNTs. The images of CNTs before conjugated with enzymes (A), the images of CNT after conjugated with HRP (CNT-HRP) (B) and conjugated with HRP and GOD (CNT–HRP–GOD) (C), respectively. The scale bars represent 50 nm.

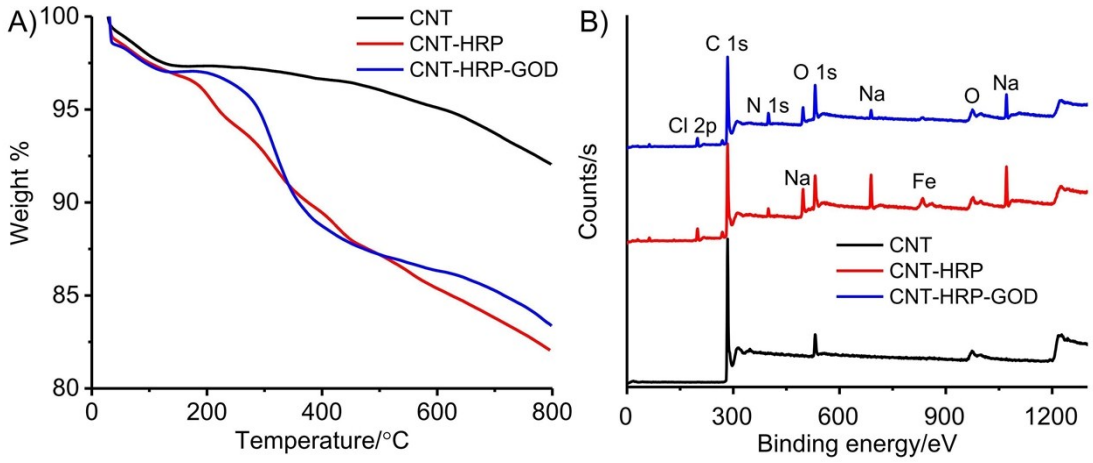

Fig. S2 The TGA and XPS measurements of CNTs. The TGA (A) and XPS (B) spectra of CNTs in the absence of enzymes (CNT) and after conjugated with GOD and/or HRP, respectively.

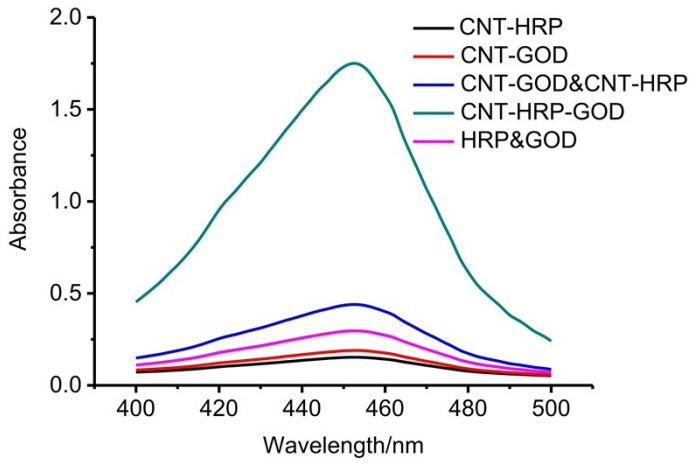

Fig. S3 The glucose detection mechanism validation experiment. The absorption spectra of solutions in the presence of CNT-HRP, CNT-GOD, CNT-GOD and CNT-HRP, CNT-HRP-GOD, HRP and GOD, respectively. The concentration of glucose is 100 μM.

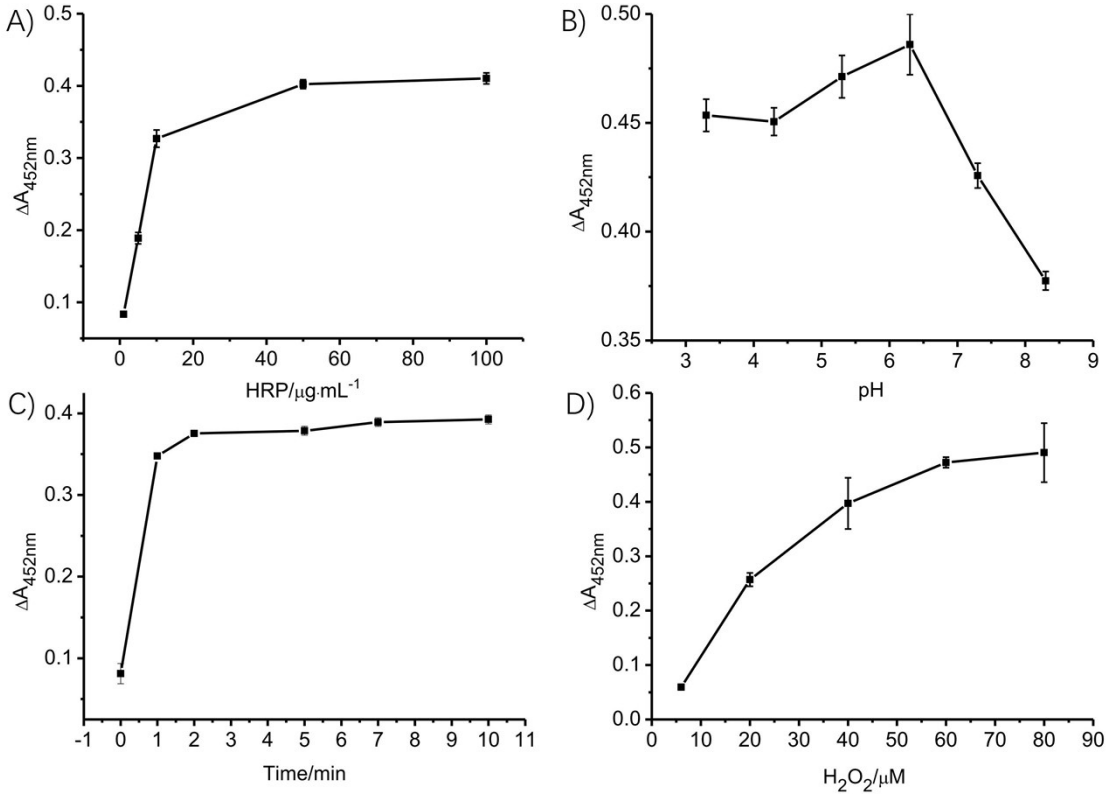

Fig. S4 The optimization of the experimental conditions for the detection of Fe^{2+}. The ΔA_{452nm} of solutions in the absence or presence of 20 μM Fe^{2+} as a function of the total concentrations of CNT-HRP (A). The ΔA_{452nm} changes of solutions in the absence or presence of 20 μM Fe^{2+} as a function of the pH. The ΔA_{452nm} changes of solutions in the absence or presence of 20 μM Fe^{2+} as a function of the reaction time between Fe^{2+} and H_2O_2 (C). The ΔA_{452nm} changes of solutions in the absence or presence of 20 μM Fe^{2+} as a function of the concentrations of H_2O_2 (D). The error bars represent the relative standard deviation of three experimental results.

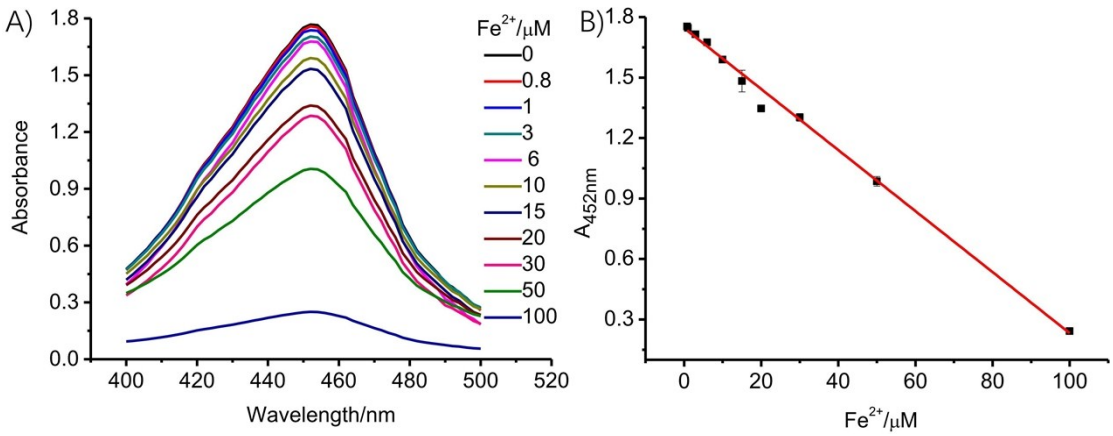

Fig. S5 The Fe^{2+} detection using CNT-HRP materials. The absorption spectra of the solutions in the presence of different amounts of Fe^{2+} (A). The corresponding A_{452nm} changes of the solutions as a function of the concentrations of Fe^{2+} from 0 to 100 μM (B). The error bars represent the relative standard deviation of three experimental results.

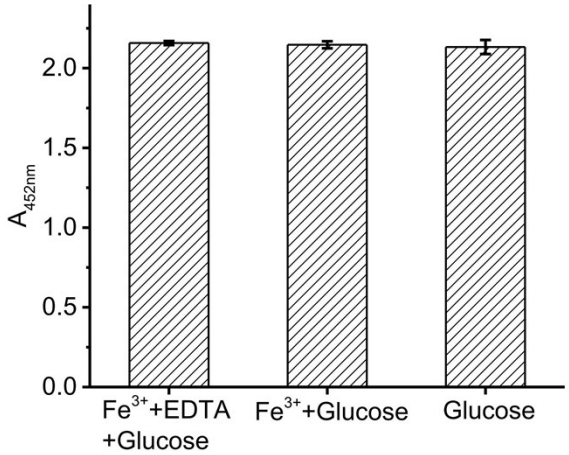

Fig. S6 The interference of Fe^{3+} on the detection of glucose. The A_{452nm} of solutions in the presence of glucose, glucose and Fe^{3+}, glucose and Fe^{3+} in the presence of EDTA, respectively. The concentrations of Fe^{3+}, glucose and EDTA are 20 μM, 100 μM and 500 μM. respectively. The error bars represent the relative standard deviation of three experimental results.

There are not dramatically differences between these samples. This may because that the HRP had much higher catalytic ability compared with Fe^{3+}, the influence of Fe^{3+} on the system can be ignored if there are not too much Fe^{3+}, therefore, in this system, the signals are not changed a lot no matter there is EDTA or not.

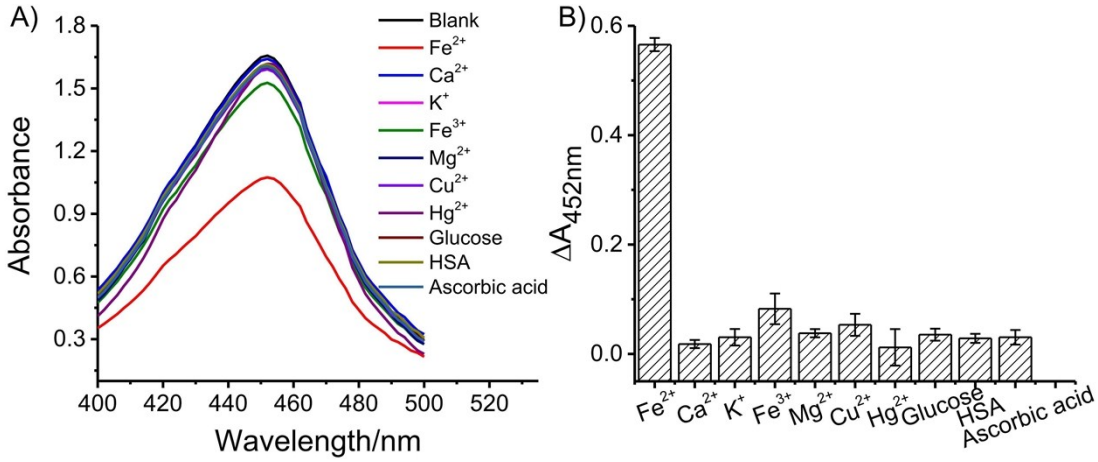

Fig. S7 The selectivity experiment. The absorption spectra of the solutions in the absence of metallic ions (blank) and in the presence of Fe^{2+}, Ca^{2+}, K^{+}, Fe^{3+}, Mg^{2+}, Cu^{2+}, Hg^{2+}, glucose, HSA and ascorbic acid, respectively (A). The ΔA_{452nm} of solutions in the presence of Fe^{2+}, Ca^{2+}, K^{+}, Fe^{3+}, Mg^{2+}, Cu^{2+}, Hg^{2+}, glucose, HSA and ascorbic acid, respectively (from left to right). The concentration of each compound is 50 μM. The error bars represent the relative standard deviation of three experimental results.

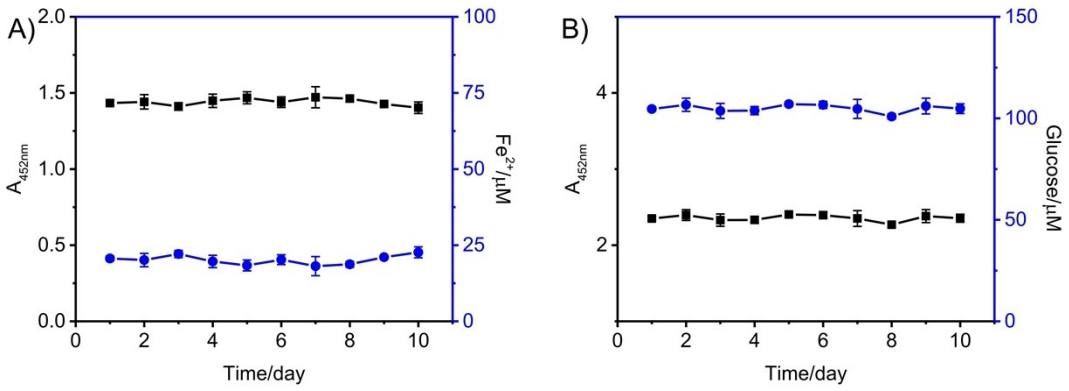

Figure S8. The stability experiment. The A_{452nm} of solutions in the presence of 20 μM Fe^{2+} (left) and the calculated concentrations of Fe^{2+} (right) in different days (A). The A_{452nm} of solutions in the presence of 100 μM glucose (left) and the calculated concentrations of glucose (right) in different days (B), respectively. The error bars represent the relative standard deviation of three experimental results.

Table S1. Comparison of our work with previous methods to detect glucose.

Analytical Method	Linear range	Limit of detection	References
Electrochemistry	2-40 μM	3 μM	J. Phys. Chem. C, 2010, 11, 12920-12924
Electrochemistry	6 μM-2.2 mM	6 μM	Biosens. Bioelectron., 2009, 25, 889-895
Colorimetric assay	1-100 μM	1 μM	Anal. Chim. Acta, 2013, 796, 92-100.
Colorimetric assay	—	20 μM	Nano Res. 2011, 4, 908-920.
Colorimetric assay	5-800 μM	0.553 μM	Sens. Actuators, B, 2017, 245, 221-229
Electrochemistry	80 μM-12 mM	20 μM	Biosens. Bioelectron., 2009, 25, 901-905
Electrochemistry	2-12 mM	25 μM	Biosens. Bioelectron., 2017, 92, 81-86.
Fluorescent assay	80-420 μM	11 μM	Tetrahedron, 2012, 68, 8899-8904
Fluorescent assay	2-100 μM	0.42 μM	Anal. Chem., 2014, 86, 12348-12354
Colorimetric assay	1-100 μM	0.3 μM	This work

Table S2. Comparison of our work with previous methods to detect Fe^{2+}.

Analytical Method	Linear range	Limit detection	References
Colorimetric assay	6.5-33 μM	6 μM	Nanochem. Res. 2016, 1, 214-221
Fluorescent assay	0.5-2.0 μM	60 nM	J. Nanopart. Res., 2017, 19, 84
Fluorescent assay	2.5-37.5 μM	—	RSC Adv., 2013, 3, 111-116
Fluorescent assay	0.1-7 μM	12 nM	Chem. Eur. J. 2011, 17, 10520-10523
Electrochemistry	5-100 μM	0.6 μM	Electrochim. Acta, 2015, 50, 3191-3199
Colorimetric assay	0.8-100 μM	0.22μM	This work

83 **Table S3.** Results of the detection of Fe^{2+} in human serum albumin (HSA) samples

84 using the CNT-HRP materials based colorimetric method. The concentration of HSA

85 is 100 μM.

Sample No.	Added (μM)	Mean found ± SD (μM)	Recovery (%)	RSD (%)
HSA1	10	10.3±0.5	103	0.45
HSA2	20	19.7±1.4	98.5	1.00
HSA3	30	30.7±2.0	102	1.66

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