Electronic supplementary information

An enzymatic reaction mediated glucose sensor activated by MnO_2 nanosheets acting as oxidant and catalyst

Guanwen Yan [a], Yuan Zhang [b], Weihua Di [a*]

[a] *State Key Laboratory on Integrated Optoelectronics, College of Electronic Science and Engineering, Jilin University, Changchun 130012, People's Republic of China.*

[b] *College of Instrumentation & Electrical Engineering, Jilin University, Changchun 130012, PR China*

E-mail: whdi@jlu.edu.cn (W. Di); Tel: 86-431-85168240-8325, Fax: 86-431-85168240-8325

[*] Corresponding authors: 2699 Qianjin Street, Changchun 130012, China. E-mail: whdi@jlu.edu.cn (W. Di), Tel: 86-431-85168240-8325, Fax: 86-431-85168240-8325

Fig. S1. Upon the addition of H_2O_2, the MnO_2 solution with deep brown color becomes a colorless one gradually, accompanying the generation of bubbles.

The generated bubbles in the reaction of MnO_2 with H_2O_2 was verified with $[(Ru(dpp)_3)]Cl_2$, an O_2 sensing probe that the fluorescence can be strongly quenched by O_2. In the experiment, a given volume of MnO_2 solution was added into a 1 cm glass cuvette containing 1 mL of $[(Ru(dpp)_3)]Cl_2$ solution, and mixed well. The fluorescence intensity of $[(Ru(dpp)_3)]Cl_2$ at 625 nm as a function of time was recorded upon adding 50 μL of H_2O_2 solution (100 μM). The measurement was conducted with a fluorescence spectrophotometer (Hitachi F-4500, Japan) equipped with a xenon lamp. The excitation wavelength was 380 nm. As shown in Fig. S2, the fluorescence intensity of $[(Ru(dpp)_3)]Cl_2$ was reduced gradually with time, indicating that the fluorescence of $[(Ru(dpp)_3)]Cl_2$ was quenched by O_2 generated through the reaction between MnO_2 and H_2O_2.

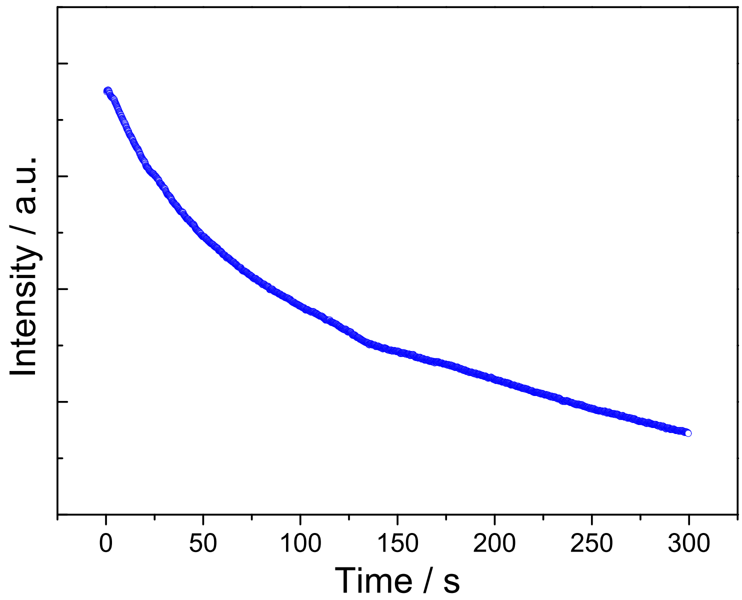

Fig. S2. The fluorescence intensity of $[(Ru(dpp)_3)]Cl_2$ at 625 nm as a function of time upon addition of H_2O_2 into MnO_2 solution.

Moreover, it is found that the reactivity of MnO_2 with H_2O_2 depended strongly on the solution pH values. To demonstrate the effect of solution pH on the reactivity of MnO_2 with H_2O_2, the experiments were conducted as below. The equivalent quantities of MnO_2 were dispersed in 5 mL citrate buffer with different pH values ranging from 6.5 to 4.8 and MiliQ water with pH 7.4, respectively. Then, 50 μL of H_2O_2 solution (100 μM) was added and reacted at room temperature for 3 min. The supernatant was immediately moved to a quartz cuvette for UV-vis absorption measurement. The absorbance of MnO_2 solution with the addition of H_2O_2 decreases remarkably with the decrease of pH value (Fig. S3). For a parallel comparison, we also measured the absorption spectra of MnO_2 solution under different pH conditions, but without the addition of H_2O_2. We can see that the absorbance of MnO_2 solution without the addition of H_2O_2 decreases slightly with the decrease of pH values ranging from 7.4 to 4.8. The above results indicate that the acidic reaction condition with a low pH value benefits the reaction of MnO_2 nanosheets with H_2O_2, and that the presence of H_2O_2 accelerates the degradation of MnO_2 in acidic solution.

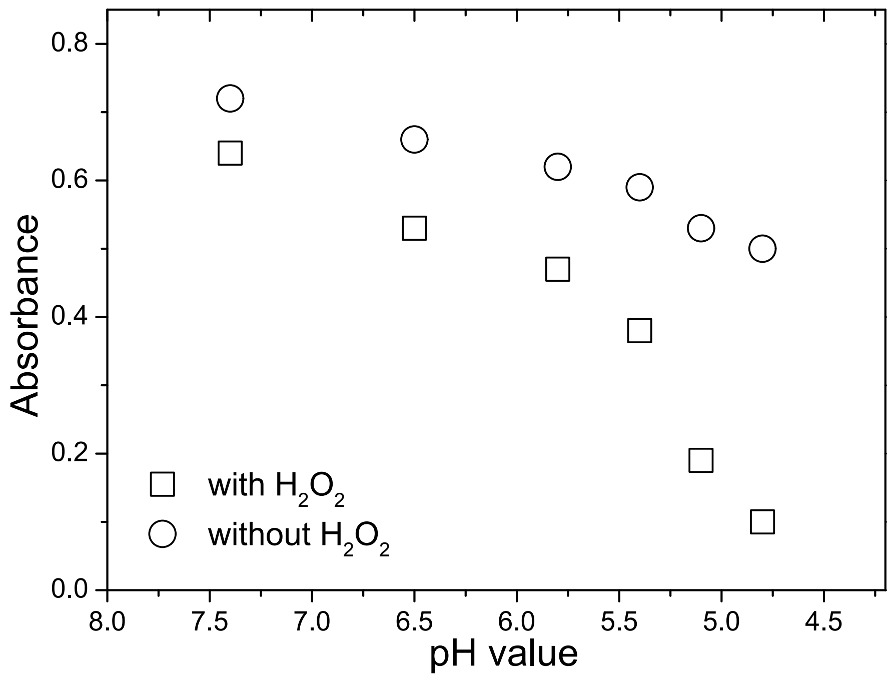

Fig. S3. A comparison of the MnO_2 solution absorbance with and without the addition of H_2O_2 under the reaction conditions with different pH values. The reaction time was fixed at 3 min.

Indeed, the gluconic acid generated in the glucose oxidation can modify pH value of the resulting solution well. Fig. S4 shows the dependence of solution pH on glucose concentration added. With the increase of glucose concentration up to 160 μM, the pH value decreases from ~6.5 to ~4.8, making the solution acidic. It is well known that the quantity of the products is proportional to that of reactants. With the increase of glucose concentration, the amount of gluconic acid increases, resulting in the decrease of pH value continuously.

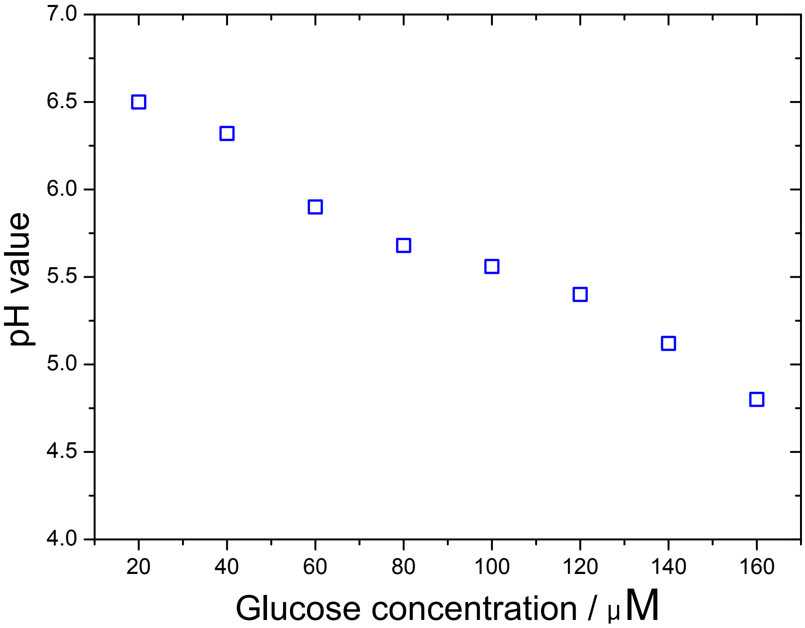

Fig. S4. The resulting pH values of glucose/GOx reaction system as a function of glucose concentration with a fixed concentration of GOx.