Electronic supplementary information:

Signal amplification performance of the proposed immunosensor

In this strategy, the amplified electrochemical signal was achieved by the corporate electrocatalysis of the ultrafine Pd NPs and HRP toward H_2O_2 reduction. The ultrafine Pd NPs supported on flower-like SnO_2 showed intrinsic peroxidase-like electrocatalytic activity, resulting in the enhancement of electrochemical signal and improvement of sensitivity of immunosensor. On one hand, to prove the effect of Pd NPs on the electrochemical signal, two different sensing platform (Au/Pd@flower-like SnO_2 and Au/flower-like SnO_2) were employed respectively. **Fig. S2A** shows the DPV signals of different modified electrodes in 0.1 M pH 7.0 PBS containing 2.0 mM H_2O_2 under optimal experimental conditions. For the Au/Pd@flower-like SnO_2 modified electrode sensing platform, a much stronger electrochemical signal was obtained. In contrast, a poor electrochemical signal was observed at the Au/flower-like SnO_2 modified electrode platform. Obviously, the participation of Pd NPs enhanced the electrochemical signal, which paved the way for the fabrication of sensitive immunosensor. On the other hand, to verify the effect of HRP on the signal, two different Ab2 bioconjugates (Au@CMK-3-MB-Ab2-HRP and Au@CMK-3-MB-Ab2) were employed respectively. **Fig. S2B** shows the DPV signals of different modified electrodes in 0.1 M pH 7.0 PBS containing 2.0 mM H_2O_2 under optimal conditions. For the modified electrode with Au@CMK-3-MB-Ab2-HRP bioconjugate, a much higher electrochemical signal was received. On the contrary, a poor

electrochemical signal was observed at the modified electrode with Au@CMK-3-MB-Ab2 bioconjugate. Thus, the employment of HRP was also very important for the signal amplification.

Selection of optimal experiment conditions:

The goal of this study was to control the optimal experimental conditions to obtain the excellent performance of the proposed immunosensors for PSA detection. In the sandwichtype immunoassays, incubation time for the antigen-antibody interaction and pH of assay solution influenced the sensitivity of the developed immunoassay. Certainly, the optimum incubation temperature of antigen-antibody interaction should be close to the normal temperature of human body (37 ^{o}C). However, considering the practical feasibility in real life, all the experiments in this study were carried out at room temperature.

The pH of the detection solution might influence not only the electrochemical performance of the immunosensor, but also the activity of HRP and immobilized immunoproteins. As shown in **Fig. S3A**, the current was increased with the increase of pH value from pH 6.0 to 7.0 and then decreased. The decrease of current response at strong acidic and alkaline solution might be on account of the decrease in bioactivity of the enzyme. Maximum current is obtained at pH 7.0, which is near the physiological condition and is chosen for subsequent experiments.

The incubation time is another important parameter for capturing PSA and Ab2 bioconjugate. The proposed immunosensors were incubated with 10 ng ml^{-1} PSA

with different incubation time. As shown in **Fig. S3B**, the electrochemical response increased with the increase of incubation time of PSA, and tended to level off after 60 min. When changed Ab2 bioconjugate to join in time, it can be seen from **Fig. S3C** that the electrochemical response also tended to level off at the time of 60 min. Therefore, 60 min was chosen as the incubation time for the determination of PSA in the following experiments.

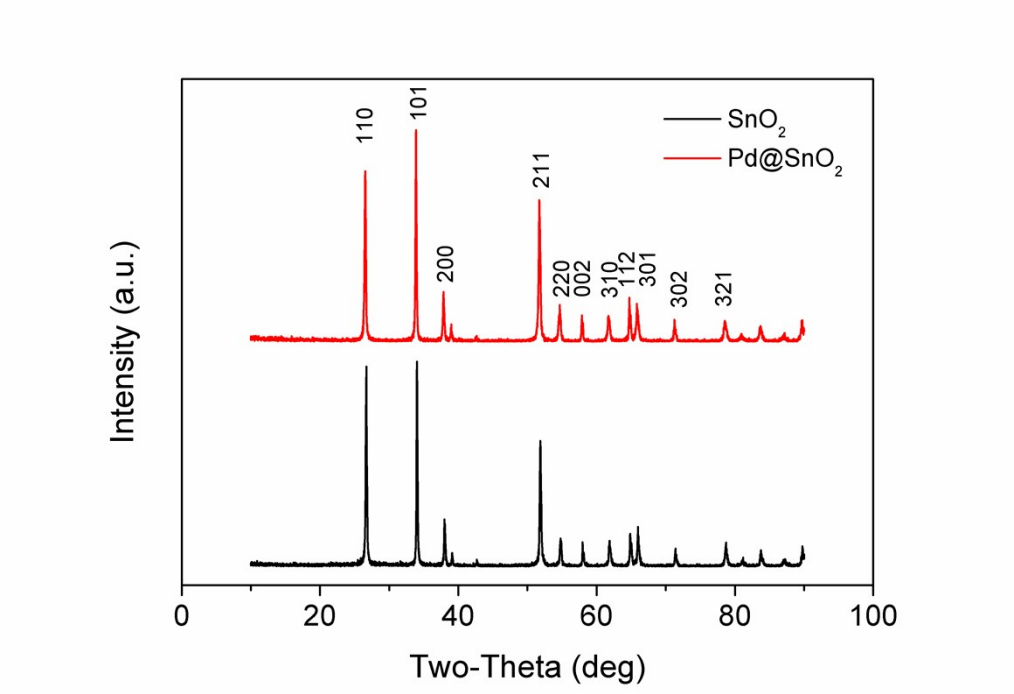

Fig. S1 XRD patterns of SnO_2 and Pd@SnO_2 samples.

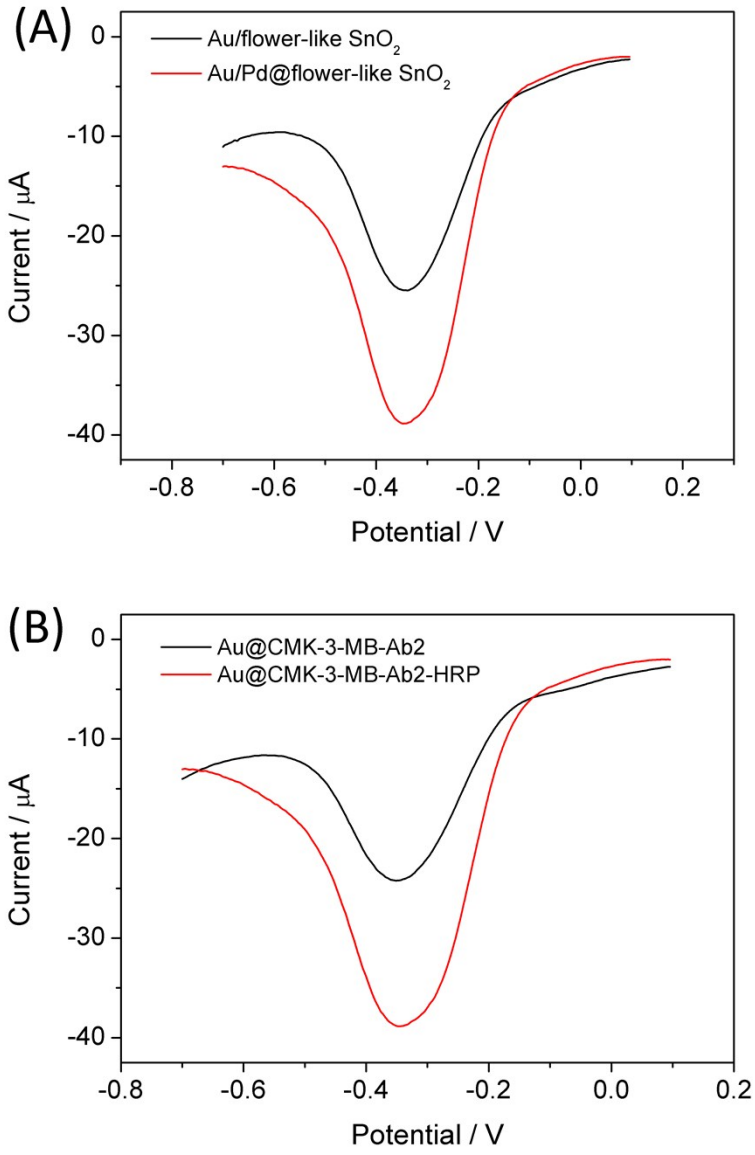

Fig. S2 DPV responses of the immunosensor for different sensing platform (Au/Pd@flower-like SnO_2 and Au/flower-like SnO_2) **(A)** and for different Ab2 bioconjugate (Au@CMK-3-MB-Ab2-HRP and Au@CMK-3-MB-Ab2) **(B)** in 0.1 M pH 7.0 PBS containing 2.0 mM H_2O_2.

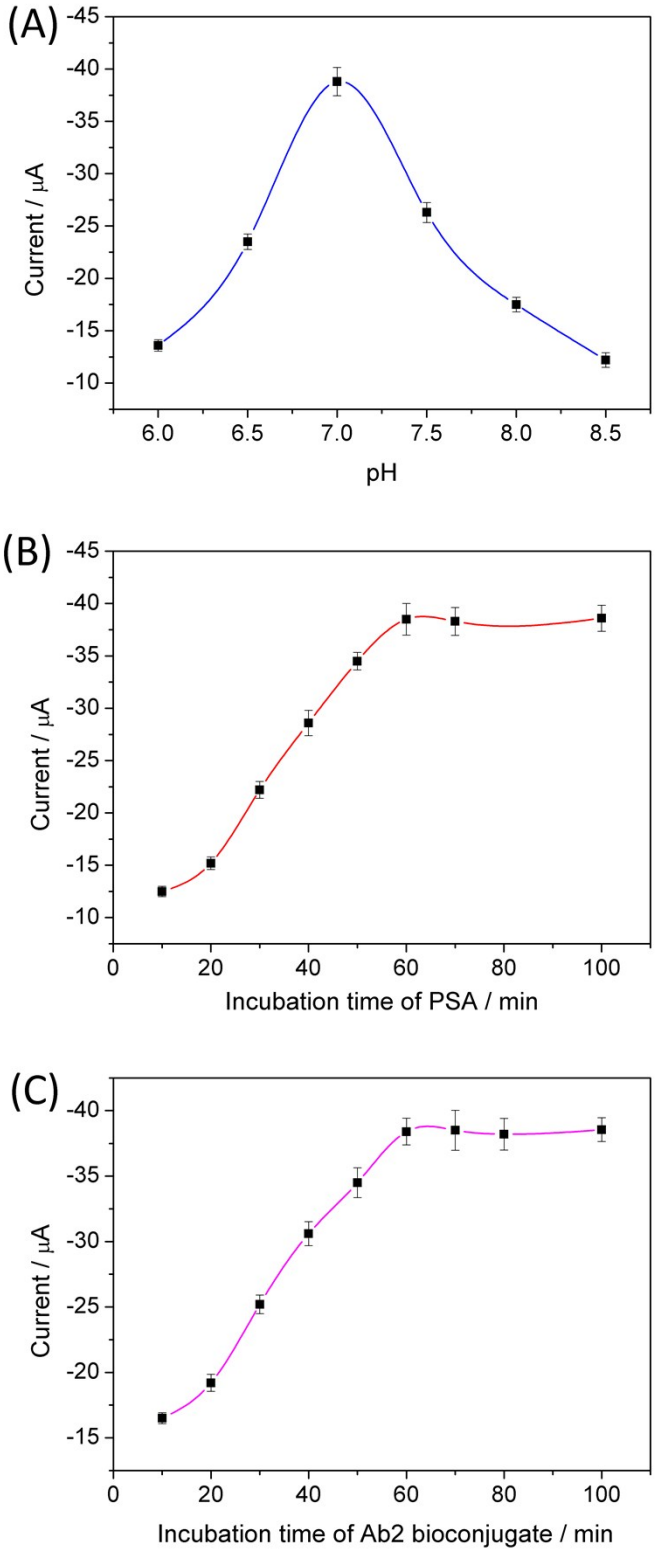

Fig. S3 (A) The effect of pH of detection PBS. **(B)** Incubation time for capturing PSA on the electrochemical response. **(C)** Incubation time for recognizing Ab2 bioconjugate on the current response.