---Electronic Supplementary Information---

Functional Glycoprotein Competitive Recognition and Signal Amplification Strategy for Carbohydrate-Protein Interaction Profiling and Cell Surface Carbohydrate Expression Evaluation

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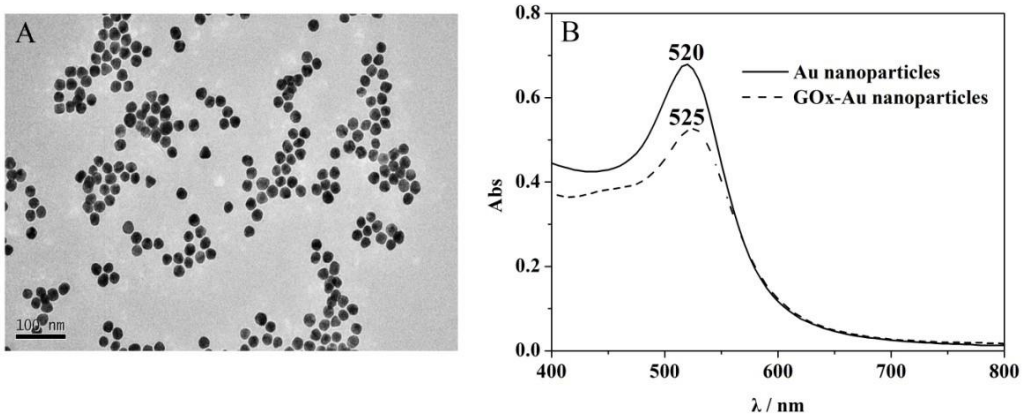

Fig. S1 (A) TEM image of GOx@Au nanoparticles. (B) UV-vis spectra of Au nanoparticles and GOx@Au nanoparticles.

Binding assay of mannose and mannan to immobilized Con A

In the binding experiments between Con A and mannose or mannan, the Con A/Au electrode, which had blocked with BSA already, was immersed into a 100 μL PBS solution containing 0.48 mM Ca^{2+}, 0.48 mM Mn^{2+}, 3.4 nM GOx@Au nanoparticles and mannose (or mannan) at a certain concentration for 2 h. Then the electrode was washed with PBS and subjected to the ECL detection.

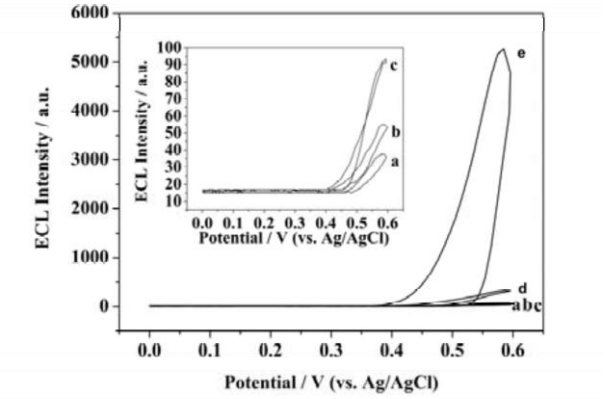

Fig. S2 ECL-potential curves at: GOx@Au/BSA/GE (a), Au nanoparticles/BSA/Con A/GE (b), Bare Electrode (c) and mannan competed GOx@Au/BSA/Con A/GE (d) in a 0.1 M PBS (pH 7.86) solution containing 100 μM luminol with 0.1 M glucose. The concentration of mannan was 2.7×10^{-3} mg mL^{-1}. The inset shows the amplification of these curves from (a) to (c). Scan rate, 100 mVs^{-1}. The voltage of PMT was maintained at 600 V.

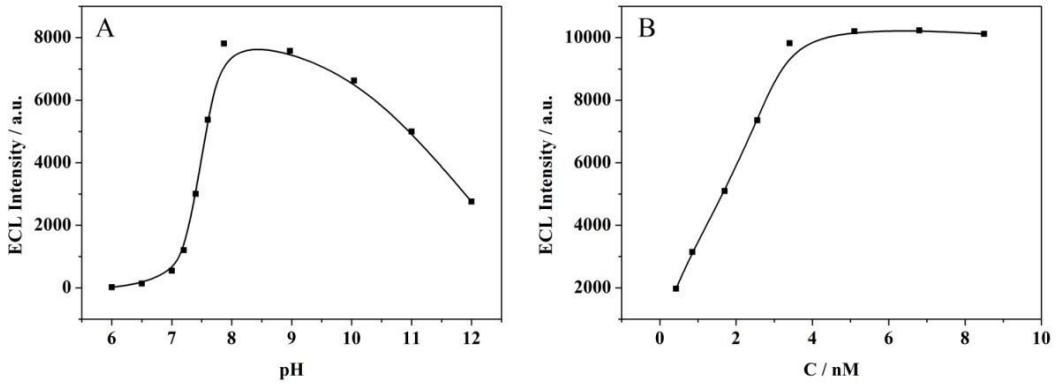

Fig. S3 (A) ECL profile of GOx@Au/Cells/BSA/Con A/GE in different pH of 0.1 M PBS containing 100 μM luminol and 0.1 M glucose. The concentration of K562 cell was 5×10^{5} cells mL^{-1}. (B) ECL profile of GOx@Au/BSA/Con A/GE in the presence of different concentration of GOx@Au nanoparticles solution.

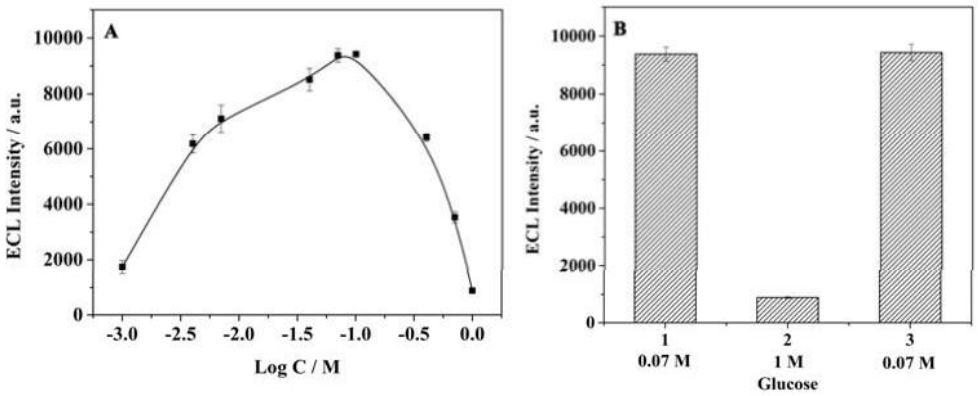

Fig. S4 (A) The ECL Intensity of GOx@Au/BSA/Con A/GE as a function of the concentration logarithm of glucose in the electrolyte. (B) ECL profile of GOx@Au/BSA/Con A/GE detected in different concentration of glucose successively.

With the increasing concentration of glucose, the ECL intensity increased and then reached a maximal value. However, if the concentration of glucose continued to increase, the ECL signal decreased rapidly, which was caused by the change of pH value on the electrode surface rather than glucose displacing the probes.[1] As we all know, GOx catalyzes glucose and then produces hydrogen peroxide and gluconic acid. When the concentration of glucose was too high, the gluconic acid can't be diffused into PBS solution immediately, which will lower the pH value on the electrode surface. As it was shown in Fig. S3A, pH had a great influence on the ECL intensity. Therefore, when the environmental glucose concentration was too high, the ECL intensity would decrease rapidly. This was proved by the data shown in Fig. 4B, in which the GOx@Au/BSA/Con A/GE was detected in 0.07 M, 1 M, 0.07 M glucose successively. If the probes was displaced by glucose when the electrode was detected in 1 M glucose, the ECL intensity of step 3 (detected in 0.07 M glucose again) would less than that of step 1 (detected in 0.07 M glucose). But the situation was opposite, which meant that the probes didn't be replaced and the decrease of ECL intensity in high glucose concentration was caused by the decrease of pH value on the electrode surface. Therefore, we choose 0.1 M as the glucose concentration in our experiments.

REFERENCES

1. D. Y. Jung, J. J. Magda and I. S. Han, *Macromolecules*, 2000, 33, 3332-3336.