Electronic Supplementary Information

Gold-platinum bimetallic nanocluster with enhanced peroxidase-like activity and its integrated agarose hydrogel-based sensing platform for colorimetric analysis of glucose level in serum

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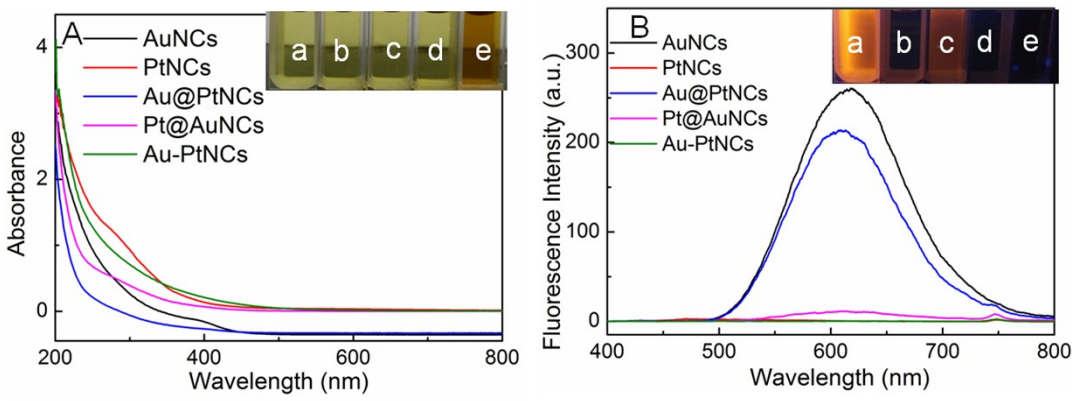

Fig. S1 (A) UV-vis absorption spectra and (B) fluorescence spectra of the prepared AuNCs, PtNCs, Au@PtNCs, Pt@AuNCs, and Au-PtNCs at Au/Pt molar ratio of 1:1. Insets: (a-e) the corresponding photographs of their aqueous solution under daylight and UV light, respectively.

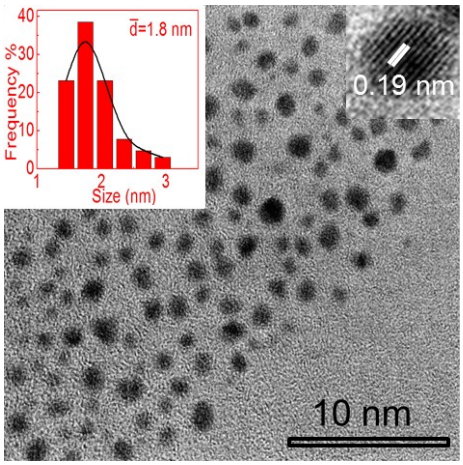

Fig. S2 TEM image of PtNCs. Left inset: size distribution histogram; right inset: HRTEM image.

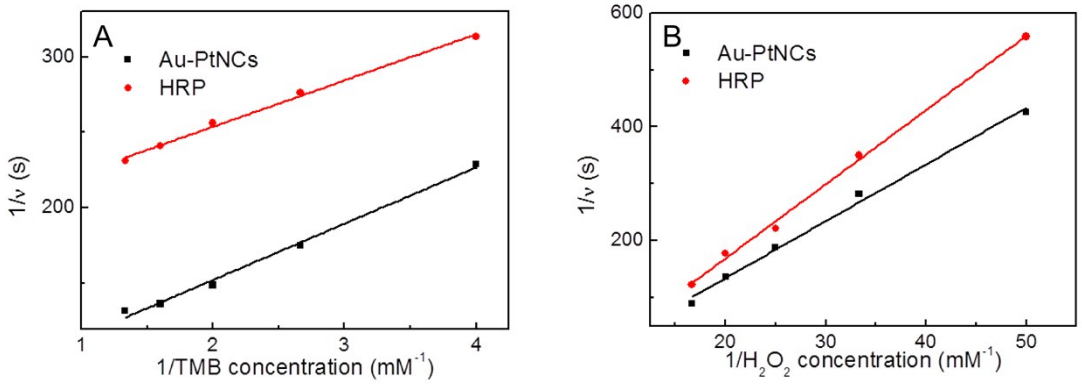

Fig. S3 Double reciprocal plots of activities of Au-PtNCs and HRP with the concentration of one substrate (A: H_2O_2 or B: TMB) fixed and the other varied.

Table S1 Comparison of the apparent Michaelis-Menten constant (K_m) and maximum reaction rate (V_{max}) between Au-PtNCs and HRP. All test conditions were at 45 °C in a pH 4.0 NaAc-HAc (0.2 M) buffer.

Catalyst	Substrate	K_m (mM)	V_{max} (10^{-8} M s^{-1})
Au-PtNCs	TMB	0.362	11.366
Au-PtNCs	H_2O_2	0.111	17.386
HRP	TMB	0.167	5.314
HRP	H_2O_2	0.522	61.444

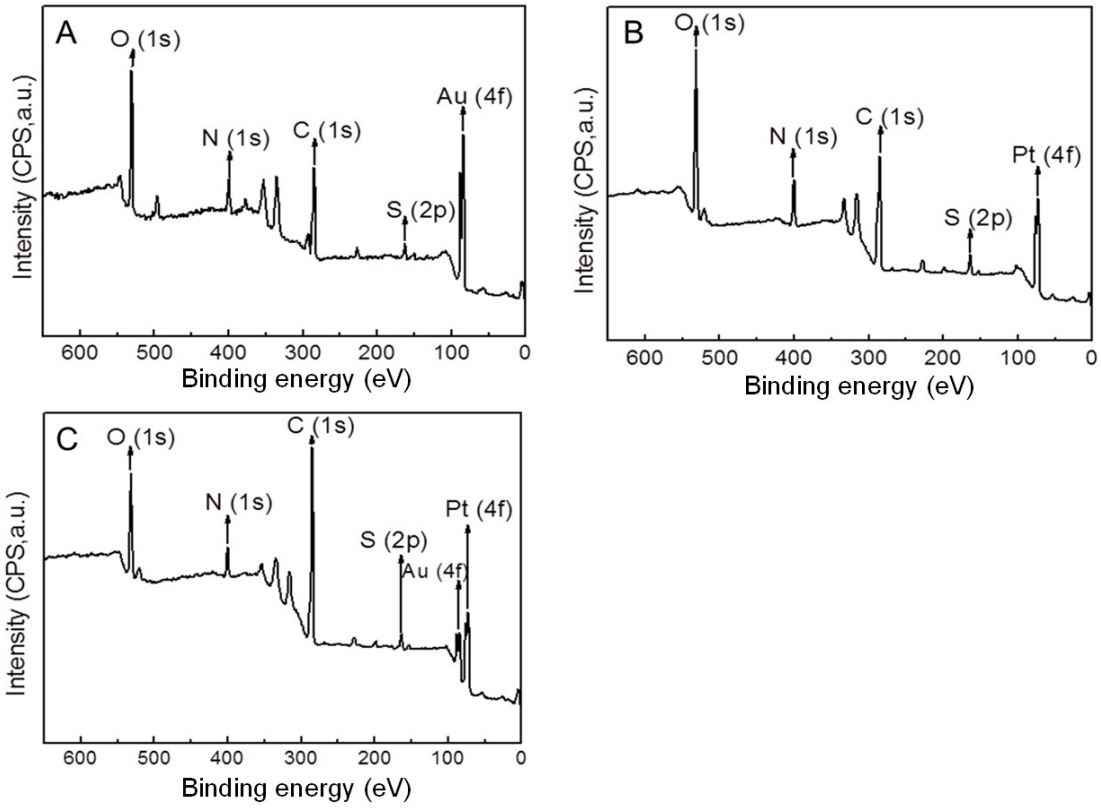

Fig. S4 XPS survey spectra of (A) AuNCs, (B) PtNCs, and (C) Au-PtNCs.

Table S2 Data of binding energy of Au 4f, and Pt 4f for AuNCs, PtNCs, and Au-PtNCs.

Catalyst	Binding energy (eV)			
	Au $4f_{5/2}$	Au $4f_{7/2}$	Pt $4f_{5/2}$	Pt $4f_{7/2}$
AuNCs	87.8	84.1	–	–
PtNCs	–	–	75.9	72.5
Au-PtNCs	87.9	84.2	75.8	72.5

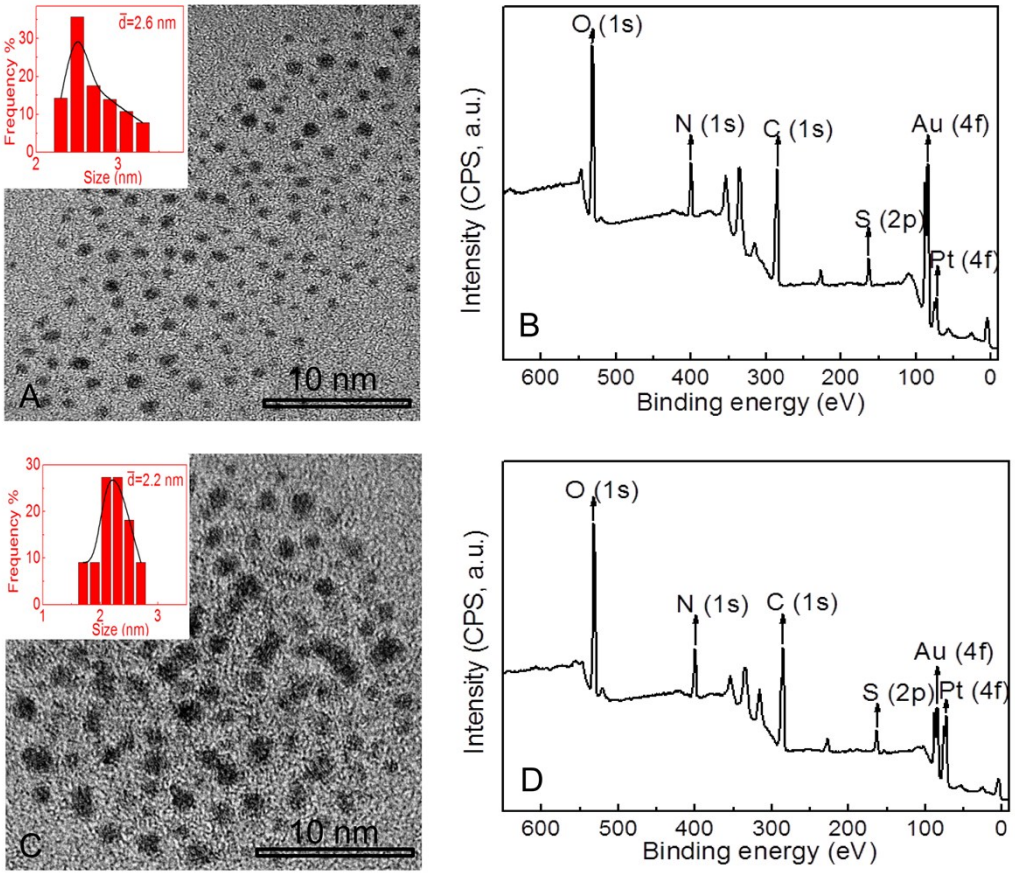

Fig. S5 TEM images of (A) Au@PtNCs and (C) Pt@AuNCs. Insets: the corresponding size distribution histograms. XPS survey spectra of (B) Au@PtNCs and (D) Pt@AuNCs.

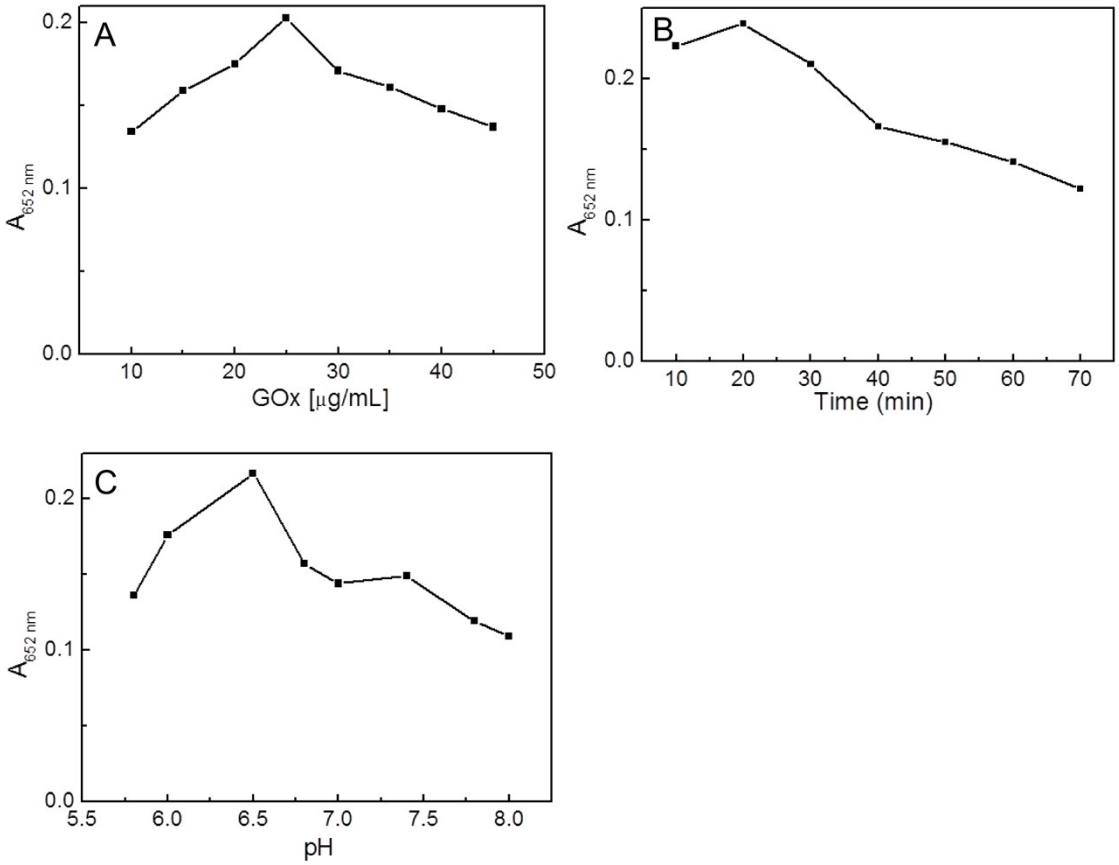

Fig. S6 The dependence of (A) GOx concentration, (B) incubation time, and (C) solution pH on absorbance changes at 652 nm of TMB in the oxidation of glucose catalyzed by GOx. Experiments were carried out using Au-PtNCs (7.5 μg/mL), glucose (40 μM), and TMB (0.5 mM) at 37 °C.

The reaction rate depended on the concentration of GOx, and the absorbance at 652 nm reached its maximum at 25 μg/mL, as exhibited in Fig. S6A. The absorbance change was also monitored as a function of incubation time (Fig. S6B). It was revealed that A_{652nm} increased with increasing time up to 20 min, after which the absorbance decreased over time. Therefore, the incubation time was set at 20 min. It was also found that A_{652nm} remarkably increased with increasing pH up to 6.5 and then decreased when over 6.5. So, pH 6.5 was selected as the optimized pH for the oxidation of glucose (Fig. S6C).

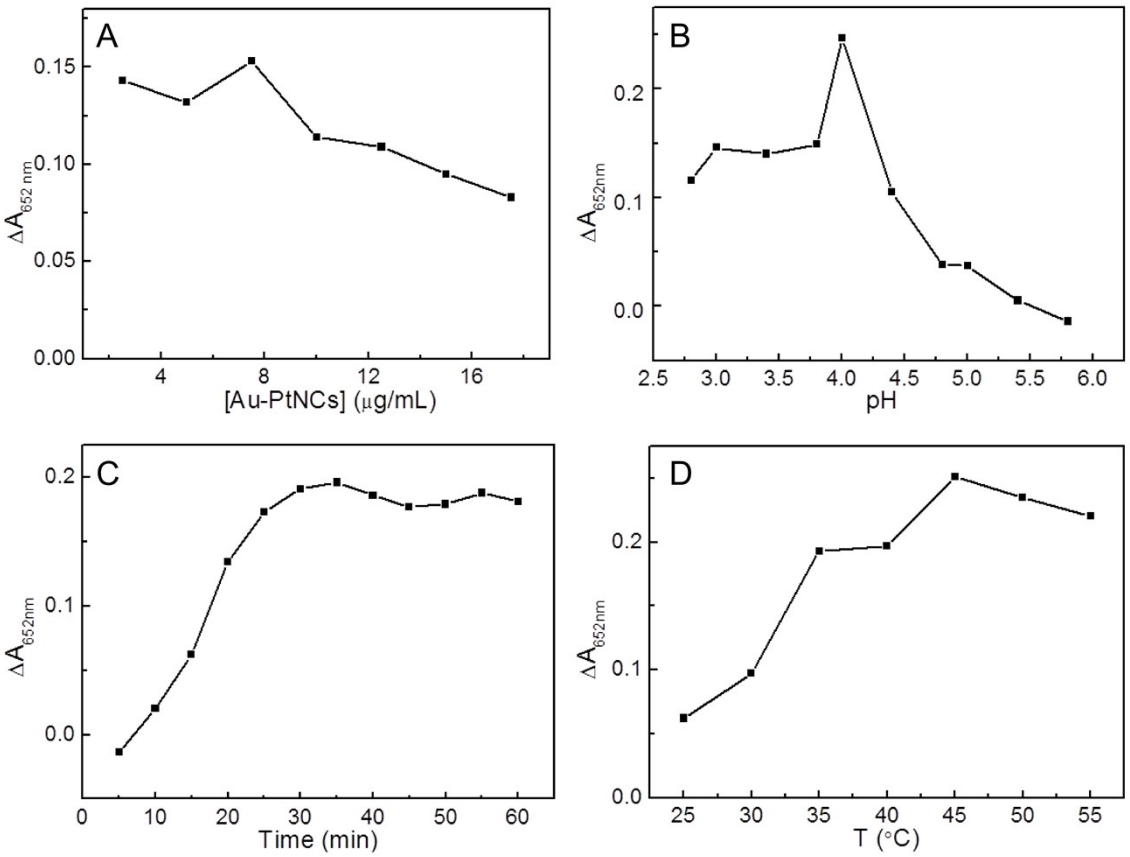

Fig. S7 Peroxidase-like activity of Au-PtNCs depended on (A) Au-PtNCs concentration, (B) pH, (C) reaction time, and (D) temperature for the oxidation of TMB catalyzed by H_2O_2 generated in the oxidation of glucose. Experiments were carried out using GOx (25 μg/mL), glucose (40 μM), and TMB (0.5 mM).

In order to investigate the effect of the amount of Au-PtNCs as novel peroxidase mimics used for oxidizing TMB, we measured ΔA (A - A_0, A and A_0 are the maximum absorbance at 652 nm in the presence and absence of glucose, respectively). The result indicated that the maximumΔA was obtained when the amount of Au-PtNCs was 7.5 μg/mL (Fig. S7A). Also, the absorbance enhancement efficiency was highly dependent on pH value of the buffer and the highest point was obtained at pH 4.0 (Fig. S7B). Fig. S7C showed the biggest absorbance change appeared at 30 min. The effect of temperature was studied from 25 to 55 °C (Fig. S7D). It showed that the catalytic activity gradually increased with the increase of temperature, while after 45 °C it decreased. Hence, 45 °C was chosen as the experimental temperature.

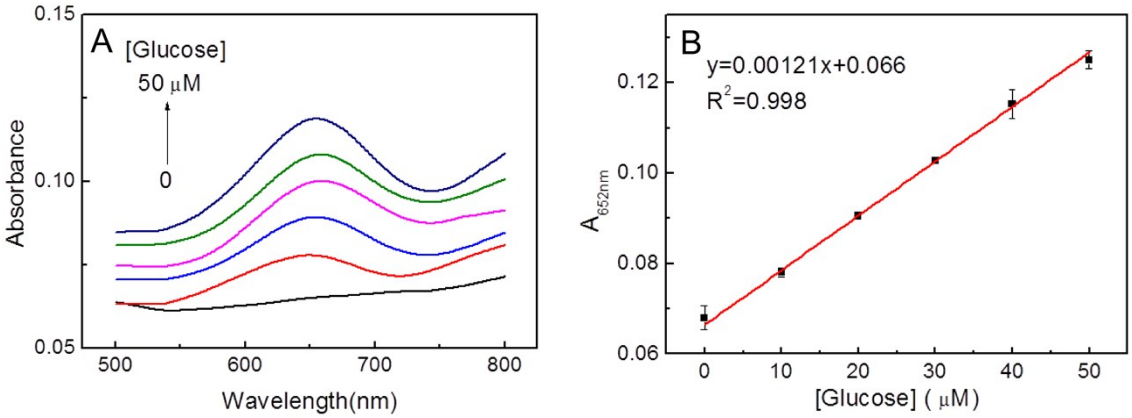

Fig. S8 (A) Absorption spectra of AuNCs-GOx-TMB system in the presence of different glucose concentrations (0, 10, 20, 30, 40, and 50 μM). (B) Linear calibration curve of the absorbance at 652 nm against glucose concentration.

Table S3 Comparison of analytical performances of various colorimetric methods using inorganic peroxidase mimetics for glucose detection.

Material	Linear range (μM)	LOD (μM)	Ref.
AuNCs-Ft[a]	2000 −10000	-	28
CuNCs	100 − 2000	100	44
Carbon nanodots	1 − 500	0.4	45
GK[b]-PdNPs[c]	10 − 1000	6.0	46
Fe-MIL-88NH_2	2 − 300	0.48	47
Yeast extract-stabilized PtNCs	0 − 200	0.28	48
Co_3O_4@CeO_2	0 − 40	1.9	49
γ-Fe_2O_3/SiO_2NPs	0 − 20	3.2	50
Au@PtNRs[d]	45 − 400	45	51
Dendrimer-encapsulated PtNPs	1 − 50	1	52
Au-PtNCs	5 − 55	2.4	This work

[a] apoferritin paired, [b] gum kondagogu, [c] nanoparticles, [d] nanorods.

Table S4 Comparison of quantitative results of glucose levels in human serum samples by enhanced peroxidase-like activity of Au-PtNCs and the commercial glucometer.

Sample	Our assay (mM)	Glucometer (mM)
1	7.8 ± 0.3	9.0 ± 0.4
2	7.2 ± 0.3	7.8 ± 0.3
3	7.9 ± 0.2	7.7 ± 0.2
4	11.3 ± 0.1	10.9 ± 0.3
5	14.3 ± 0.3	14.8 ± 0.2
6	15.5 ± 0.3	16.2 ± 0.3

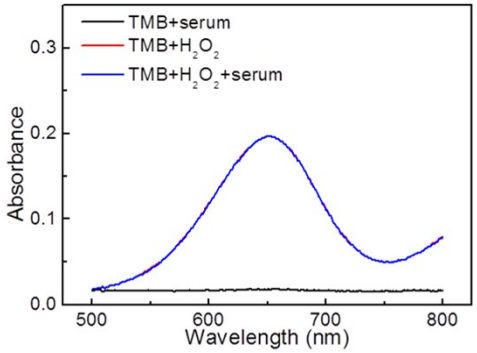

Fig. S9 Absorption spectra of TMB + serum, TMB + H_2O_2, and TMB + H_2O_2 + serum.