Supporting information

Highly sensitive colorimetric detection of copper ions based on regulating the peroxidase-like activity of Au@Pt nanohybrids

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Preparation of Pt NPs

Pt nanoparticles were synthesized according to the report.[1] A solution of $H_2PtCl_6 \cdot (H_2O)_6$ (0.2%, 36 mL) was added to boiling deionized water (464 mL) for 1 min. Subsequently, a mixture (11 mL) of 1% sodium citrate and 0.05% citric acid was added to a boiling solution of $H_2PtCl_6 \cdot (H_2O)_6$. After 30 s, a freshly prepared $NaBH_4$ (0.08%, 5.5 mL) solution containing 1% sodium citrate and 0.05% citric acid was rapidly injected to the resulting solution. After 10 min, a solution of the formed Pt NPs was cooled down to room temperature. TEM image show that the diameter of the Pt NPs was 5 nm.

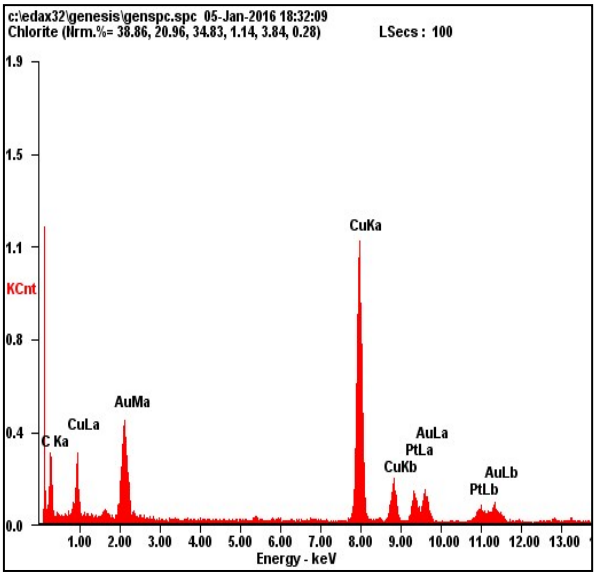

Fig. S1 EDX spectrum of Au@PtNHs

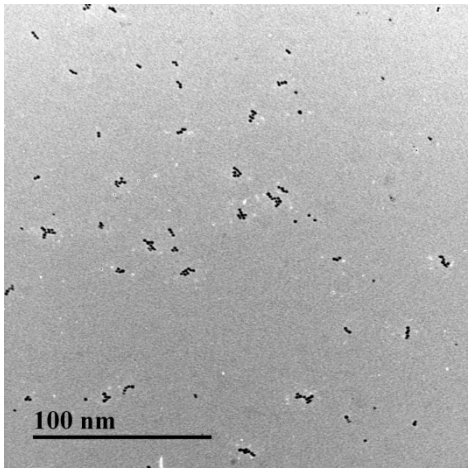

Fig. S2 TEM image of PtNPs.

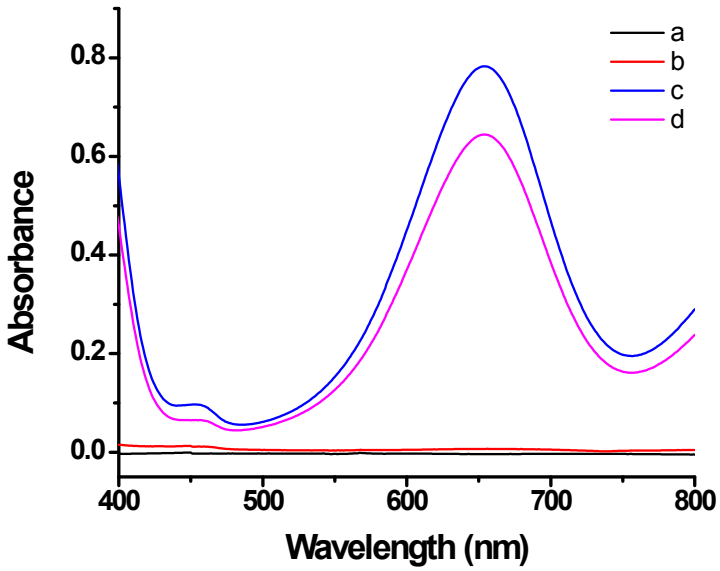

Fig. S3 Inhibition of L-cysteine toward the peroxidase-like activity of PtNPs.

UV-vis spectra of (a) PtNPs-TMB-H_2O_2 reaction solution, (b) L-cysteine-PtNPs -TMB-H_2O_2 reaction solution, (c) TMB-H_2O_2 reaction solution and (d) PtNPs solution. [L-cysteine], 2.0 μM; [Cu^{2+}], 200 nM.

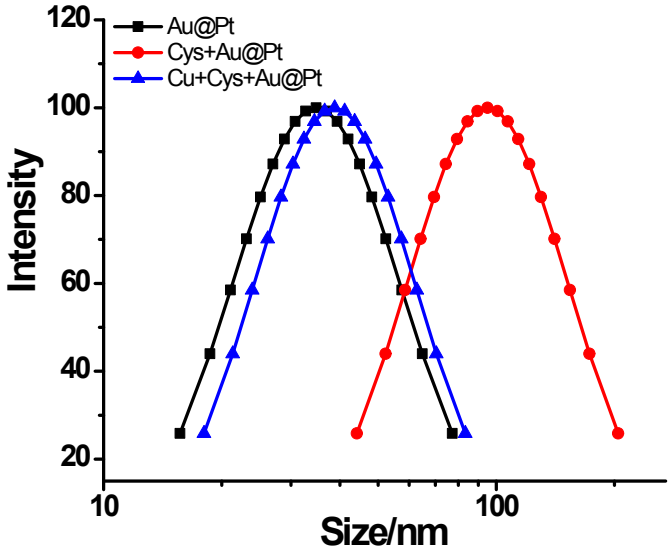

Fig. S4 The size distribution of the Au@PtNHs before and after incubated with L-Cys and the mixture of Cu^{2+} and L-Cys.

Cu^{2+} and L-Cys were first incubated for 30 min and then mixed with Au@PtNHs) for 10 min for DLS measurements.

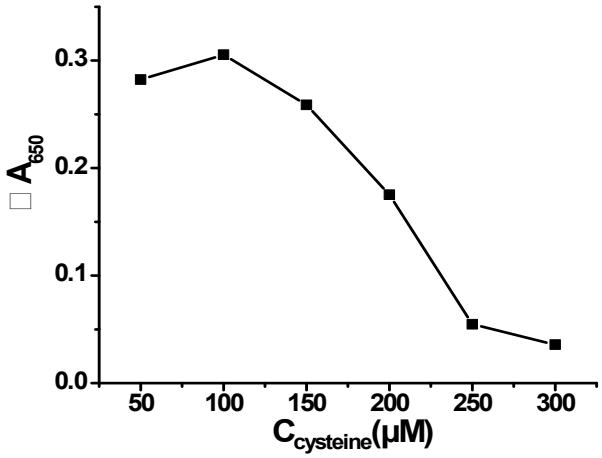

Fig. S5 Different concentrations of L-cysteine were investigated.

[Au@PtNHs] = 12 pM,[PB buffer] = 5 mM (pH 7.0), [H_2O_2] = 0.4 M, [TMB] =1.0 mM, [citrate buffer] =0.04 M (pH 4.5) ;Incubation time for the mixture of L-cysteine and Cu^{2+}, 20min; Incubation time for the mixture of L-cysteine, Cu^{2+} and Au@PtNHs, 10 min; color-developing time, 10min.

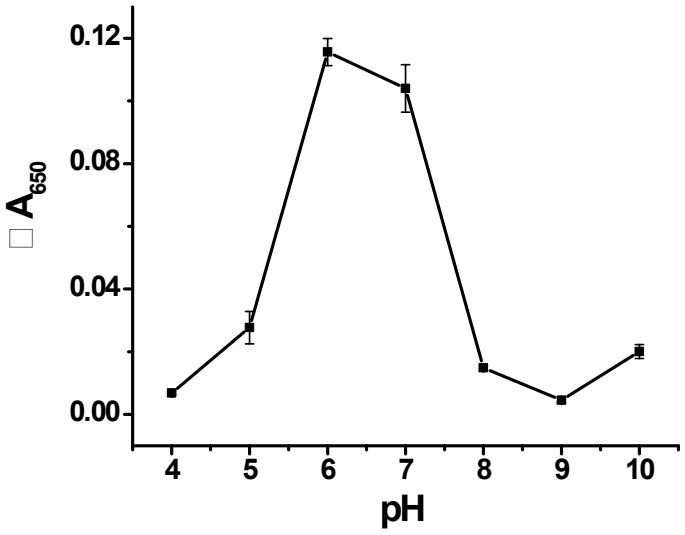

Fig. S6 Different pH values of Phosphate buffer were investigated.
[Au@PtNHs] = 12 pM, [cysteine] = 100 μM, [PB buffer] = 5 mM, [H_2O_2] =0.4 M, [TMB] =0.3 mM, [citrate buffer] =0.04 M (pH 4.5) ; Incubation time for the mixture of L-cysteine and Cu^{2+}, 20 min; Incubation time for the mixture of L-cysteine ,Cu^{2+} and Au@PtNHs, 10 min; color-developing time, 10min.

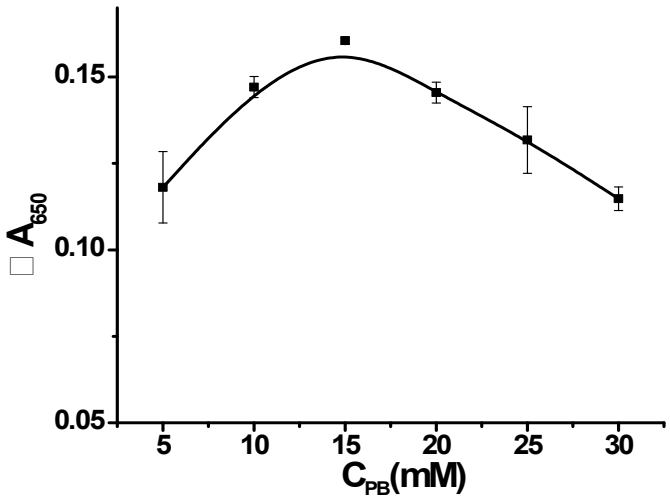

Fig. S7 Different concentrations of Phosphate buffer (pH 6.0) were investigated. [Au@PtNHs] = 12 pM, [cysteine] = 100 μM, [H_2O_2] =0.4 M, [TMB] =0.3 mM, [citrate buffer] =0.04 M (pH 4.5) ;Incubation time for the mixture of L-cysteine and Cu^{2+}, 20 min; Incubation time for the mixture of L-cysteine ,Cu^{2+} and Au@PtNHs, 10 min; color-developing time, 10min.

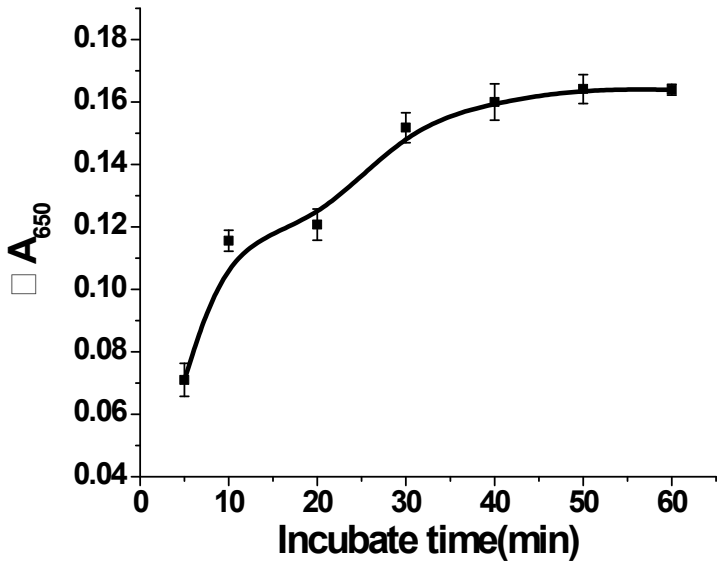

Fig. S8 Different reaction time between L-cysteine and Cu^{2+} was investigated. [Au@PtNHs] = 12pM, [cysteine] = 100 μM, [PB buffer] = 15 mM (pH 6.0), [H_2O_2] = 0.4 M, [TMB] =0.3 mM, [citrate buffer] =0.04 M (pH 4.5) ; Incubation time for the mixture of L-cysteine, Cu^{2+} and Au@PtNHs, 10 min; color-developing time, 10min.

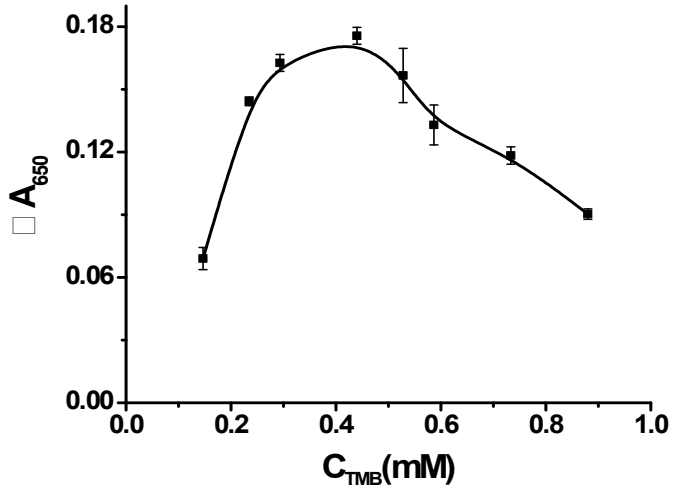

Fig. S9 Different concentrations of TMB were investigated.

[Au@PtNHs] = 12 pM, [L-cysteine] = 100μM, [PB buffer] = 15mM (pH 6.0), [H_2O_2] =0.4 M, [citrate buffer] =0.04 M (pH 4.5) ; Incubation time for the mixture of L-cysteine and Cu^{2+}, 30 min; Incubation time for the mixture of L-cysteine,Cu^{2+} and Au@PtNHs, 10 min, color-developing time, 10 min.

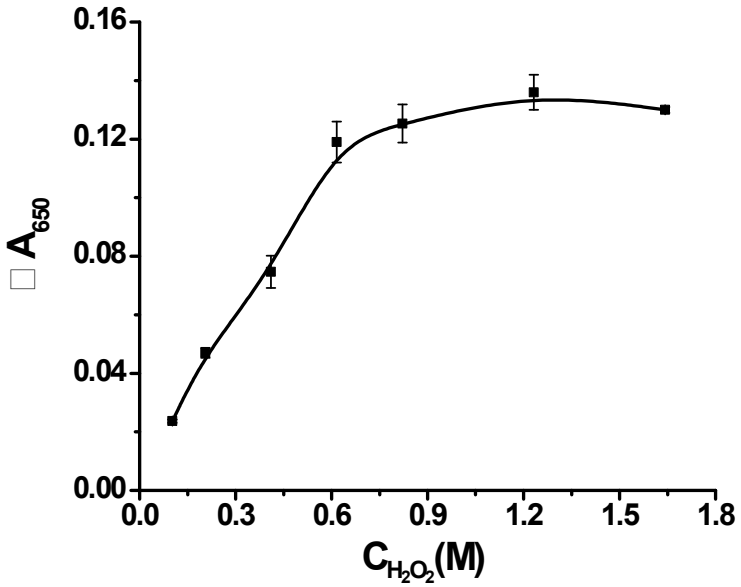

Fig. S10 Different concentrations of H_2O_2 were investigated.
[Au@PtNHs] = 12 pM, [cysteine] = 100 μM, [PB buffer] = 15 mM (pH 6.0), [TMB] = 0.44 mM, [citrate buffer] =0.04 M (pH 4.5) ;Incubation time for the mixture of L-cysteine and Cu^{2+},30min;Incubation time for the mixture of L-cysteine ,Cu^{2+} and Au@PtNHs, 10 min, color-developing time, 10min.

Table S1 Comparison of several colorimetric methods for Cu2+ detection based on nanoparticles

Probes	LOD		Linear range	Ref.
	By UV-vis spectrometry	By the naked eyes		
Gold nanoparticles	0.04 μM	2.0 μM	0.2 - 4 μM	[2]
Azide-tagged gold nanoparticles	1.8 μM	1.8 μM	1.8 - 200 μM	[3]
Silver/dopamine nanoparticle	50.0 nM	—	0.05 - 8 μM	[4]
Thiomalic acid functionalized Ag nanoparticles	1 nM	—	1 - 50 nM	[5]
Polyamine-functionalized gold nanoparticles	30 nM	—	0.1 - 1 μM	[6]
Gold nanoparticles	30 nM	—	0.05 - 1.85 μM	[7]
Gold nanoparticles	5 nM	40 nM	10 - 80 nM	[8]
gold nanorods	1.6 nM	—	5 nM - 500 mM	[9]
Gold nanorods	4.96 nM	10 nM	10 - 300 nM	[10]
Silver-coated gold nanorods	3 nM	—	3 - 1000 nM	[11]
Ag nanoparticles	0.25 μM	0.75 μM	0.25- 2.0 μM	[12]
A monoazo dye, Chromotrope 2R	3.4 nM	—	5.0 - 1000 nM	[13]
Au@PtNHs	4.0 nM	20 nM	20.0 -500 nM	(this work)

Table S2 Determination of Cu^{2+} in tap water samples (n=3)

Spiked (nM)	Found (nM)	Recovery (%)	RSD (%)
0	33.9[a]	-	5.7
20.0	53.4	97.5	4.4
50.0	88.5	109.2	6.6
100.0	130.3	96.4	3.2
200.0	244.7	105.4	3.9

[a] The sample was also detected by graphite furnace AAS method and the result was 32.5 nM. The relative deviation of 2 values was lower than 5%.

Table S3 Determination of Cu^{2+} in green tea samples (n=3)

Green tea samples	Measured by AAS (μg/g)	Measured by this method (μg/g)
1	20.2±1.3	21.5±1.9
2	24.1±1.1	24.9±1.5
3	32.8±1.5	31.9±2.3

Equation S1

$$6RS^- + 2Cu^{II} \rightarrow RSSR + 2RS^-Cu^{I}{}^-SR$$

$$RS^-Cu^{I}{}^-SR + O_2 \rightarrow RS^-Cu^{I}{}^{\bullet}SR + O_2^{-\bullet}$$

$$2O_2^{-\bullet} + 2H^+ \rightarrow O_2 + H_2O_2$$

$$RS^-Cu^{I}{}^{\bullet}SR \rightarrow 1/2RSSR + RS^-Cu^{I}$$

$$RS^-Cu^{I} + O_2 + 2H^+ \rightarrow 1/2RSSR + H_2O_2 + Cu^{II}$$

$$\xrightarrow{Cu^{2+}}$$

The total catalytic equation: $2RSH + O_2 \rightarrow RSSR + H_2O_2$

The detailed and total catalytic equations for the copper catalysed oxidation of L-cysteine (RSH).

References

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