Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Rapid colorimetric sensing for ascorbic acid based on the excellent peroxidase-like activity of Pt deposited on $ZnCo_2O_4$ spheres

Dexin Yin[a], Xiaoyan Cao[a], Xiangwei Liu[a], Yang Zhou[c], Zhenxue Liu[a], Dongmei Wang[a,*], Qingyun Liu[a,*], Xianxi Zhang[b], and Xiao Zhang[d]

Synthesis of $ZnCo_2O_4$ Microspheres

$Co(CH_3COO)_2 \cdot 4H_2O$ (8 mmol), $Zn(CH_3COO)_2 \cdot 2H_2O$ (4 mmol) was added to 80 mL of ethylene glycol, stirred for 30 min, and transferred into Teflon-lined stainless steel autoclaves at 180 °C for 12 h. The product was centrifuged and washed several times with ethanol and dried at 60 °C overnight.

Synthesis of Pt/$ZnCo_2O_4$ Microspheres

30 mg of polyvinylpyrrolidone (PVP) was added to 50 ml of ethylene glycol by ultrasonic stirring to dissolve, and the prepared $ZnCo_2O_4$ (50 mg) was added to the above solution, and the mixture was ultrasonically stirred to be uniformly dispersed. 5 mg of K_2PtCl_4 was dissolved in 0.6 mL of deionized water and added to the above system. Heat at reflux at 110 °C for 2 h. The product was centrifuged, washed with water and ethanol, and dried at 60 °C overnight.

Peroxidase-like Activity and Steady-State Kinetic Assay of Pt/$ZnCo_2O_4$ Microspheres

The peroxidase-like activity of Pt/$ZnCo_2O_4$ microspheres was studied in the aid of oxidation of chromogenic substrate (TMB) by H_2O_2. Typically, Pt/$ZnCo_2O_4$ (200 μL, 0.06 mg/mL) and H_2O_2 (200 μL, 0.25 M) was added to acetic acid buffer solution (1400 μL, pH = 4.0), followed by adding of TMB solution (200 μL, 1 mM). After 3 min, the absorbance of reaction systems was monitored by a UV-1810 PC spectrophotometer at 652 nm. In order to study the effect of different reaction parameters on the oxidation reaction, the effects of different reaction conditions such

as pH (2.0-9.0) and temperature (15-60 °C) on the activity of $Pt/ZnCo_2O_4$ were investigated by the same method to obtain the optimal reaction conditions.

The kinetics of the catalytic reaction was investigated via monitoring the specific absorption spectra (652 nm, time course mode) by changing the concentration of H_2O_2 or TMB at pH = 4. The Michaelis-Menten constant (K_m) was calculated according to the Michaelis−Menten equation, $1/v = (K_m /V_{max}) \times (1/[S]) + 1/V_{max}$. In the equation, v is the initial reaction velocity, K_m and V_{max} are the Michaelis−Menten constant and the maximum reaction velocity, respectively. [S] is the concentration of substrate.

Colorimetric Determination of H_2O_2 and ascorbic acid

The detection of H_2O_2 was tested as follows: $Pt/ZnCo_2O_4$ (200 μL, 0.06 mg/mL) and H_2O_2 (200 μL) with different concentrations were added to acetic acid buffer solution (1400 μL, pH = 4.0), followed by adding of TMB solution (200 μL, 1 mM). After reacting for 3 min at the optimum temperature (30°C), reaction system was tested the absorbance at 652 nm.

The detection of ascorbic acid was tested as follows: $Pt/ZnCo_2O_4$ (200 μL, 0.06 mg/mL), H_2O_2 (200 μL, 0.125 M), TMB solution (200 μL, 0.5 mM) were added to acetic acid buffer solution (1400 μL, pH = 4.0) for 2 min. Immediately, add 200 μL of ascorbic acid with different concentrations into the above reaction system, and measured on a UV−vis spectrophotometer.

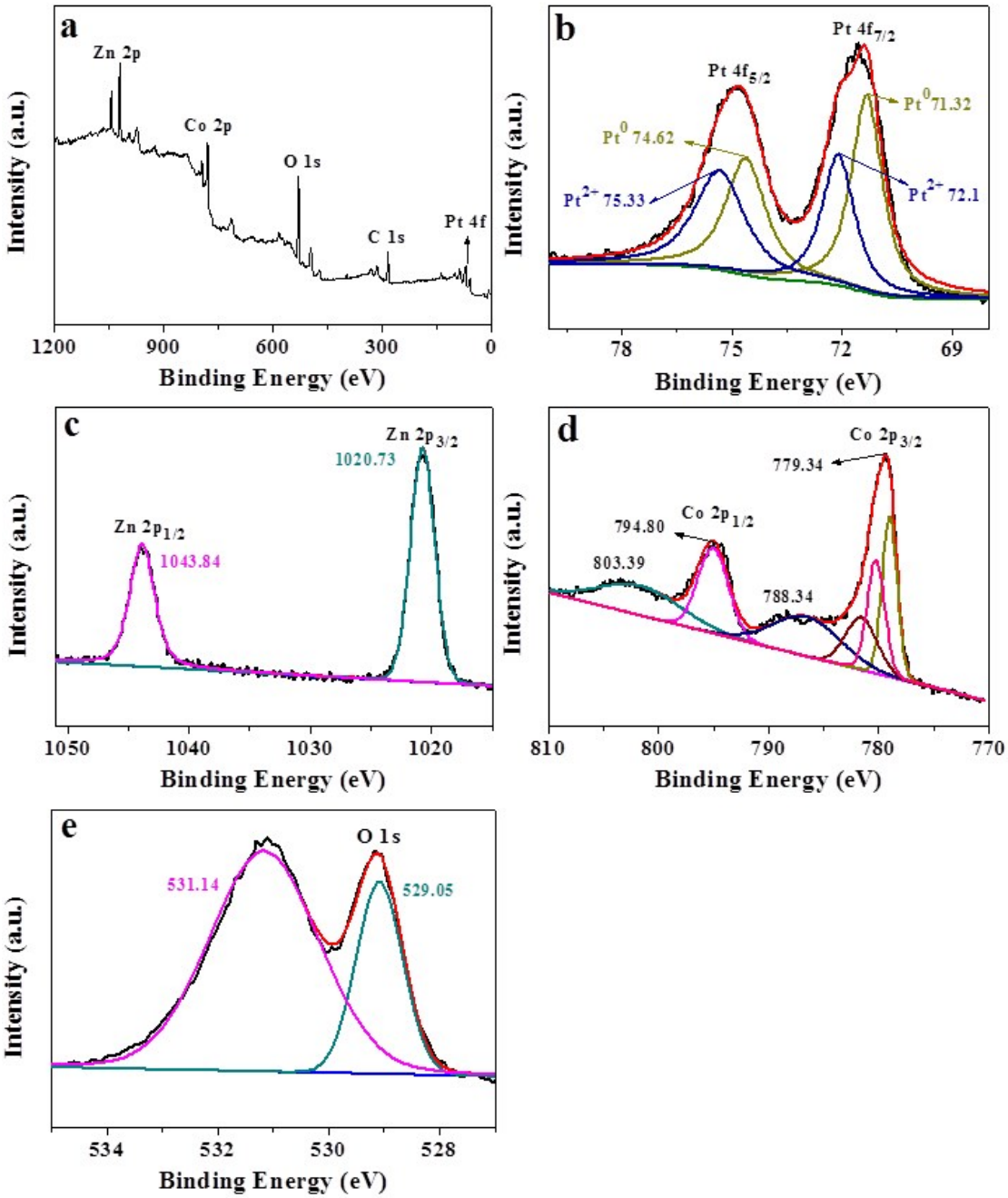

Fig. S1 XPS spectra of Pt/$ZnCo_2O_4$: Survey spectra (a), Pt 4f (b), Zn 2p (c), Co 2p (d) and O 1s (e), respectively.

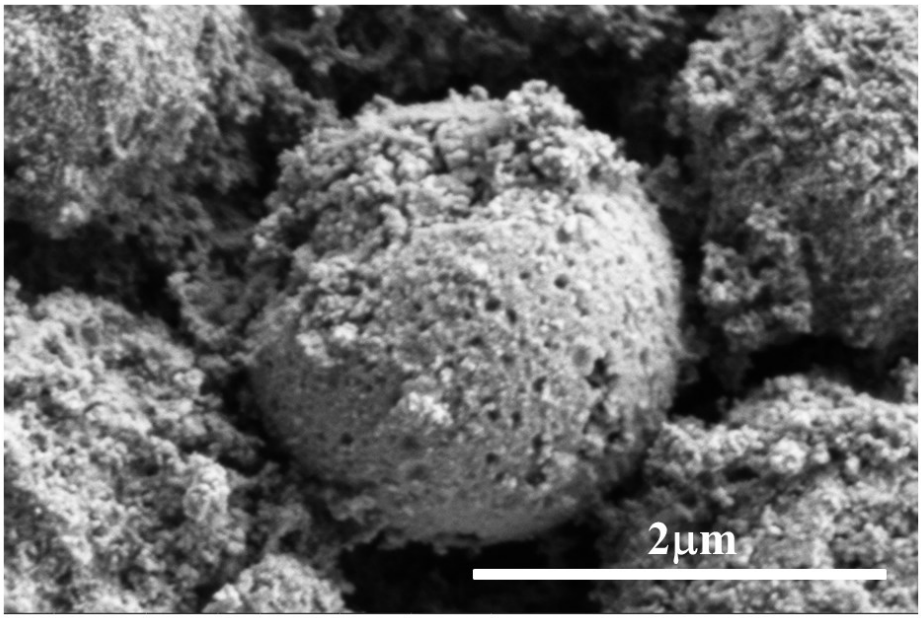

Fig. S2 SEM image of $ZnCo_2O_4$ microspheres.

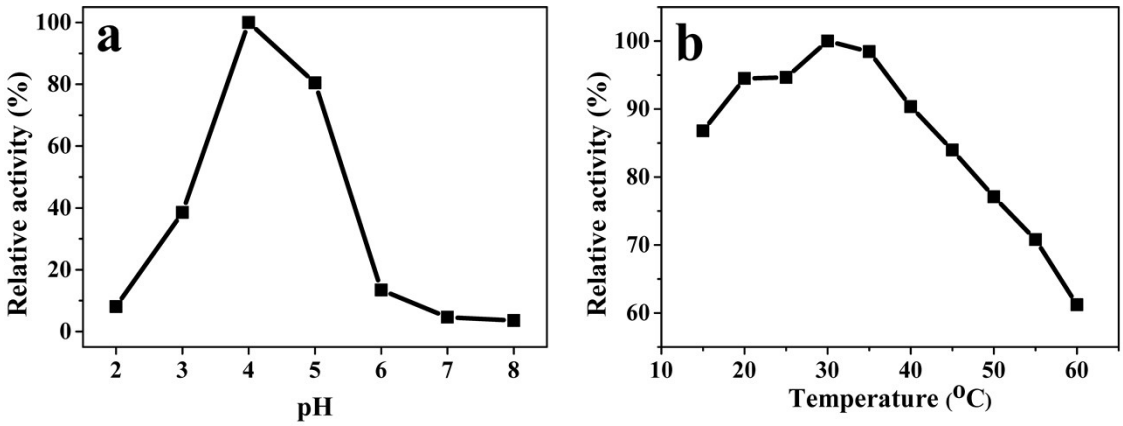

Fig. S3 Optimization of experimental conditions: pH values of the reaction buffer from 2 to 8 (a) and temperatures from 15 to 60 °C (b), respectively.

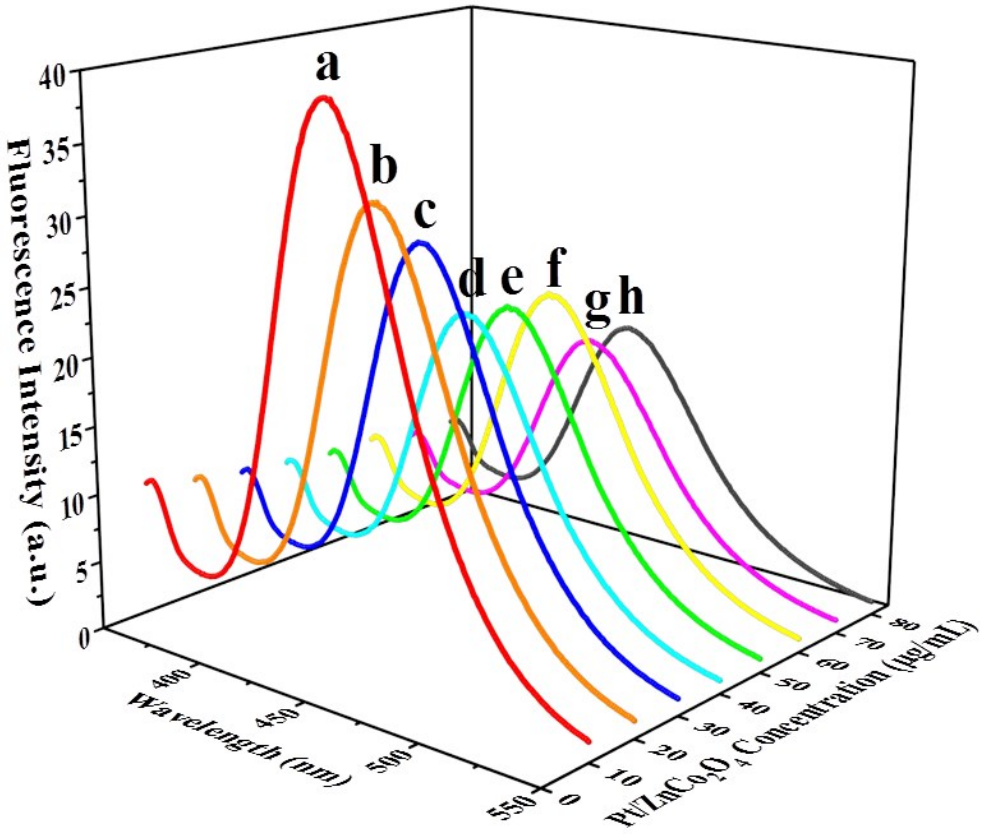

Fig. S4 Fluorescent spectra using terephthalic acid (TA) as a fluorescent probe. $Pt/ZnCo_2O_4$ concentration (from a to h): 10, 20, 30, 40, 50, 60, 70 and 80 μg/mL, respectively. Conditions: H_2O_2 (25 mM), TA (5 mM), pH=4 and temperature (30 °C).

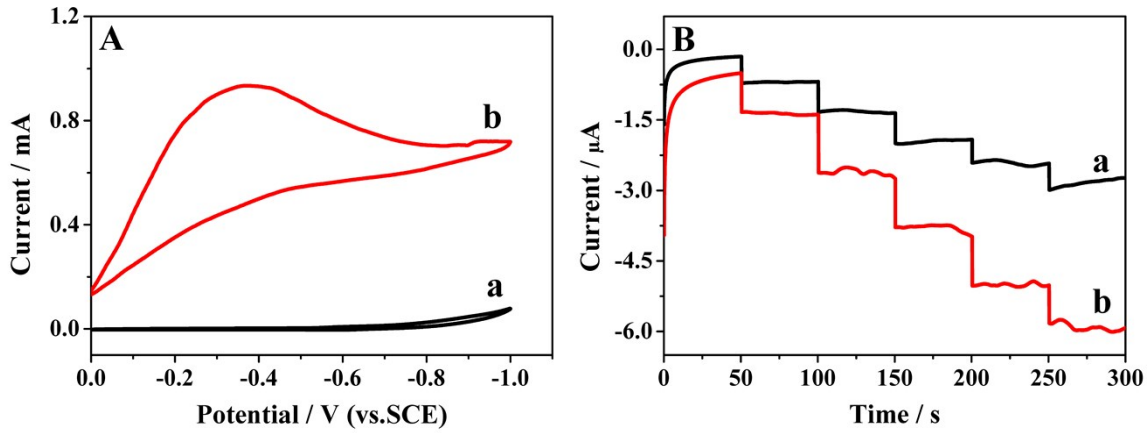

Fig. S5 (A) Cyclic voltammograms of the $Pt/ZnCo_2O_4$ modified GCE in 100 mM phosphate buffer saline (PBS) plus 100 mM NaCl (pH = 5.7) in absence (a) and in presence of 100 mM H_2O_2

(b). Scan rate, 50 mV s^{-1}. (B) Amperometric response of bare GCE (a) and the $Pt/ZnCo_2O_4$ modified GCE (b) in 100 mM phosphate buffer saline (PBS) plus 100 mM NaCl (pH = 5.7) at applied potential of 0.6 V upon successive additions of 100 mM H_2O_2 100 μL.

Table S1 Kinetic parameters for the oxidation of substrates by different nanoperoxidase mimics.

Catalysts	K_m (mM)		V_{max} (10^{-8} M s^{-1})		ref
	H_2O_2	TMB	H_2O_2	TMB	
Co_3O_4@CeO_2	7.09	0.140	43.3	25.0	[63]
Ag@Fabric	7.61	0.19	14.4	15.1	[64]
BSA/Pt-NPs	68.4	0.217	28.7	15.4	[65]
CuCNPs	282.1	0.183	16.8	14.5	[66]
Fe/CeO_2 NRs	47.6	0.176	16.6	8.6	[67]
Graphene-Au NPs	26.4	0.38	15.41	18.30	[68]
HRP	3.702	0.434	8.71	10	[62]
$Pt/ZnCo_2O_4$	0.73	0.1357	8.35	80.68	This work

Table S2 Comparison based on different nanoperoxidases for AA detection.

Catalyst	Method	Linear range (μM)	Detection limit (μM)	Reference
$Pt/ZnCo_2O_4$	Colorimetric	1-15	0.456	This work
MIL-53 (Fe)	Colorimetric	28.6-190.5	15	[69]
N-CQDs	Colorimetric	5−40	1.773	[70]
MOF-808	Colorimetric	30−1030	15	[71]

SnO_2	Electrochemistry	80-1360	20	[72]
hnp-PtCu	Electrochemistry	30–800	17.5	[73]
CuO/Pt	Colorimetric	1-600	0.796	[74]
Cu-Pt nanoalloys	Colorimetric	1-10	–	[75]
Pt/CeO_2	Colorimetric	0.5−30	0.080	[76]
$Pt/IMo_6O_{24}/GO$	Electrochemistry	50–4000	6.4	[77]

Table S3 Analytical results of AA in commercial vitamin C tablets.

Sample	Claimed	Found	Recovery (%)	RSD (%)
1	10 μM	(11.59 ± 0.442) μM	115.9	3.8
2	10 μM	(9.65 ± 0.158) μM	96.5	1.6