Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.

Supplementary Information

Fluorescent and colorimetric dual-mode assay of alkaline phosphatase activity via destroying oxidase-like CoOOH nanoflakes

Shi Gang Liu, Lei Han, Na Li, Na Xiao, Yan Jun Ju, Nian Bing Li*, and Hong Qun Luo*

Key Laboratory of Eco-Environments in Three Gorges Reservoir Region (Ministry of Education), School of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, P.R. China

*Corresponding Author. E-mail address: linb@swu.edu.cn (NB Li); luohq@swu.edu.cn (HQ Luo).

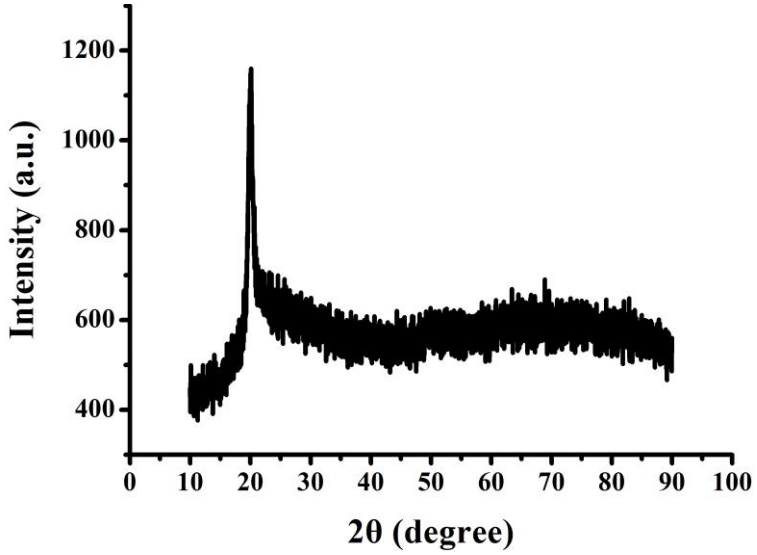

Fig. S1 XRD spectrum of the CoOOH nanoflakes.

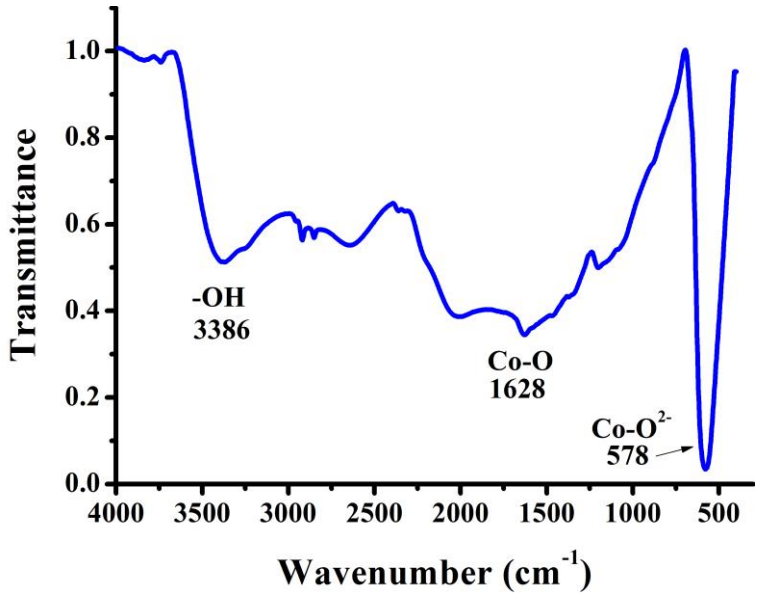

Fig. S2 FT-IR spectrum of the CoOOH nanoflakes.

.

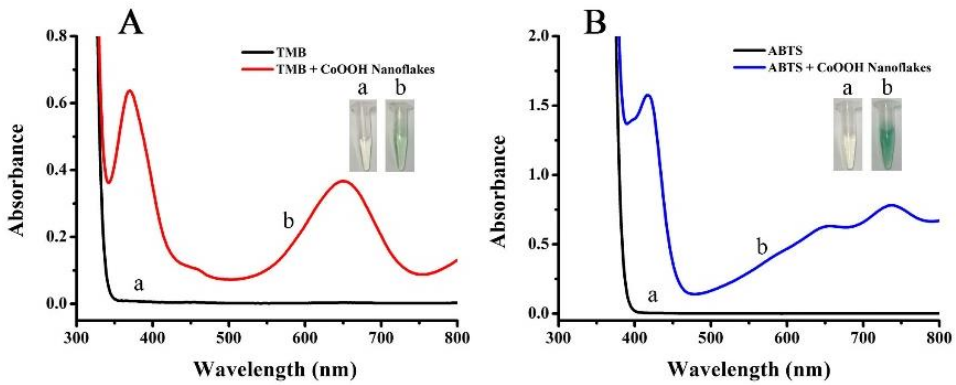

Fig. S3 UV-vis absorption spectra of (A) TMB solution (a), TMB + CoOOH nanoflakes solution (b), and (B) ABTS solution (a), ABTS + CoOOH nanoflakes solution (b). Insets are photographs of corresponding solutions under visible light. Concentrations: TMB, 1 mM; ABTS, 500 μM; CoOOH nanoflakes, 40 mg/L. Reaction conditions: 60 ^{o}C for 1 h; PBS buffer, pH 5.5.

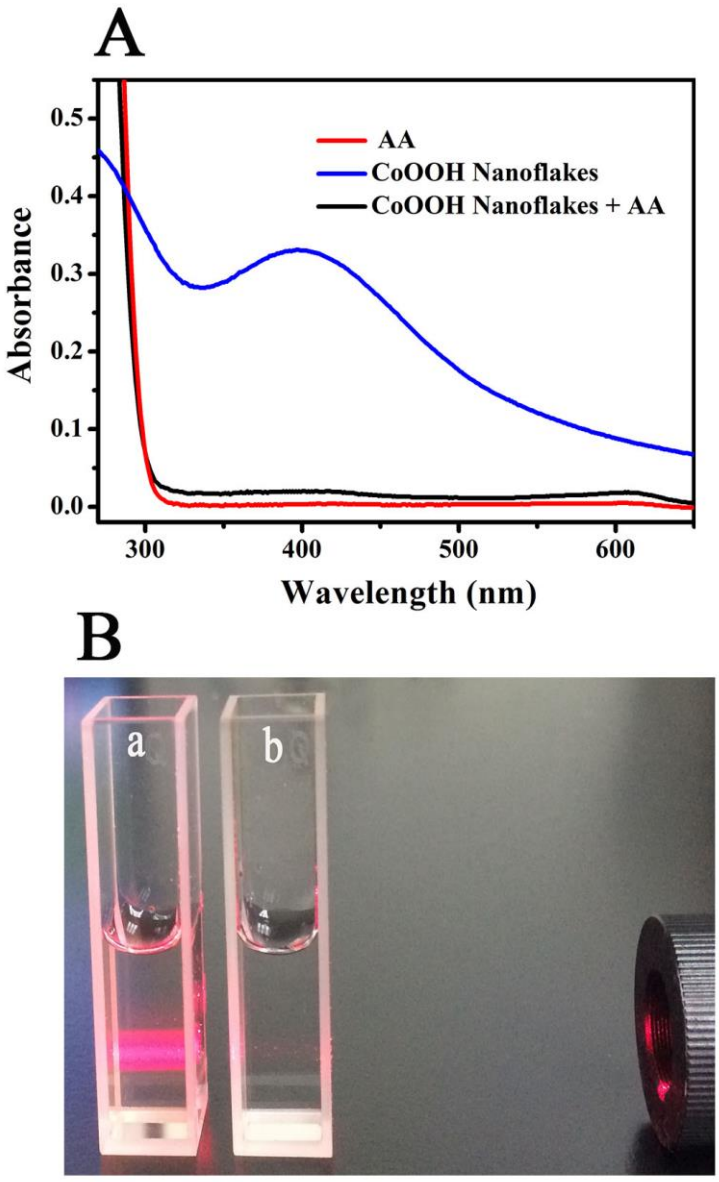

Fig. S4 (A) UV-vis absorption spectra of CoOOH nanoflakes (160 mg/L) in the absence and presence of AA (200 μM). (B) Tyndall effect of the CoOOH nanoflakes in the absence (a) and presence (b) of AA under radiation by a 635 nm laser pointer.

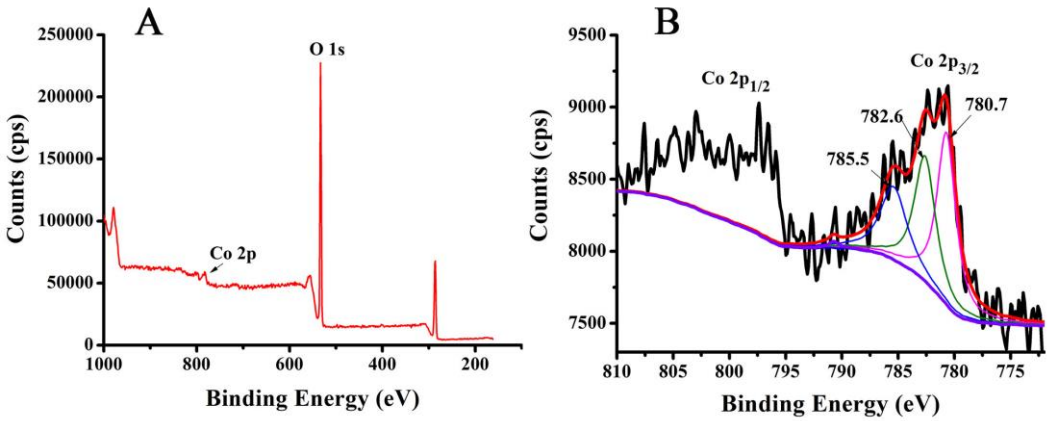

Fig. S5 XPS spectrum (A) and Co 2p spectrum (B) of CoOOH nanoflakes reduced by AA. It can be found that after reduction by AA, the peak of Co 2p on the XPS spectrum is greatly decreased for the reduced product of CoOOH nanoflakes compared to that of CoOOH nanoflakes, and high-resolution Co $2p_{3/2}$ spectrum can be fitted into three peaks including 780.7, 782.6, and 785.5 eV, which is apparently different from the Co $2p_{3/2}$ spectrum of CoOOH nanoflakes (780.2, 781.3, and 790.4 eV). The shift of the peaks implies the variation of cobalt oxidation state from Co(III) to Co(II).[S1]

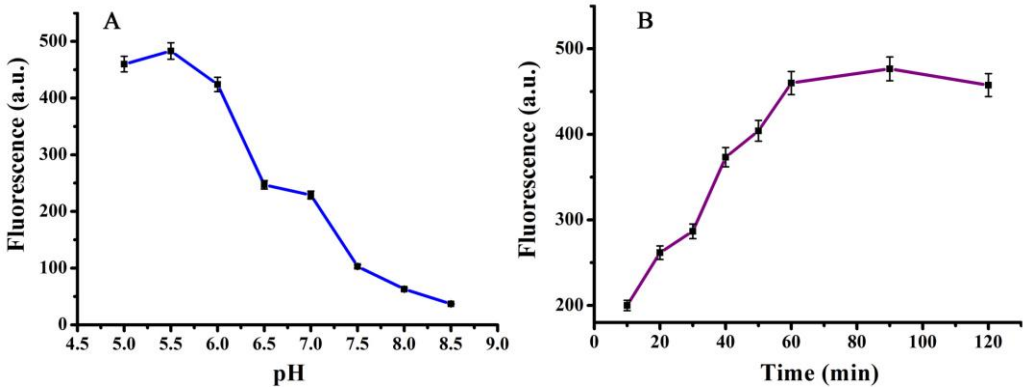

Fig. S6 Optimization of sensing conditions. Effects of pH (A) and incubation time (B) on the oxidase-like activity of CoOOH nanoflakes. Conditions: (A) OPD, 300 μM; CoOOH nanoflakes, 40 mg/L; 60 ^{o}C for 1 h; PBS buffer; (B) OPD, 300 μM; CoOOH nanoflakes, 40 mg/L; 60 ^{o}C; PBS buffer, pH 5.5.

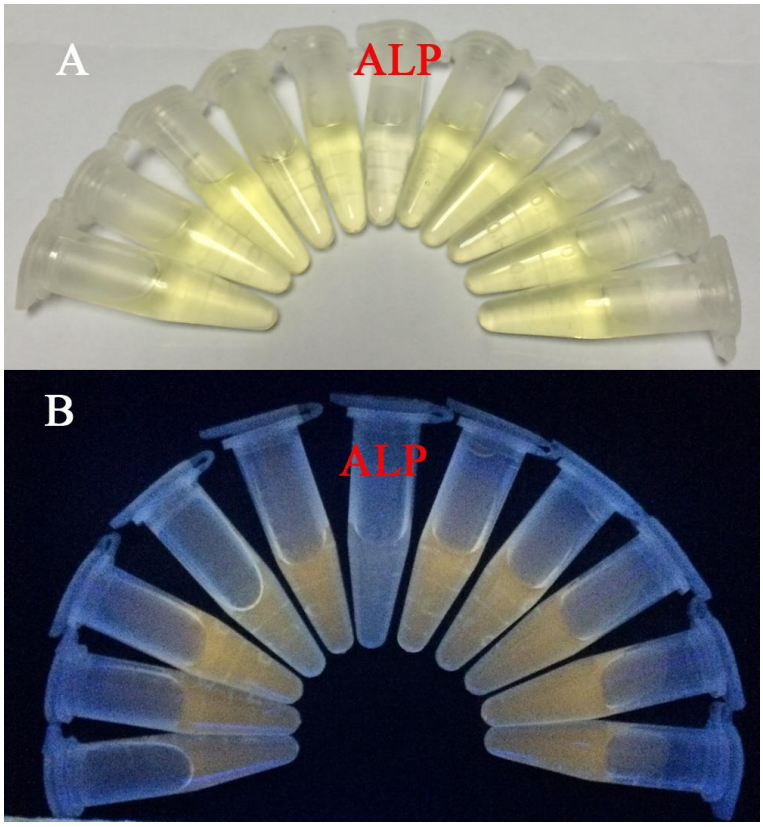

Fig. S7 Selectivity of the proposed method for ALP assay. Photographs of the reaction solutions (from left to right: Thr, GOx, HRP, BSA, Glu, ALP, K^+, Na^+, Ca^{2+}, Zn^{2+}, and Mg^{2+}) under visible light (A) and UV light of 365 nm (B).

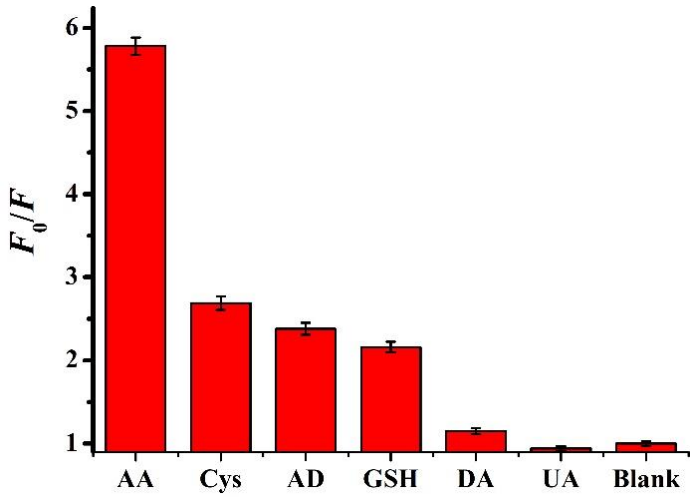

Fig. S8 Effect of biological reducing molecules on fluorescence of OPD/CoOOH nanoflakes system. F_0 and F denote the fluorescence intensity of the system in the absence and presence of reducing molecules. AA, ascorbic acid; Cys, cysteine; AD, adrenaline; GSH, glutathione; DA, dopamine; UA, uric acid. Concentrations of all the species are 100 μM; OPD, 300 μM; CoOOH nanoflakes, 40 mg/L. Reaction conditions: 60 ^{o}C for 1 h; PBS buffer, pH 5.5.

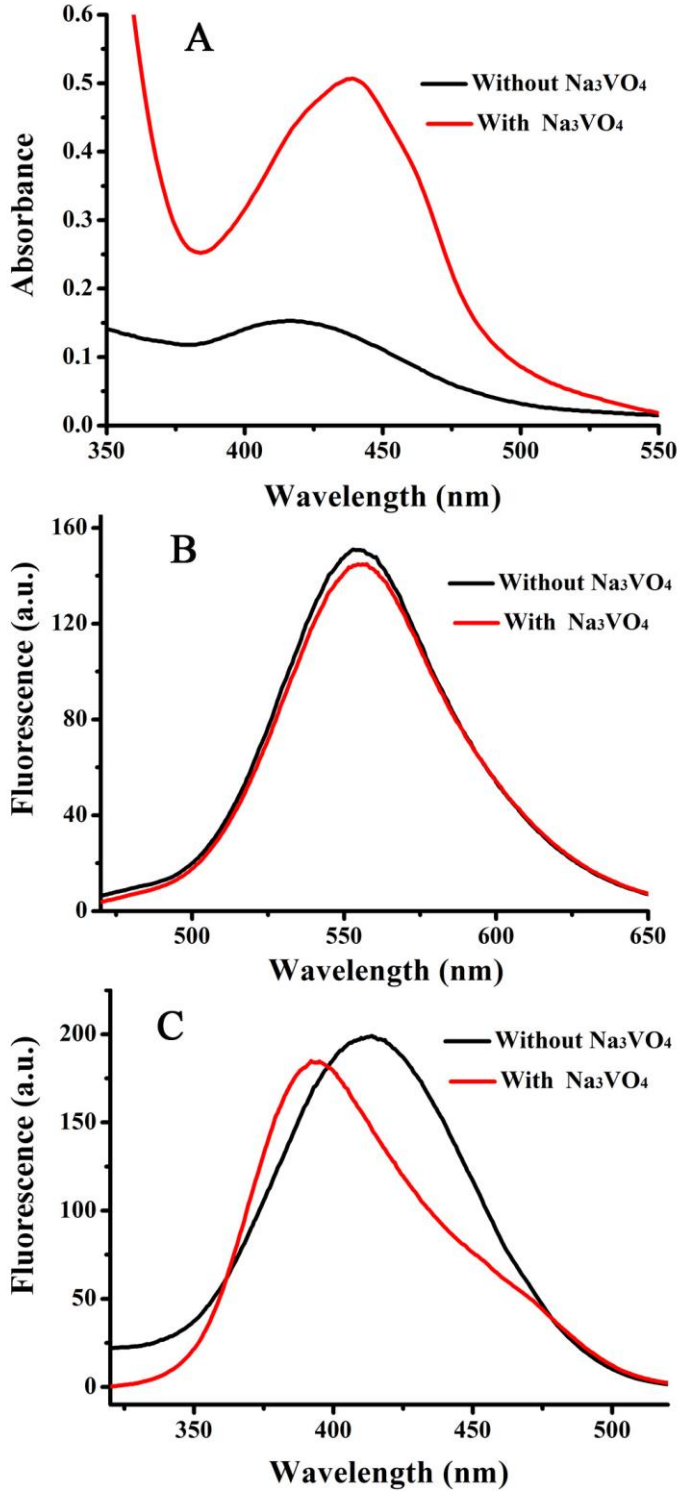

Fig. S9 (A) UV-vis absorption spectra of the reaction system in the absence and presence of Na_3VO_4 (7.5 mM). (B) and (C) are fluorescence emission spectra and excitation spectra of the reaction system in the absence and presence of Na_3VO_4 (7.5 mM), respectively. Sensing system: AAP, 2 mM; ALP, 200 U/L; CoOOH nanoflakes, 40 mg/L; OPD, 300 μM.

Table S1. Comparison of ALP assay in analytical performance.

Material	Assay mode	Detection of ALP		Ref.
		Linear range (U/L)	Detection limit (U/L)	
Au nanoparticles	UV-Vis	100 – 600	10	S2
Ce nanoparticles	UV-Vis	0.04 – 2	0.04	S3
CdSe quantum dots	Electrochemistry	2 – 25	2	S4
Au nanoclusters	Fluorescence	10 – 200	0.05	S5
Polymer nanoparticles	Fluorescence	25 – 200	10	S6
Au nanoclusters	Fluorescence	0.02 – 50	0.002	S7
Small molecule	Fluorescence	10 – 2000	3	S8
Carbon dots	Fluorescence	0.01 – 25	0.001	S9
CoOOH/OPD	Fluorescence, UV-Vis	0.04 – 160, 0.04 – 160	0.026, 0.032	This work

Table S2. Detection of ALP in human serum samples using a clinical method and the developed method (n = 3).

Sample	Clinical method		Our method			
	Added (U/L)	Detected (U/L)	Added (U/L)	Detected (U/L)	Recovery (%)	RSD (%)
1	0	52.5	0	55.6	/	6.26
	20	73.0	20	76.8	106.0	3.58
	50	103.2	50	105.2	99.2	1.22
2	0	59.8	0	63.2	/	5.18
	20	82.4	20	85.1	109.5	4.66
	50	112.6	50	114.6	102.8	2.50

References

(S1) J. Yang, H. Liu, W. N. Martens, and R. L. Frost, *J. Phys. Chem. C*, 2009, 114, 111-119.

(S2) C. M. Li, S. J. Zhen, J. Wang, Y. F. Li and C. Z. Huang, *Biosens. Bioelectron.* 2013, 43, 366-371.

(S3) A. Hayat, B. Gonca and S. Andreescu, *Biosens. Bioelectron.* 2014, 56, 334-339.

(S4) H. Jiang and X. Wang, *Anal. Chem.* 2012, 84, 6986-6993.

(S5) M. I. Halawa, W. Gao, M. Saqib, S. A. Kitte, F. Wu and G. Xu, *Biosens. Bioelectron.* 2017, 95, 8-14.

(S6) J. Deng, P. Yu, Y. Wang and L. Mao, *Anal. Chem.* 2015, 87, 3080-3086.

(S7) H. Liu, M. Li, Y. Xia and X. Ren, *ACS Appl. Mater. Interfaces* 2017, 9, 120-126.

(S8) S. J. Li, C. Y. Li, Y. F. Li, J. Fei, P. Wu, B. Yang, J. Ou-Yang and S. X. Nie, *Anal. Chem.* 2017, 89, 6854-6860.

(S9) G. Li, H. Fu, X. Chen, P. Gong, G. Chen, L. Xia, H. Wang, J. You and Y. Wu, *Anal. Chem.* 2016, 88, 2720-2726.