RSC Advances

This article can be cited before page numbers have been issued, to do this please use: Y. Xu, X. Wu, J. Shen and H. Zhang, *RSC Adv.*, 2015, DOI: 10.1039/C5RA17900A.

View Article Online
DOI: 10.1039/C5RA17900A

Journal Name

ARTICLE

Highly selective and sensitive recognition of histidine based on the oxidase–like activity of Cu^{2+} ions

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Yan Xu,[a] Xiao-Qiong Wu,[a] Jiang-Shan Shen,[a,b*] and Hong-Wu Zhang[a*]

Developing simple, highly sensitive and selective sensing systems for histidine (His) is important due to its biological significance. In this report, Cu^{2+} ions serving as the oxidase mimic towards *O*-phenylenediamine (OPD) was in detail investigated. Experimental results revealed that the oxidase-like activity of Cu^{2+} ions is substantially higher than that of Cu/CuO nanoparticles. On the basis of these findings, a simple, highly sensitive and selective PL sensing platform for His could be developed, with a limit of detection (LOD) as low as 0.33 μM. Furthermore, the experiments of His recovery in human urine samples were successfully conducted by employing the established sensing system with satisfactory results.

Introduction

Histidine (His) is one of natural α-amino acids, which acts as an important constituent of proteins. His containing an imidazole moiety can function as a neurotransmitter and a regulator of metal transmission in the biological systems.[1] Deficiency of His results in the impaired nutritional state in patients with chronic kidney disease.[2] Therefore, developing highly selective and sensitive methods for detecting His is of importance due to its biological significance. Until now, a number of approaches have been developed for the detection of His, including high-performance liquid chromatography, electrochemistry, UV-vis absorption spectra, photoluminescence (PL) spectra.[3-14] In particular, constructing PL based sensors have recently attracted considerable attentions due to the high sensitivity of PL spectrometry. Most of these reported investigations of probing His focused on metal-complexes,[15-17] particularly Cu^{2+}-complexes,[18-22] as chemosensing ensembles, which could promise a high selectivity towards His. However, the procedures of preparing metal-complexes in general are tedious, time-consuming and troublesome, and employed organic solvents are environmentally unfriendly. Therefore, it is of importance to develop a novel, simple, highly sensitive and selective PL sensor for His.

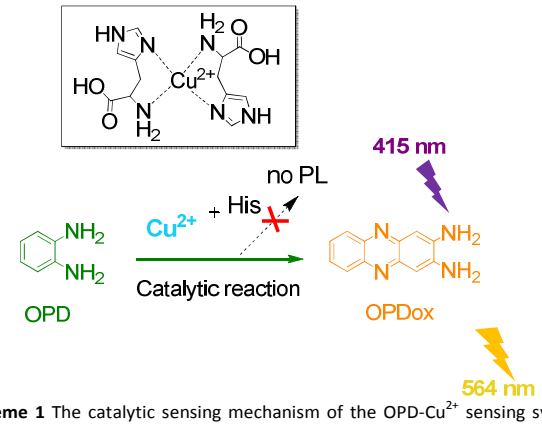
Artificial enzyme mimics have recently become a very important and exciting branch of biomimetic chemistry,[23, 24] since that, (1) they can serve as highly stable and low-cost alternatives to natural enzymes; (2) quite a number of artificial enzyme mimics have been found and prepared. Therefore, a wide range of applications of artificial enzyme mimics have been explored.[25-29] In particular, numerous nanomaterials have been developed for serving as artificial enzyme mimics with oxidase-, peroxidase- and catalase-like activity,[30-36] which were widely employed in the field of chemo-/biosensing by means of PL or UV-vis absorption spectra for the detection of a series of targets including metal ions, anions, toxic substance and biomolecules. Recently, we found that Fe^{3+} ions possess much higher peroxidase-like activity than that of Fe_3O_4 magnetic nanoparticles.[37] Therefore, as the counterpart of Fe^{3+} ions, are Cu^{2+} ions having similar peroxidase-like or oxidase-like activity? However, to the best of our knowledge, such investigation is lack at present. Furthermore, it should be noted that, although several Cu^{2+}-complexes have been employed as PL sensors for His based on the displacement mechanism, developing the sensing system for His, relying on the catalytic reaction of artificial enzyme mimics, has not been reported so far.

Herein, we employed Cu^{2+} ions as the oxidase mimic for catalysing the oxidation of *O*-phenylenediamine (OPD) to form a photoluminescent compound. The oxidase-like activity of Cu^{2+} ions was found to be higher than that of Cu/CuO nanoparticles. Introducing a certain amount of His could significantly suppress the oxidation reaction of OPD catalysed by Cu^{2+} ions, due to the specific strong interaction between His and Cu^{2+} ions (Scheme 1). Good linear relationship between PL intensity and His concentration could be established, and a limit of detection (LOD) was calculated to be sub μM level. High selectivity has also been revealed by performing control experiments of other 19 natural α-amino acids, although

[a,a] *Key Laboratory of Urban Pollutant Conversion, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen, 361021, China. E-mail: jsshen@hqu.edu.cn; hwzhang@iue.ac.cn*
[b,b] *College of Materials Science and Engineering, Huaqiao University, Xiamen, 361021, China*
† Footnotes relating to the title and/or authors should appear here.
Electronic Supplementary Information (ESI) available: Electronic supplementary information (ESI) available: Fig. S1–S10. See DOI: 10.1039/x0xx00000x

View Article Online
DOI: 10.1039/C5RA17900A

cysteine showed somewhat interference due to it bearing one thiol group with strong binding capacity towards most of transition heavy metal ions. The experiments of His recovery in human urine samples were further performed by employing the established sensing system, and satisfactory results could be obtained.



Scheme 1 The catalytic sensing mechanism of the OPD-Cu^{2+} sensing system for His.

Experimental Section

Materials and Instruments

Materials. OPD (98.5%, AR), HOAc (99.5%, AR), NaOAc (99%, AR), $Cu(CH_3COO)_2.H_2O$ (99%, AR), HCl (36%-38%, AR), Tris(hydroxymethyl) aminomethane (Tris, BR), acetonitrile (99%, AR), ascorbic acid, and other inorganic salts were purchased from Guo Yao (Shanghai, China). 3, 3', 5, 5'-tetramethyl benzidine (TMB, 99%), amino acids (L-form), and other biomolecules were purchased from Sigma-Aldrich. *p*-Acetoamidophenol was obtained from Aladin. All chemicals were used in the experiments without further purification. All solutions were prepared with ultrapure water purified by a Milli-Q system.

Instruments. PL spectra were recorded by a F-4600 Fluorescence spectrophotometer. Transmission electron microscopy (TEM) experiments were done on a HITACHI H-7650 system. The Cu content of the CuO nanoparticles solution was obtained using a Thermo ELECTRON CORPORATION M6. X-Ray power diffractions (XRD) were performed on Panalytical X'pert PRO diffractometer equipped with Cu κα radiation (λ=1.5418Å).

Procedures

Measurements of oxidase-like Activity. To investigate the oxidase-like activity of Cu^{2+} ions, the catalytic oxidation of OPD was carried out in the 50 mM Tris-HCl buffer solution of pH 7.4 containing 15% acetonitrile (by volume). In a typical experiment, 100 μL 5 mM OPD and 10 μL 50 μM Cu^{2+} ions solutions were added into 890 μL 50 mM Tris-HCl buffer solution of pH 7.4 containing 15 % acetonitrile (by volume). Then, the mixed solution reacted at 65 ^{o}C for 1 h. After the resulting solution was cooled to room temperature, the measurements of PL spectra were conducted by a F-4600 Fluorescence spectrophotometer with an excitation wavelength at 415 nm. To investigate the effects of reaction time, pH, temperature, OPD concentration, Cu^{2+} ions concentration and the volume ratio of acetonitrile in the buffer solution (v/v, %), PL intensity at 564 nm was measured when reaction time was changed from 10 min to 90 min, pH was adjusted from 4.8 to 8.5, the temperature was varied from 25 ^{o}C to 80 ^{o}C, OPD concentration was varied from 0.1 mM to 3 mM, Cu^{2+} ions concentration was changed from 0.05 μM to 5 μM, and the volume ratio of acetonitrile in the buffer solution was varied from 5 % to 30 %, respectively. Error bars were obtained by measuring three parallel solutions.

Sensing His. For sensing His, firstly, a certain amount of Cu^{2+} ions solution and a certain amount of His stock solution were mixed for 10 min (the results of relationship between the interaction time and PL intensity at 564 nm of the sensing system was shown as in Fig. S1), then, the mixed solution was introduced into 50 mM Tris-HCl buffer solution of pH 7.4 containing 15 % acetonitrile (by volume) and 0.5 mM OPD. The resulting solution reacted at 65 ^{o}C for 1 h. After the resulting solution was cooled to room temperature, measurements of PL spectra were conducted by a F-4600 Fluorescence spectrophotometer. To investigate the sensing selectivity, other 19 natural α-amino acids employed their L-form and other biomolecules were also tested in this sensing system and their concentrations were 15 μM. Error bars were obtained by measuring three parallel solutions.

His recovery in Human Urine samples. Human urine samples were collected from healthy volunteers, and no additional pretreatment was required, except for directly diluted with ultrapure water. 1 mL urine sample was transferred to 5.0 mL centrifuge tube, then 10 μL His solution and 490 μL ultrapure water were added to obtain a total volume of 1.5 mL, resulting in that spiked His concentrations in the tubes were 0 (blank sample), 400, 800 μM, respectively. To detect His in diluted urine samples, a certain amount of Cu^{2+} ions solution and 10 μL spiked urine were mixed for 10 min, then, the mixed solution was introduced into 50 mM Tris-HCl buffer solution of pH 7.4 containing 15% acetonitrile (by volume) and 0.5 mM OPD, to afford a total volume of 1 mL. The reaction solution reacted at 65 ^{o}C for 1 h. After the resulting solution was cooled to room temperature, measurements of PL spectra were conducted by a F-4600 Fluorescence spectrophotometer.

Synthesis of CuO nanoparticles. The cupric oxide nanoparticles were prepared *via* a previously reported quick-precipitation method.[35] 1.0083 g copper acetate was dissolved in 150 mL ultrapure water, and then the solution was mixed with 0.5 mL glacial acetic acid in a round-bottomed flask equipped with a refluxing device. The solution was heated to boil under vigorous stirring. Then, 10 mL 0.08 g. mL^{-1} NaOH aqueous

View Article Online
DOI: 10.1039/C5RA17900A

solution was rapidly added to the above mentioned boiled solution, where a large amount of black precipitates immediately formed. The precipitates were centrifuged, washed three times with ethanol, and dried by air at room temperature.

Measurement of the total Cu content of CuO nanoparticles solution. The total Cu content of CuO nanoparticles solution was analysed by a flame atomic absorption spectrometry. The CuO nanoparticles stock solution was prepared by adding certain volumes of HCl solution (1.2 M) for ensuring that CuO was completely converted into Cu^{2+} ions. The Cu standard solutions with five different concentrations were employed to obtain the calibration curve, and then the Cu content of the nanoparticles solution was calculated by measuring three parallel solutions of CuO nanoparticles.

Results and discussion

The oxidase-like activity of Cu^{2+} ions was firstly investigated by employing OPD, TMB and *p*-Acetoamidophenol as the substrates, respectively. It was found that, when 0.5 μM Cu^{2+} ions was introduced into 50 mM Tris-HCl buffer solution of pH 7.4 containing 15 % acetonitrile (by volume) and 0.5 mM OPD under 65 ^{o}C of temperature, the original colourless solution gradually turned into light yellow, and the resulting solution could change to emit yellow light from its original nonfluorescent under a 365 nm UV lamp (Fig. 1b, c). This observation revealed that Cu^{2+} ions can possess the extraordinary oxidase-like activity, similar to that of metal or metal oxides/sulfides nanomaterials.[35, 38-40] This catalytic reaction would be greatly suppressed if Cu^{2+} ions or oxygen in the measured solution were absent (the results of the control experiments of free dissolved oxygen were shown in Fig. S2). However, for TMB employed as the substrate, neither obvious colour substances, nor fluorescent substances, could be observed, under similar experimental conditions. For *p*-Acetoamidophenol catalysed by Cu^{2+} ions, only very weak PL emission could be observed. Furthermore, PL / UV-vis absorption spectra supported these observations (Fig. 1a). For OPD as the substrate, maximum wavelength of PL emission spectrum could be obtained at 564 nm (Fig. 1a, black line). The reaction time-dependent PL intensity at 564 nm of the OPD–Cu^{2+} system was showed in Fig. 2.

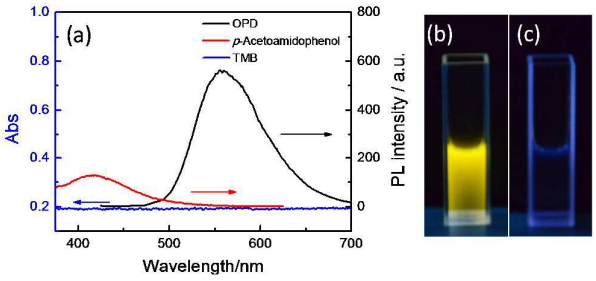


Fig. 1 PL spectra of OPD (black line, λ_{ex}=415 nm) and *p*-Acetoamidophenol (red line, λ_{ex}=330 nm), and UV-vis absorption spectrum of TMB (blue line) catalysed by Cu^{2+} ions (a). Typical PL photographs of OPD catalysed by Cu^{2+} ions (b), and of original OPD (c), illuminated by 365 nm UV lamp in dark room. Experimental conditions: OPD, *p*-Acetamidophenol and TMB concentration were set to be 0.5 mM; temperature of 65 ^{o}C; 50 mM Tris-HCl buffer solution of pH 7.4 containing 15% acetonitrile (by volume); the reaction time of 1 h.

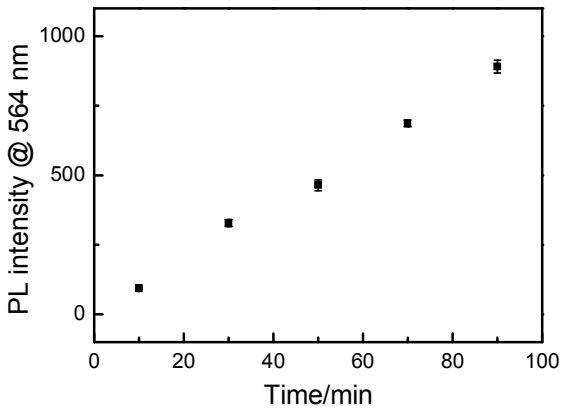


Fig. 2 Reaction time-dependent oxidase-like activity of Cu^{2+} ions towards OPD. Experimental conditions: [OPD] = 0.5 mM; [Cu^{2+} ions] = 0.5 μM; temperature of 65 ^{o}C; 50 mM Tris-HCl buffer solution of pH 7.4 containing 15% acetonitrile (by volume).

The catalytic activity of Cu^{2+} ions towards OPD was found to be dependent on pH, temperature, OPD and Cu^{2+} ions concentrations, too (Fig.3-6). pH effect on the catalytic activity of Cu^{2+} ions showed a change tendency, in which the catalytic activity first enhanced and then decreased, when pH was increased from 4.7 to 8.5 (Fig. 3), indicated by the change of PL intensity at 564 nm with varying pH. Taken together pH of the biological condition, 50 mM Tris-HCl buffer solution of pH 7.4 was thus employed in further experiments. When the temperature was set from 25 ^{o}C to 80 ^{o}C, the catalytic activity demonstrated an enhancement (Fig. 4). Furthermore, the effect of OPD concentration was investigated, and the results were showed in Fig. 5. Experimental results revealed that, when OPD concentration was changed from 0.1 mM to 3.0 mM, PL intensity at 564 nm gradually enhanced with increasing OPD concentration. The effect of Cu^{2+} ions concentration also indicated that, with increasing Cu^{2+} ions concentration from 0.05 μM to 5 μM, not only accelerating reaction, but also enhancement of PL intensity, could be observed (Fig. 6). Importantly, even if Cu^{2+} ions concentration was lowered to 0.1 μM which was 3 orders of magnitude lower than that of OPD fixed at 0.5 mM, a significant reaction could still occur, indicative of the extremely high oxidase-like activity of Cu^{2+} ions towards OPD. It should be noted that, we recently reported that Fe^{3+} ions possess much higher peroxidase-like activity than that of Fe_3O_4 nanoparticles.[37]

Similarly, in the absence of Cu^{2+} ions, the time, pH and temperature effect on the PL intensity of only OPD system were investigated, too. It was revealed that, the changes were similar to those of cases in the presence of Cu^{2+} ions (Fig. S3-S5), besides PL intensity at 564 nm was significantly lowered.

View Article Online
DOI: 10.1039/C5RA17900A

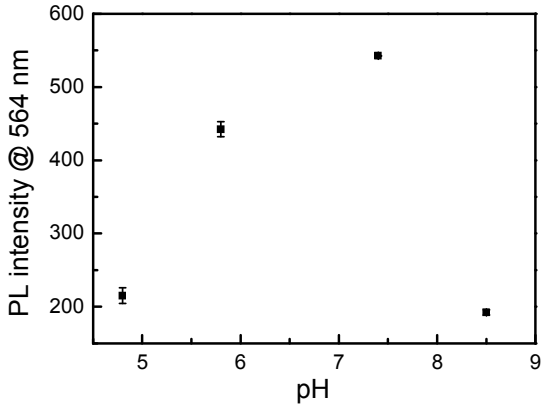


Fig.3 pH-dependent oxidase-like activity of Cu^{2+} ions towards OPD. Experimental conditions: [OPD] = 0.5 mM; [Cu^{2+} ions] = 0.5 μM; temperature of 65 ^{o}C; buffer solution of varied pH containing 15% acetonitrile (by volume); the reaction time of 1 h.

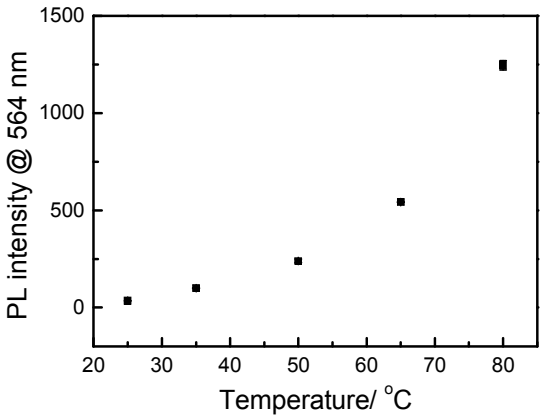


Fig. 4 Temperature-dependent oxidase-like activity of Cu^{2+} ions towards OPD. Experimental conditions: [OPD] = 0.5 mM; [Cu^{2+} ions] = 0.5 μM; 50 mM Tris-HCl buffer solution of pH 7.4 containing 15% acetonitrile (by volume); the reaction time of 1 h.

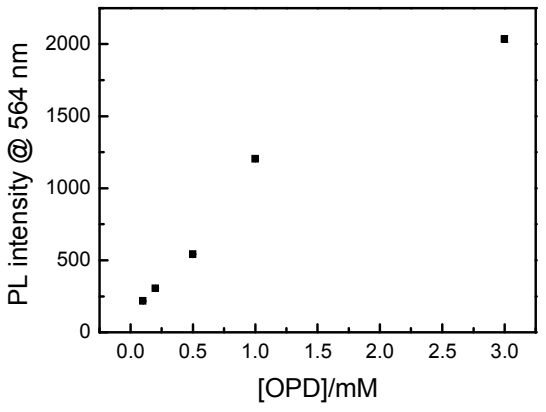


Fig. 5 The relationship between PL intensity @ 564 nm and OPD concentration. Experimental conditions: [Cu^{2+} ions] = 0.5 μM; temperature of 65 ^{o}C; 50 mM Tris-HCl buffer solution of pH 7.4 containing 15% acetonitrile (by volume); the reaction time of 1 h.

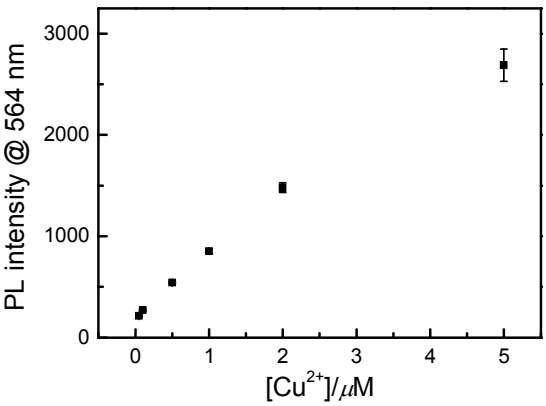


Fig. 6 The relationship between PL intensity @ 564 nm and Cu^{2+} ions concentration. Experimental conditions: [OPD] = 0.5 mM; temperature of 65 ^{o}C; 50 mM Tris-HCl buffer solution of pH 7.4 containing 15% acetonitrile (by volume); the reaction time of 1 h.

We suggested that the reversible conversion between Cu^{2+} and Cu^{+} ions was responsible for the observable catalytic activity of Cu^{2+} ions. Since in traditional inorganic chemistry it is well known that, Cu^{+} ions can be stabilized by the weak coordination of acetonitrile,[41, 42] introducing acetonitrile into this catalytic system was expected to be helpful for stabilizing Cu^{+} ions. This suggestion was supported by the experiment of the effect of volume ratio of acetonitrile to buffer aqueous (v/v, %) on the catalytic activity of Cu^{2+} ions. Experimental results exhibited that, the catalytic activity of Cu^{2+} ions was substantially enhanced when the volume ratio was changed from 0 to 15 %, however, further increasing the volume ratio could lead to the decrease of the catalytic activity (Fig.7). The decrease of the catalytic activity of Cu^{2+} ions caused by the addition of excessive acetonitrile should originate from that the redox potential of the catalyst generally decreased when polarity of the solvent was lowered. Therefore, 15 % acetonitrile content (by volume) was chosen to obtain preferable catalytic activity of Cu^{2+} ions in the related experiments.

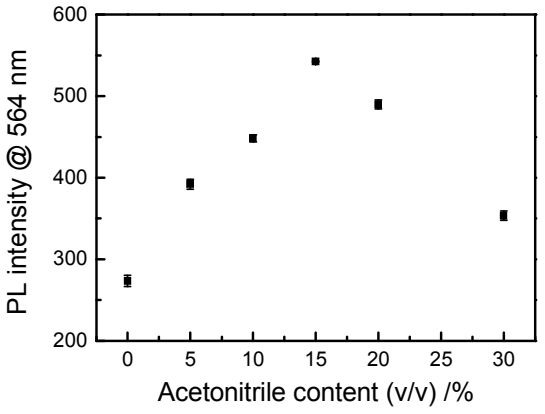


Fig. 7 Acetonitrile content (by volume) -dependent oxidase-like activity of Cu^{2+} ions towards OPD. Experimental conditions: [Cu^{2+} ions] = 0.5 μM; [OPD]

View Article Online
DOI: 10.1039/C5RA17900A

= 0.5 mM; temperature of 65 °C; 50 mM Tris-HCl buffer solution of pH 7.4 containing varied acetonitrile content (by volume); the reaction time of 1 h.

It is known that, the stability of Cu nanoparticles is usually poor, and Cu nanoparticles are easy to be converted into CuO nanoparticles when Cu nanoparticles aqueous solution contains oxygen. Therefore, it was wondered that whether CuO nanoparticles have similar catalytic performance towards OPD compared with that of Cu^{2+} ions? Experimental results revealed that, OPD could be catalysed by CuO nanoparticles (the results of XRD and TEM characterization were shown in Fig.S6-S7)[35] to form an oxidation production, too, similar to that of the case of Cu^{2+} ions. This result has also been observed by other groups.[33] However, when Cu^{2+} ions concentration in copper salt and Cu content of CuO nanoparticles solution were set to be exactly same, the catalytic activity of CuO nanoparticles was found to be significantly poorer than that of Cu^{2+} ions (Fig. 8). Furthermore, the catalytic activity of Cu^{2+} ions obviously decreased when a certain amount of ascorbic acid was added to the OPD– Cu^{2+} catalytic system (Fig. 9), because ascorbic acid could fast reduce Cu^{2+} ions to *in situ* form Cu/CuO nanoparticles (Fig. S8). This observation further supported that the catalytic activity of Cu^{2+} ions is superior to that of CuO nanoparticles. It should be noted that, likely only the superficial copper (unbinding or binding Cu^{2+} ions) in the surface of nanoparticles could act as catalysts for catalysing the oxidation reaction of OPD, similar to our recent observations.[37]

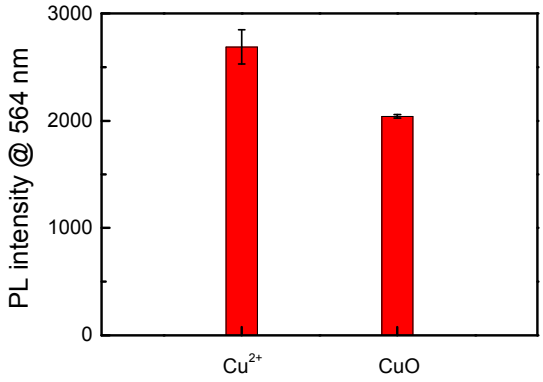


Fig. 8 Comparison of the oxidase-like activity of Cu^{2+} ions and CuO nanoparticles towards OPD. Experimental conditions: both Cu^{2+} ions concentration in copper salt and Cu content of CuO nanoparticles solution were set to be same, 5 μM; [OPD] = 0.5 mM; temperature of 65 °C; 50 mM Tris-HCl buffer solution of pH 7.4 containing 15% acetonitrile (by volume); the reaction time of 1 h.

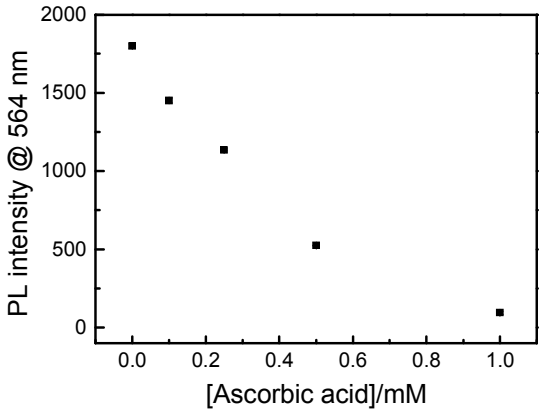


Fig. 9 The effect of ascorbic acid concentration on the oxidase-like activity of Cu^{2+} ions towards OPD. Experimental conditions: [Cu^{2+} ions] = 3 μM; [OPD] = 0.5 mM; temperature of 65 °C; 50 mM Tris-HCl buffer solution of pH 7.4 containing 15% acetonitrile (by volume); the reaction time of 1 h.

Considering the strong complexation capability of His towards Cu^{2+} ions, the catalytic reaction of the OPD– Cu^{2+} system should be inhibited by adding His. Indeed, it was found that, introducing a certain amount of His, the oxidation reaction of OPD catalysed by Cu^{2+} ions was His concentration-dependent. As shown in Fig. 10, the catalytic oxidation reaction was gradually suppressed with increasing His concentration, and good linear relationship was found between [His] and the PL intensity at 564 nm wavelength. The linear correlation of PL =414.7–16.8 [His] (R^2= 0.991) was obtained over the tested concentration range of His from 0.5 to 30 μM when 0.5 μM Cu^{2+} ions was employed. The limit of detection (LOD) for His was estimated to be 0.47 μM ($3\sigma/k$, n = 11). Decreasing Cu^{2+} ions concentration to 0.1 μM, LOD of this sensing system for His was lowered to be 0.33 μM (Fig. S9). These LODs were much lower than those of most of reported cases.[43-45] The inhibition of the catalytic reaction should be ascribed to forming Cu^{2+}-2His compounds due to high stability constant of Cu^{2+}-His, which could result in reducing the amount of unbound Cu^{2+} ions.[46, 47] Other 19 natural α-amino acids were employed to test the selectivity of this sensing system. The results showed that, under similar experimental conditions, employing other amino acids did not suppress the catalytic reaction, besides that, cysteine bearing a thiol group showed somewhat interference, since it has strong binding capacity towards most of transition heavy metal ions (Fig. 11). Furthermore, other structurally similar biomolecules such as Adenine and Cytosine were employed for conducting control experiments, too, and the results revealed that PL spectral interferences were hardly observed (Fig. S10). This result indicated that this established sensing system has good selectivity. A comparison of our present sensing system and other reported references were summarized, as shown in Table 1. Compared with tedious and troublesome synthesis of receptors or expensive instruments in the reported references, our present sensing system shows some merits of simplicity, facile operation, and sensitivity.

View Article Online
DOI: 10.1039/C5RA17900A

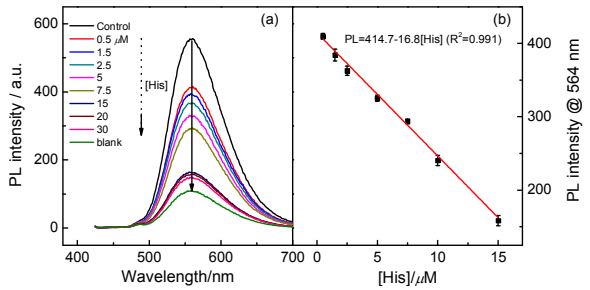


Fig. 10 His concentration-dependent PL intensity changes at 564 nm wavelength of the Cu^{2+}–OPD system (a), and linear relationship plot between PL intensity at 564 nm and His concentration (b). The reaction time was set as 1 h. [Cu^{2+} ions] = 0.5 μM; [OPD] = 0.5 mM; temperature of 65 ^{o}C; 50 mM Tris-HCl buffer solution of pH 7.4 containing 15% acetonitrile (by volume).

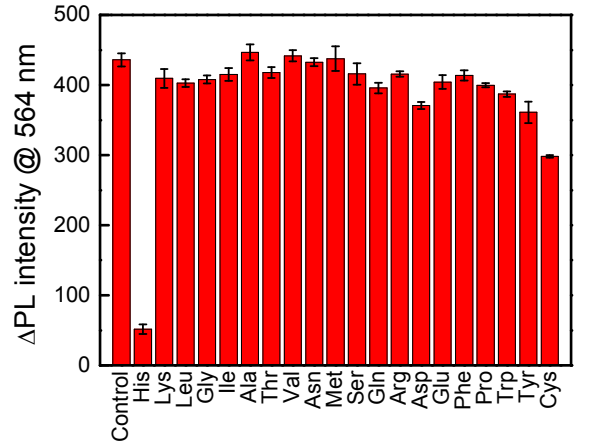


Fig. 11 The difference of ΔPL intensity at 564 nm wavelength of the Cu^{2+}–OPD system in the presence of His and other 19 amino acids, respectively. The reaction time was set as 1 h. His and other amino acids concentrations were 15 μM; [Cu^{2+} ions] = 0.5 μM; [OPD] = 0.5 mM; temperature of 65 ^{o}C; 50 mM Tris-HCl buffer solution of pH 7.4 containing 15% acetonitrile (by volume). Note that, ΔPL was obtained from that the PL intensity at 564 nm of every group subtracted that of blank (the OPD system in the absence of Cu^{2+} ions).

To evaluate the applicability, the experiments of His recovery in human urine samples were performed by employing our present sensing system. Two human urine samples were collected, and detailed experimental operation was referred to the experimental section. As shown in Table 2, the quantitative recoveries (96.3% to 102.5%) of spiked His have revealed that this sensing system can have good practical sensing application. Meanwhile, affording His concentration (402 to 610.5 μM) in the human urine samples are consistent with its normal levels (normal level, 130-2100 μM in urine)[48] and that by other developed sensors.[43, 48, 49]

Table 1 Comparison of the LODs of reported references and our present work

No.	Ref.	Method	LOD (μM)
1	[50]	HPLC	1.1
2	[51]	Capillary electrophoresis	0.14
3	[52]	Electrochemical analysis	5
4	[53]	CL	0.1
5	[54]	PL	0.3
6	[44]	PL	1.6
7	This work	PL	0.33

Table 2 His recovery experiments in the diluted human urine samples (n = 3)

Sample	Spiked /μM	Measured /μM	Recovery /%	Found concentration /μM
Sample A	0	2.68±0.07		402.0±9.8
	4	4.10±0.18	102.5±4.5	
	8	7.70±0.05	96.3±0.7	
Sample B	0	4.07±0.16		610.5±23.7
	4	3.88±0.11	97.0±2.8	
	8	8.13±0.11	101.6±1.4	

Note that, the urine sample A and sample B were directly diluted to 150 times by 50 mM Tris-HCl buffer solution of pH 7.4.

Conclusion

Cu^{2+} ions could be employed as the oxidase mimic to catalyse the oxidation reaction of OPD to "turn on" its PL. The catalytic reaction was investigated in detail for obtaining optimal experimental conditions. It was found that, when OPD was employed as the substrate, the oxidase-like activity of Cu^{2+} ions was substantially better than that of Cu/CuO nanoparticles. Due to the strong binding of His towards Cu^{2+} ions, a simple, highly selective and sensitive sensing platform was thus established for His. Furthermore, this sensing system was successfully employed for detecting His in the human urine samples with satisfactory His recovery. All in all, the PL sensing system for His established in this work has several intriguing enlightenments: (i) Cu^{2+} ions serving as the oxidase mimic is much more simple and stable, compared with its nanomaterials counterparts such as Cu/CuO nanoparticles, because the preparation procedures of nanomaterials are in general troublesome and most of nanomaterials are intrinsic instable during storage and preparation; (ii) our experimental results can afford much more useful insights for the nature of the observed oxidase/peroxidase-like activity of Cu/CuO nanoparticles.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grants no. 21377124), and by the project of new faculty of Huaqiao University (Grant no. 15BS202).

View Article Online
DOI: 10.1039/C5RA17900A

Notes and references

1. Y. Kusakari, S. Nishikawa, S.-i. Ishiguro and M. Tamai, *Current eye research*, 1997, **16**, 600-604.
2. M. Watanabe, M. E. Suliman, A. R. Qureshi, E. Garcia-Lopez, P. Bárány, O. Heimbürger, P. Stenvinkel and B. Lindholm, *The American journal of clinical nutrition*, 2008, **87**, 1860-1866.
3. N. Tateda, K. Matsuhisa, K. Hasebe, N. Kitajima and T. Miura, *Journal of Chromatography B: Biomedical Sciences and Applications*, 1998, **718**, 235-241.
4. R. P. Deo, N. S. Lawrence and J. Wang, *Analyst*, 2004, **129**, 1076-1081.
5. F. Darain, C. Ban and Y.-B. Shim, *Biosensors and Bioelectronics*, 2004, **20**, 857-863.
6. Z. Huang, J. Du, J. Zhang, X.-Q. Yu and L. Pu, *Chemical communications*, 2012, **48**, 3412-3414.
7. P. G. Sutariya, A. Pandya, A. Lodha and S. K. Menon, *Analyst*, 2014, **139**, 4794-4798.
8. D. L. Ma, W. L. Wong, W. H. Chung, F. Y. Chan, P. K. So, T. S. Lai, Z. Y. Zhou, Y. C. Leung and K. Y. Wong, *Angewandte Chemie*, 2008, **120**, 3795-3799.
9. A. Buryak and K. Severin, *Angewandte Chemie*, 2004, **116**, 4875-4878.
10. Y. Zhou and J. Yoon, *Chemical Society reviews*, 2012, **41**, 52-67.
11. E. Oliveira, C. Santos, P. Poeta, J. L. Capelo and C. Lodeiro, *Analyst*, 2013, **138**, 3642-3645.
12. R. M. Kong, X. B. Zhang, Z. Chen, H. M. Meng, Z. L. Song, W. Tan, G. L. Shen and R. Q. Yu, *Analytical chemistry*, 2011, **83**, 7603-7607.
13. X. Lou, L. Zhang, J. Qin and Z. Li, *Langmuir*, 2010, **26**, 1566-1569.
14. H. Li and Y. Bian, *Nanotechnology*, 2009, **20**, 145502.
15. J. Du, Z. Huang, X.-Q. Yu and L. Pu, *Chemical communications*, 2013, **49**, 5399-5401.
16. Q.-H. You, A. W.-M. Lee, W.-H. Chan, X.-M. Zhu and K. C.-F. Leung, *Chemical communications*, 2014, **50**, 6207-6210.
17. Y. He, X. Wang, J. Zhu, S. Zhong and G. Song, *Analyst*, 2012, **137**, 4005-4009.
18. H. Agarwalla, N. Taye, S. Ghorai, S. Chattopadhyay and A. Das, *Chemical communications*, 2014, **50**, 9899-9902.
19. B. Wang, Y. Gao, H.-W. Li, Z.-P. Hu and Y. Wu, *Org. Biomol. Chem.*, 2011, **9**, 4032-4034.
20. Y. Zhou, T. Zhou, M. Zhang and G. Shi, *Analyst*, 2014, **139**, 3122-3126.
21. J.-T. Hou, K. Li, K.-K. Yu, M.-Y. Wu and X.-Q. Yu, *Organic & biomolecular chemistry*, 2013, **11**, 717-720.
22. J. Sun, F. Yang, D. Zhao, C. Chen and X. Yang, *ACS applied materials & interfaces*, 2015, **7**, 6860-6866.
23. H. Wei and E. Wang, *Chemical Society reviews*, 2013, **42**, 6060-6093.
24. Y. Lin, J. Ren and X. Qu, *Accounts of chemical research*, 2014, **47**, 1097-1105.
25. A. Singh, S. Patra, J.-A. Lee, K. H. Park and H. Yang, *Biosensors and Bioelectronics*, 2011, **26**, 4798-4803.
26. K. S. McKeating, S. Sloan-Dennison, D. Graham and K. Faulds, *Analyst*, 2013, **138**, 6347-6353.
27. W. Shi, Q. Wang, Y. Long, Z. Cheng, S. Chen, H. Zheng and Y. Huang, *Chemical communications*, 2011, **47**, 6695-6697.
28. G.-L. Wang, X.-F. Xu, L. Qiu, Y.-M. Dong, Z.-J. Li and C. Zhang, *ACS applied materials & interfaces*, 2014, **6**, 6434-6442.
29. Y. Song, K. Qu, C. Zhao, J. Ren and X. Qu, *Advanced Materials*, 2010, **22**, 2206-2210.
30. A. Asati, S. Santra, C. Kaittanis, S. Nath and J. M. Perez, *Angewandte Chemie International Edition*, 2009, **48**, 2308-2312.
31. A. Asati, C. Kaittanis, S. Santra and J. M. Perez, *Analytical chemistry*, 2011, **83**, 2547-2553.
32. M. Liang, K. Fan, Y. Pan, H. Jiang, F. Wang, D. Yang, D. Lu, J. Feng, J. Zhao and L. Yang, *Analytical chemistry*, 2012, **85**, 308-312.
33. X. Yang and E. Wang, *Analytical chemistry*, 2011, **83**, 5005-5011.
34. D. Zhao, Y. Zheng, M. Li, S. A. Baig, D. Wu and X. Xu, *Ultrasonics sonochemistry*, 2014, **21**, 1714-1721.
35. W. Chen, J. Chen, Y.-B. Feng, L. Hong, Q.-Y. Chen, L.-F. Wu, X.-H. Lin and X.-H. Xia, *Analyst*, 2012, **137**, 1706-1712.
36. Z. Wang, X. Yang, J. Yang, Y. Jiang and N. He, *Analytica chimica acta*, 2015, **862**, 53-63.
37. X.-Q. Wu, Y. Xu, Y.-L. Chen, H. Zhao, H.-J. Cui, J.-S. Shen and H.-W. Zhang, *RSC Advances*, 2014, **4**, 64438-64442.
38. W. Chen, L. Hong, A.-L. Liu, J.-Q. Liu, X.-H. Lin and X.-H. Xia, *Talanta*, 2012, **99**, 643-648.
39. W. He, H. Jia, X. Li, Y. Lei, J. Li, H. Zhao, L. Mi, L. Zhang and Z. Zheng, *Nanoscale*, 2012, **4**, 3501-3506.
40. W. Chen, J. Chen, A. L. Liu, L. M. Wang, G. W. Li and X. H. Lin, *ChemCatChem*, 2011, **3**, 1151-1154.
41. M. Meyer, A.-M. Albrecht-Gary, C. O. Dietrich-Buchecker and J.-P. Sauvage, *Inorganic Chemistry*, 1999, **38**, 2279-2287.
42. J. Eersels, J. Mertens and J. Herscheid, *Journal of Radioanalytical and Nuclear Chemistry*, 2011, **288**, 291-296.
43. W. Bian, F. Wang, Y. Wei, L. Wang, Q. Liu, W. Dong, S. Shuang and M. M. Choi, *Analytica chimica acta*, 2015, **856**, 82-89.
44. X. Wang, Q. Miao, T. Song, Q. Yuan, J. Gao and G. Liang, *Analyst*, 2014, **139**, 3360-3364.
45. X. Huang, Y. Lin, J. Chen, Y. Chen, Y. Li and W. Gao, *New Journal of Chemistry*, 2015.
46. T. P. Kruck and B. Sarkar, *Canadian Journal of Chemistry*, 1973, **51**, 3563-3571.
47. R. Leberman and B. Rabin, *Transactions of the Faraday Society*, 1959, **55**, 1660-1670.
48. P. M. Kovach and M. Meyerhoff, *Analytical chemistry*, 1982, **54**, 217-220.
49. P. Wu and X.-P. Yan, *Biosensors and Bioelectronics*, 2010, **26**, 485-490.
50. S. Wadud, M. M. Or-Rashid and R. Onodera, *Journal of Chromatography B*, 2002, **767**, 369-374.
51. J. Meng, W. Zhang, C.-X. Cao, L.-Y. Fan, J. Wu and Q.-L. Wang, *Analyst*, 2010, **135**, 1592-1599.
52. M. K. Amini, S. Shahrokhian and S. Tangestaninejad, *Analytical chemistry*, 1999, **71**, 2502-2505.
53. M. Hosseini, M. R. Ganjali, Z. Vaezi, B. Arabsorkhi, M. Dadmehr, F. Faridbod and P. Norouzi, *Sensors and Actuators B: Chemical*, 2015, **210**, 349-354.
54. Y. He, X. Wang, J. Zhu, S. Zhong and G. Song, *Analyst*, 2012, **137**, 4005-4009.

View Article Online
DOI: 10.1039/C5RA17900A

Highly selective and sensitive recognition of histidine based on the oxidase–like activity of Cu^{2+} ions

Yan Xu,[a] Xiao-Qiong Wu,[a] Jiang-Shan Shen,[a,b*] and Hong-Wu Zhang[a*]

[a] Key Laboratory of Urban Pollutant Conversion, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen, 361021, China.

[b]College of Materials Science and Engineering, Huaqiao University, Xiamen 361021, China.

E-mail: jsshen@hqu.edu.cn; hwzhang@iue.ac.cn; Fax: +86-592-619-0773; Tel: +86-592-619-0773

A simple, highly sensitive and selective PL sensing platform for histidine have been developed, based on the oxidase–like activity of Cu^{2+} ions.