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# MnO<sub>2</sub> *in situ* formed into the pores of C-dots/ZIF-8 hybrid nanocomposites as an effective quencher for fluorescence sensing ascorbic acid†

Guangming Li,<sup>ab</sup> Nan Lv,<sup>ab</sup> Jilin Zhang<sup>\*a</sup> and Jiazuan Ni<sup>a</sup>

A sensitive fluorescent nanosensor based on MnO<sub>2</sub> quenching fluorescent carbon quantum dots was facilely developed by MnO<sub>2</sub> *in situ* formed in the pores of C-dots/ZIF-8 hybrid nanocomposite. The C-dots/ZIF-8 hybrid nanocomposite was synthesized *via* a rapid method within 5 min at room temperature. Then, the MnO<sub>2</sub> was directly incorporated into the ZIF-8 framework *via* redox reaction between the C-dots/ZIF-8 hybrid nanocomposite and KMnO<sub>4</sub>. The resulting fluorescent nanosensor exhibited a relatively uniform particle size of about 100 nm, good water-dispersibility and a highly selective fluorescence response toward ascorbic acid with a detection limit as low as 83 nM and a linear range of 0.5–8 μM.

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## Introduction

Zeolitic imidazolate frameworks (ZIFs) are a subclass of metal-organic frameworks consisting of tetrahedral transition metal ions (zinc/cobalt) bridged by imidazole or imidazolate type linkers. As one of the most promising MOFs, ZIF-8 has received great attention because of its large surface area, unique pore volume, easy preparation, and good water dispersibility.<sup>1,2</sup> When scaled down to the nanoscale level, it can give rise to novel applications in fluorescent probes, delivery vehicles, and therapeutic agents.<sup>3</sup> For example, the fluorescent probe of copper ions has been synthesized by encapsulating BPEI functionalized photoluminescence (PL) carbon dots (C-dots) into the ZIF-8 MOFs.<sup>4</sup> Research results indicated that the accumulation effect of ZIF-8 MOFs can greatly amplify the sensing signal from the C-dots. However, the process of encapsulation is time-consuming (*e.g.* 24 h),<sup>4</sup> and it thus needs to be improved. To date, the hybrid nanocomposites based on ZIF-8 MOFs have shown remarkable properties depending on the incorporated foreign nanoparticles with versatile functions. In most cases, an *in situ* ZIF-8 crystal growth route for construction of the hybrid nanocomposites was applied using foreign nanoparticles as a template.<sup>5–9</sup> However, such hybrid nanocomposites constructed using ZIF-8 as a matrix and the foreign nanoparticles *in situ* formed in the pores of the ZIF-8 are rarely reported, which may be more suitable for those foreign nanoparticles whose morphology and stability cannot be easily controlled.

Recently, manganese dioxide (MnO<sub>2</sub>) has been demonstrated to be particularly attractive for bio-applications due to their wide absorption band, redox activity, and good biocompatibility.<sup>10,11</sup> By taking advantage of their broad absorption spectrum (250–550 nm), which overlaps with the fluorescence excitation and/or emission spectra of most types of fluorescent dyes, MnO<sub>2</sub> has been widely studied as a rational quencher for fluorescent sensing systems.<sup>12–14</sup> However, due to the strong tendency of manganese oxide to precipitate or coagulate during the synthesis, most MnO<sub>2</sub> materials for sensing application have larger size and poor water-dispersibility.<sup>12,15–17</sup> In addition, MnO<sub>2</sub>, as a surface modification material, introduced in the fluorescence sensing systems, often results in agglomeration of fluorescent nanoparticles.<sup>18–20</sup> Hence, a MnO<sub>2</sub>-assistant fluorescent sensor with smaller size and good water-dispersibility for fluorescence sensing is an urgent need.

Ascorbic acid (AA) is an essential nutrient for humans and certain other animals. Ascorbate is a powerful reducing agent, which is capable of rapidly scavenging a number of reactive oxygen species by electron transfer at typical biological pH values. It is well known that the radicals such as the hydroxyl radical are damaging to humans and animals at the molecular level due to their possible interaction with nucleic acids, proteins, and lipids.<sup>21</sup> Certainly, it is very necessary to monitor and determine the content of AA in food and pharmaceutical products to ensure adequate intake using a sensitive fluorescent nanosensor.<sup>22</sup>

In this study, we developed a rapid method for preparing C-dots/ZIF-8 hybrid materials within 5 min and achieved the construction of the C-dots/ZIF-8/MnO<sub>2</sub> *via in situ* formation of MnO<sub>2</sub> using ZIF-8 as a matrix. Due to the broad absorption of MnO<sub>2</sub>, it can act as an effective energy quencher adaptable to fluorescent C-dots. When AA was introduced into the

<sup>a</sup>State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Changchun 130022, P. R. China. E-mail: zjl@ciac.ac.cn

<sup>b</sup>University of Science and Technology of China, Hefei 244100, P. R. China

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nanosensor, the quenched fluorescence could be restored *via* reduction of the quencher  $\text{MnO}_2$  to  $\text{Mn}^{2+}$  by AA. Based on this mechanism, we designed and synthesized the novel C-dots/ZIF-8/ $\text{MnO}_2$  hybrid nanocomposite as a selective and sensitive nanosensor for AA fluorescence sensing.

## Experimental

### Materials

Bovine serum albumin was purchased from Aladdin Industrial Corporation. Ethylenediamine was purchased from Beijing Yili Fine Chemical Co. Ltd. Ascorbic acid was procured from Shanghai Huishi Biochemical Reagents Co., Ltd. Reagent grade NaCl, KCl,  $\text{Ca}(\text{NO}_3)_2$ , sodium citrate, glucose and sodium glutamate, were obtained from Beijing Chemical Works. Glutathione and cysteine were purchased from Aladdin Industrial Corporation. Soluble starch and DL-tartaric acid were obtained from Guangdong Xilong Co., Ltd. Vitamin C soluble tablet with 0.1 g of AA content was obtained from Cisen Pharmaceutical Co., Ltd.

### Characterization

Powder X-ray diffraction (XRD) patterns were collected on a Bruker D8-FOCUS X-ray diffractometer using Cu K $\alpha$  radiation. Fourier transform infrared (FTIR) spectra of the samples were recorded on a BRUKER Vertex 70 FTIR spectrometer using a standard KBr pellet technique. Fluorescence measurements were carried out using a Hitachi F-7000 spectrofluorometer. The transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were taken with a FEI Tecnai G<sup>2</sup> S-Twin transmission electron microscope operated at 200 kV. Scanning electron microscopy (SEM) images and energy dispersive X-ray spectrum (EDS) were acquired on a field emission scanning electron microscope (FESEM, S4800, Hitachi). Nitrogen-adsorption isotherms were measured at a liquid nitrogen temperature (77 K) using a Micromeritics ASAP 2010M apparatus.

### Preparation of the C-dots

The C-dots were synthesized according to the literature<sup>25</sup> with slight modification. In a typical synthesis procedure, citric acid (1.05 g) and ethylenediamine (670  $\mu\text{L}$ ) were dissolved in DI-water (10 mL). Then, the solution was transferred to a poly(tetrafluoroethylene) (Teflon)-lined autoclave and heated at 200 °C for 5 h. After the reaction, the reactors were cooled to room temperature naturally. The product was purified by dialysis (500 Da, MWCO) for approximately 12 h to obtain high quality C-dots. Finally, the C-dots were diluted into 50 mL using DI-water for further use.

### Preparation of C-dots/ZIF-8

First, 1.17 g  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was dissolved in 8 mL of the abovementioned C-dots solution. Second, 22.70 g 2-methylimidazole was dissolved in another 80 mL of DI water. The 2-methylimidazole solution was then poured into the mixture of zinc nitrate and C-dots solution with stirring. After stirring for

5 min, the product was collected by centrifugation and then washed with DI water several times. Finally, the C-dots/ZIF-8 nanoparticles were diluted into 10 mL DI water for further use. All the operations were performed at room temperature.

### The C-dots/ZIF-8 quenched by various amounts of $\text{KMnO}_4$

100  $\mu\text{L}$  of the abovementioned C-dots/ZIF-8 solution was mixed with different amounts of  $\text{KMnO}_4$  solution, and the purple-red colour of  $\text{KMnO}_4$  was faded. Subsequently, the mixtures were diluted to 5 mL with 0.05 M Tris-HCl buffer solution (pH = 7.4), followed by shaking and mixing. The fluorescence intensities of different mixtures were collected after another 12 h. All experiments were performed at room temperature. The excitation and emission slits were both 5.0 nm.

### Detection of the AA concentrations

For AA fluorescent sensing, the fluorescence probe based on C-dots/ZIF-8/ $\text{MnO}_2$  nanocomposite was first prepared. 15 mL  $\text{KMnO}_4$  solution ( $5 \times 10^{-4} \text{ mol L}^{-1}$ ) was slowly added into 5 mL of the abovementioned C-dots/ZIF-8 solution with stirring at room temperature. After continuous stirring for 12 h, C-dots/ZIF-8/ $\text{MnO}_2$  nanocomposite was obtained and directly diluted into 25 mL using DI-water. Then, 500  $\mu\text{L}$  of as-obtained C-dots/ZIF-8/ $\text{MnO}_2$  solution was diluted to 5 mL with 0.05 M Tris-HCl buffer solution (pH = 7.4) (termed as blank). The fluorescence intensity at 443 nm of the blank sample under excitation with light of 360 nm was measured and marked as  $F_0$ . After that, the AA solution with different concentration was added to the abovementioned solution and mixed well. The fluorescence intensities ( $F$ ) of the samples were measured under the same conditions. The selectivity for AA was confirmed by adding commonly coexisting substances (*i.e.*  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , sodium citrate, glucose, sodium glutamate, glutathione, cysteine, soluble starch, DL-tartaric acid, BSA) instead of AA in a similar way. All detection experiments were performed at room temperature. The excitation slit and the emission slit were both 5.0 nm.

### Real sample analysis

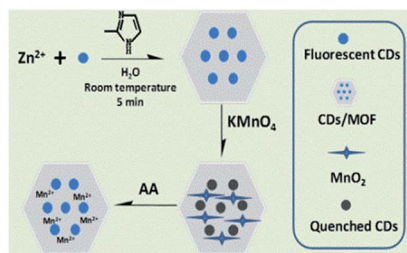
For real sample analysis, the AA content of vitamin C soluble tablet (CISEN) was evaluated using C-dots/ZIF-8/ $\text{MnO}_2$  hybrid nanocomposite as the nanosensor. Briefly, a tablet (160 mg) with 0.1 g AA content was used to prepare an appropriate concentration of the solution upon analysis using the fluorescence sensing system developed in this study.

## Results and discussion

### Synthesis and characterization of the C-dots/ZIF-8/ $\text{MnO}_2$

Scheme 1 illustrates our design rationale. Carbon dots were chosen due to their outstanding optical properties (*e.g.* resistance to photobleaching), low toxicity, dispersibility in water, excellent biocompatibility and low cost.<sup>23,24</sup> The C-dots were first produced according to a literature method.<sup>25</sup> The as-prepared C-dots have an average particle size of about 4 nm and show an optimum excitation wavelength at 360 nm (ESI, Fig. S1†). The





**Scheme 1** Schematic of the synthetic route of the C-dots/ZIF-8/MnO<sub>2</sub> and the AA detection process.

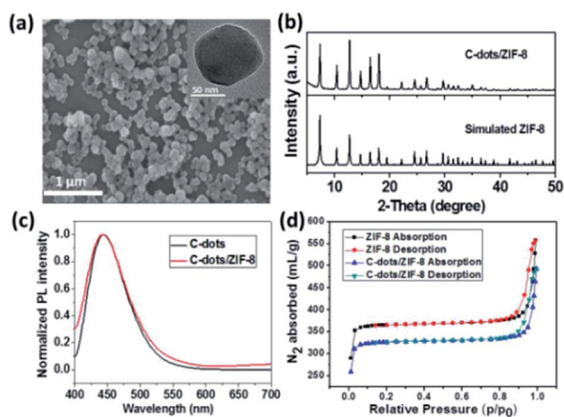
carboxylic and N-containing groups of C-dots were confirmed by FTIR analysis, which may play important roles for the formation of C-dots/ZIF-8 *via* the coordination interactions between Zn<sup>2+</sup> ions (ESI, Fig. S2†).<sup>26</sup> Subsequently, the C-dots/ZIF-8 was prepared by mixing 2-methylimidazole and the mixture of C-dots and Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O at room temperature using H<sub>2</sub>O as solvent with stirring for 5 min. The as-prepared C-dots/ZIF-8 hybrid nanocomposites were spherical and had an average size of about 100 nm (Fig. 1a). The morphology and size did not show significant differences on comparing with the pure ZIF-8 prepared under the same conditions, except for replacing the C-dots solution into water (ESI, Fig. S3†). In addition, the consistency in the XRD pattern between the C-dots/ZIF-8 and simulated ZIF-8 indicates that the introduction of C-dots did not have notable effects on the resulting crystal structure of ZIF-8 (Fig. 1b). Although C-dots could not be directly observed from the TEM image, the same fluorescence emission spectrum and the decrease in specific surface area (from 1091 to 977 m<sup>2</sup> g<sup>−1</sup>) of C-dots/ZIF-8 can be used as an indirect proof of the encapsulation of nonporous C-dots into the ZIF-8 MOFs (Fig. 1c and d).<sup>7</sup>

The C-dots/ZIF-8/MnO<sub>2</sub> nanocomposite was constructed by incubation of the C-dots/ZIF-8 with the KMnO<sub>4</sub>. The structure of the product was identified by X-ray diffraction spectroscopy. XRD diffraction peaks of the product prepared by mixing 2-

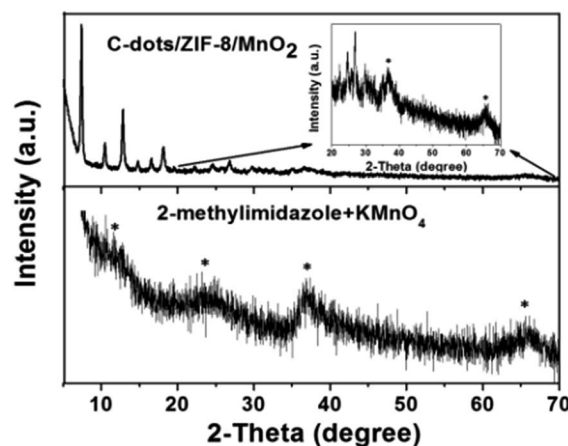
methylimidazole and KMnO<sub>4</sub> recorded at  $2\theta = 11.79, 23.63, 37.01, \text{ and } 65.57^\circ$  can be assigned to the (001), (002), (100), and (110) planes of MnO<sub>2</sub> with a turbostratic structure (Fig. 2) based on the literature.<sup>27</sup> Except for the dominant diffraction peaks of the C-dots/ZIF-8, the weak residual peaks of C-dots/ZIF-8/MnO<sub>2</sub> nanocomposite fit well with the MnO<sub>2</sub> phase by comparing with the MnO<sub>2</sub> pattern prepared by mixing 2-methylimidazole and KMnO<sub>4</sub> together under the same conditions, which demonstrates that KMnO<sub>4</sub> can be reduced to MnO<sub>2</sub> in the presence of C-dots/ZIF-8 for the formation of the stable C-dots/ZIF-8/MnO<sub>2</sub> nanocomposites. In addition, the redox reaction between the C-dots/ZIF-8 nanocomposite and KMnO<sub>4</sub> could also be proven by the fading of KMnO<sub>4</sub>'s purple-red colour. On comparing the FTIR spectrum, the M–O vibration was observed in the C-dots/ZIF-8/MnO<sub>2</sub> nanocomposites in the low frequency region, further indicating that MnO<sub>2</sub> is attached to the C-dots/ZIF-8 sample (ESI, Fig. S4†).<sup>28</sup> The absorption spectrum of the C-dots/ZIF-8/MnO<sub>2</sub> nanocomposite exhibits a wide band in the range of 300–700 nm, which is characteristic absorption of MnO<sub>2</sub> nanoparticles (ESI, Fig. S5†). Moreover, the absorption overlapped well with the fluorescence emission of C-dots.

### The application of the C-dots/ZIF-8/MnO<sub>2</sub> for AA detection

Due to the absorption overlapping well with the fluorescence emission of C-dots, MnO<sub>2</sub> could serve as an effective energy acceptor adaptable to fluorescent C-dots.<sup>17</sup> The fluorescence quenching properties of the different concentrations (from 0 to 200 μM) of KMnO<sub>4</sub> toward C-dots/ZIF-8 were investigated. As shown in Fig. 3, the fluorescence intensity of C-dots decreased gradually with increasing KMnO<sub>4</sub> concentrations. When the KMnO<sub>4</sub> concentration was higher than 50 μM, the fluorescence intensity was almost constant, which means that the fluorescence quenching had reached the maximum. Based on the principle of fluorescence detection, too large or too small fluorescence quenching may result in poor sensitivity toward the detection of ascorbic acid. Thus, 30 μM KMnO<sub>4</sub> was chosen to synthesize the C-dots/ZIF-8/MnO<sub>2</sub> nanocomposite in this study, which could cause about 85% of the fluorescence quenching.



**Fig. 1** (a) SEM image of C-dots/ZIF-8 (inset: the corresponding TEM image); (b) XRD patterns of simulated ZIF-8 and C-dots/ZIF-8; (c) normalized photoluminescence emission spectra of C-dots and C-dots/ZIF-8 under the excitation of 360 nm; (d) N<sub>2</sub> sorption isotherms of pure ZIF-8 and C-dots/ZIF-8 collected at 77 K.



**Fig. 2** XRD patterns of CDs/ZIF-8/MnO<sub>2</sub> and MnO<sub>2</sub> prepared by mixing 2-methylimidazole and KMnO<sub>4</sub> together.





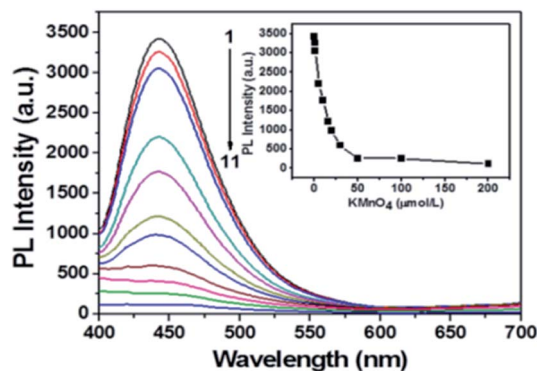


Fig. 3 The C-dots/ZIF-8 quenched by various amounts of  $\text{KMnO}_4$ . Curve 1, C-dots/ZIF-8; curves 2–11, various amounts of  $\text{KMnO}_4$  were introduced into the C-dots/ZIF-8 solution. Inset, intensity at 443 nm titrated with  $\text{KMnO}_4$ .

The TEM image reveals that the C-dots/ZIF-8/ $\text{MnO}_2$  nanocomposites have a smooth surface without  $\text{MnO}_2$  deposition, good dispersion and smaller sizes of about 100 nm (Fig. 4a). The Brunauer–Emmett–Teller (BET) isotherm of C-dots/ZIF-8/ $\text{MnO}_2$  shown in Fig. 4b exhibits a typical type I isotherm characteristic of microporous materials. The BET surface area of the C-dots/ZIF-8/ $\text{MnO}_2$  was  $\sim 991 \text{ m}^2 \text{ g}^{-1}$ . Because the manganese content from  $\text{MnO}_2$  produced under the optimized conditions was less than the EDS detection limit, the expanded tenfold manganese content of C-dots/ZIF-8/ $\text{MnO}_2$  was used to study the distribution of manganese dioxide (ESI, Fig. S6<sup>†</sup>). The elemental mapping image shows that Mn was distributed in the entire C-dots/ZIF-8 composite, indicating that  $\text{MnO}_2$  can be formed within C-dots/ZIF-8 (ESI, Fig. S7<sup>†</sup>). The possible reason for this is that the permanganate ion was preferentially adsorbed to the inside of the C-dots/ZIF-8 nanocomposite. Subsequently,  $\text{MnO}_2$  began to form *via* a redox reaction between the C-dots/ZIF-8 nanocomposite and permanganate ion.

The relationship between the concentration of ascorbic acid and the PL intensity of the C-dots/ZIF-8/ $\text{MnO}_2$  nanocomposites was further studied under the optimal conditions. The results show that a significant increase of the PL intensity can be seen with increasing concentrations of AA (Fig. 5a). The recovery efficiency  $(F - F_0)/F_0$  displayed a good linear relationship ( $R =$

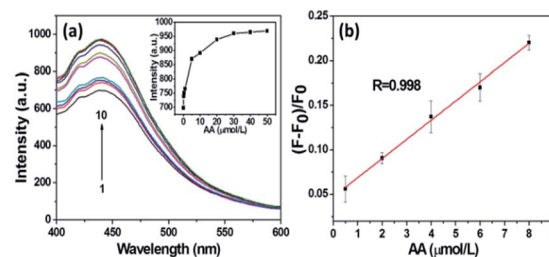


Fig. 5 (a) Fluorescence spectra of the probe in the presence of AA. Curve 1, C-dots/ZIF-8/ $\text{MnO}_2$ ; curves 2–10, various amounts of AA were introduced into the C-dots/ZIF-8/ $\text{MnO}_2$  solution (b) the plot of the fluorescence intensity *versus* AA concentration. The error bars represent the standard deviation of three measurements.

0.998) *versus* the concentration of AA in the range of 0.5–8  $\mu\text{M}$  (Fig. 5b), where  $F_0$  and  $F$  are PL intensities at 443 nm in the absence and presence of AA, respectively. The limit of ascorbic acid, based on  $3\sigma/\text{slope}$ , was estimated to be about 83 nM.

To assess the selectivity of this novel nanosensor for ascorbic acid, the influence of some electrolytes and biological species was studied in aqueous solutions. The experimental results are presented in Fig. 6. The C-dots/ZIF-8/ $\text{MnO}_2$  nanocomposites exhibited a remarkable fluorescence increase toward AA at a concentration of 8  $\mu\text{M}$ . In contrast, relatively weak fluorescence intensity changes could be observed with other molecules even at much higher concentrations. The results showed that the C-dots/ZIF-8/ $\text{MnO}_2$  nanocomposites display a highly selective fluorescence response toward AA over other non-target samples. The feasibility of our assay based C-dots/ZIF-8/ $\text{MnO}_2$  nanocomposites for fluorescence sensing AA in a real sample was tested. The sample selected was a vitamin C soluble tablet of the CISEN brand, which is commercially available to the public. The composition of each tablet includes 100 mg of AA. The results are summarised in Table S1 in the ESI.<sup>†</sup> The average

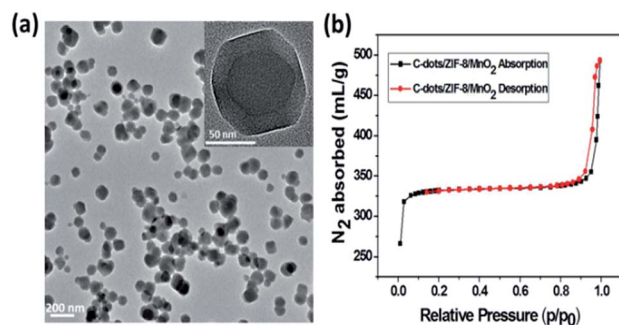


Fig. 4 (a) TEM image of the C-dots/ZIF-8/ $\text{MnO}_2$ ; (b)  $\text{N}_2$  sorption isotherms of C-dots/ZIF-8/ $\text{MnO}_2$  collected at 77 K.

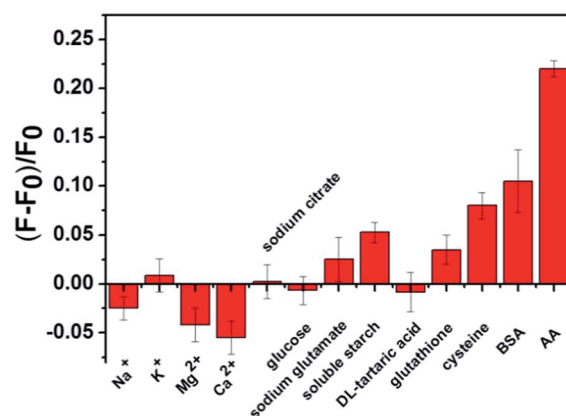


Fig. 6 Selectivity of the probe for AA over other potential interferences ( $\text{Na}^+$ : 1 mM;  $\text{K}^+$ : 0.5 mM;  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ : 0.25 mM; sodium citrate and glucose: 0.05 mM; sodium glutamate: 0.1 mM; soluble starch, DL-tartaric acid, glutathione, cysteine and bovine serum albumin: 10  $\mu\text{M}$ ; AA: 8  $\mu\text{M}$ ).  $F_0$  and  $F$  are the fluorescence intensity of the probe in the absence and presence of the target (AA) or nontarget samples, respectively.



recovery rate (103.8%) of our system indicates that this fluorescence sensing system based on C-dots/ZIF-8/MnO<sub>2</sub> was likely to be capable of real sample analysis.

## Conclusions

In conclusion, we developed a rapid method for preparing C-dots/ZIF-8 hybrid materials within 5 min at room temperature and constructed a C-dots/ZIF-8/MnO<sub>2</sub> probe for sensing ascorbic acid *via* the oxidation–reduction reaction between KMnO<sub>4</sub> and C-dots/ZIF-8. Importantly, the C-dots/ZIF-8/MnO<sub>2</sub> nanocomposites with a relatively uniform particle size about 100 nm and good water-dispersibility can serve as an effective probe for PL detection of AA with a detection limit as low as 83 nM, and the linear range is 0.5–8 μM. It is anticipated that the same strategy can also be extended to the preparation of other MnO<sub>2</sub>-containing hybrid materials for other applications (*e.g.* photocatalytic and photoelectric studies).

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