Cobalt Oxyhydroxide-Prompted Synthesis of Fluorescent Polydopamine Nanoparticles for Glutathione Detection

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Abstract

Glutathione (GSH) plays an important role in cells which is an essential endogenous antioxidant. Here, we developed a new detection platform to analyze GSH levels. In our system, fluorescent polydopamine (PDA) nanoparticles, as signal indicators, was obtained by oxidation through cobalt oxyhydroxide (CoOOH) nanosheets. When CoOOH was present, CoOOH could fleetly oxidize dopamine to fluorescent PDA nanoparticles. But once GSH was existed, CoOOH nanosheets were decomposed into Co$^{2+}$, and the oxidation between CoOOH and dopamine was prevented with the weaker fluorescence occurring. Thus, we could realize the detection of GSH concentration according to the decreased fluorescence value of the fluorescent polydopamine. This method provided a fast, simple, high sensitivity and desirable selectivity platform for GSH monitoring.

Keywords Cobalt oxyhydroxide (CoOOH) nanosheets, dopamine, oxidation-reduction reaction, fluorescent polydopamine nanoparticles, glutathione (GSH)
Introduction

Glutathione (GSH) is the most abundant thiolated tripeptide present in life species. GSH is an important endogenous antioxidant that prevents toxins and free radicals in cells.\(^1\) GSH levels are often associated with many diseases.\(^2\)\(^3\) The results of the study showed that GSH concentrations decreased in patients with liver disease, diabetes, and cataract.\(^4\)\(^5\) Chinta et al found that patients with Parkinson's disease and Alzheimer's disease also had lower GSH concentrations.\(^6\) In addition, the abnormal content of GSH is also related to the body mass index.\(^7\) Therefore, it is very important to monitor GSH concentration. To date, various methods for measuring GSH have been developed, including fluorescence-electroanalysis (FL-EC),\(^8\) liquid chromatography (LC),\(^9\) liquid chromatography-mass spectrometry (LC-MS),\(^10\) capillary electrophoresis (CE),\(^11\) and electroanalysis (EC)\(^12\) and electrochemiluminescence (ECL).\(^13\) Conventional methods for detecting cellular GSH concentration typically utilizes thiol-sensitive organic fluorophores.\(^14\)\(^15\) Despite their usefulness, the organic fluorophores cannot be measured for long periods because of photobleaching and sample labeling at large depths due to low-depth tissue penetration. Therefore, it is necessary to find a simple, fast, sensitive and low-cost method to monitor the level of GSH.

Fluorescent nanoparticles are receiving increasing attention for their potential applications in labeling, sensing and biomedicine fields.\(^16\)\(^22\) Compared with traditional organic fluorescent dyes, fluorescent nanoparticles e.g. quantum dots, polymer nanoparticles and upconverting nanoparticles have unique optical and chemical performances for example high fluorescence intensity, strong light stability and great biocompatibility.\(^23\)\(^29\) In particular, polymeric nanoparticles have become a promising material own to the strong stability in the environment and better controllable surface properties.\(^30\)

Here we have developed a new simple, sensitive and fast sensing method based on polymer fluorescent nanoparticles for GSH detection. As an important neurotransmitter in the human brain, dopamine can regulate various biological functions. Dopamine's catechol is easily oxidized to an anthracene derivative under oxidative conditions and can be self-polymerized into fluorescent polydopamine nanoparticles. Based on this property of dopamine, endogenous fluorescent PDA nanoparticles with cobalt oxyhydroxide (CoOOH)
as oxidant was successfully prepared, and further constructed a platform based on CoOOH and GSH redox reaction to detect GSH. When no GSH was present, CoOOH could oxidize dopamine to fluorescent polydopamine particles. But once the CoOOH in the system was firstly reacted with GSH, GSH could reduce it to Co$^{2+}$ with no oxidation ability, resulting in the inability to continue to oxidize dopamine to produce fluorescence. In the system we developed, the signal indicator was the fluorescent polydopamine particle. The concentration of GSH could be detected by observing changes in particle’s fluorescence. This sensing method exhibited great detection capability in GSH assay and its detection limit was as low as 1.93 μM. This method had a desirable selectivity for GSH compared to other potentially interfering substances. In addition, this means showed practical application in GSH analysis in human blood samples, and provided a meaningful detection means in clinical diagnosis and biological detection.

Experimental

Reagents and materials

Cobaltous chloride (CoCl$_2$•6H$_2$O), sodium hypochlorite (NaClO), sodium hydroxide (NaOH), sodium chloride (NaCl), magnesium chloride (MgCl$_2$), potassium chloride (KCl), calcium chloride (CaCl$_2$), hydrochloric acid, all amino acids and glucose were purchased from China National Pharmaceutical Group Corp. Dopamine, vitamin c and L-glutathione (GSH) were provided by Sigma-Aldrich. YSL (composed of tyrosine, serine and leucine), YSV (composed of tyrosine, serine and valine) was obtained from Kangzhe Pharmaceutical (Shenzhen, China). RGD (composed of arginine, glycine and aspartic acid) was provided by Puzhen Organism (Shanghai, China). The First Xiangya Hospital (Changsha, China) provided the human blood. All solutions were prepared by an electric resistance of >18.2 MΩ ultrapure water, which was obtained via a Millipore Milli-Q water purification system (Billerica, MA, USA).

Apparatus

Fluorescence spectra were from an F-7000 fluorescence spectrometer (HORIBA, Japan).
The scanning range was collected in the range of 430 nm - 600 nm and its excitation wavelength was 390 nm. TEM images were acquired by a field-emission high resolution 2100F TEM (JEOL, Japan) manipulating at a 200 kV acceleration voltage. The UV-vis absorption spectrum was obtained with UV-2450 UV-visible spectrometer (Shimadzu, Japan).

**Preparation of CoOOH**

CoOOH nanosheets was performed by the previously reported method with some modifications.\(^1\) Briefly, 500 \(\mu\)L 10 mM CoCl\(_2\) \(\cdot\)6H\(_2\)O solution was added into 125 \(\mu\)L 1.0 M NaOH and ultrasonicated for 60 s. Then, 25 \(\mu\)L 0.9 M NaClO was added and reacted 30 min under ultrasonication at 25°C. The final solution was centrifuged with 13000 rpm for 30 minutes and continuously was washed four times with sterilized water. Lastly, we dispersed the nanosheets into 1 mL sterile water and placed at 4 °C for use. The final concentration of CoOOH was about 0.75 mg mL\(^{-1}\).

**Preparation of fluorescent polydopamine**

To obtained fluorescent PDA particles, 86 \(\mu\)L water, 6 \(\mu\)L 0.75 mg mL\(^{-1}\) CoOOH nanosheets and 5 \(\mu\)L 25 mM dopamine solution were mixed in a 200 \(\mu\)L PCR tube and then the mixed solution was incubated for 40 minutes at 25 °C. Finally, 3 \(\mu\)L 0.2 M HCl was added to regulate pH.

**GSH detection**

Firstly, 45 \(\mu\)g mL\(^{-1}\) CoOOH nanosheets was incubated with different concentrations of L-glutathione for 20 minutes at room temperature. Then 1.25 mM dopamine was put into the system and reacted 40 minutes at 25 °C to obtain the fluorescent PDA. Ultimately, 3 \(\mu\)L 0.2 M HCl was introduced into the above mixture to stop the reaction.

To test GSH in whole blood, heparin was first used for anticoagulant treatment. Briefly, 200 \(\mu\)L whole blood was treated by 5 \(\mu\)L 100 mM L-serine–borate complex to inhibit gamma-glutamyltranspeptidase activity and then the mixture was centrifuged 15 min at 12 000 rpm to remove haemocytes. Finally the supernatant fluid was obtained. After supernatant fluid was diluted 50 times, it was immediately introduced into the sensing platform and other
operations were similar to above.

**Results and Discussions**

*Principle of preparing fluorescent polydopamine particles and detecting GSH*

Firstly, according to previous literature reports, CoOOH nanosheets were simply synthesized using CoCl$_2$, NaClO, and NaOH.$^{31}$ When dopamine was mixed with CoOOH nanosheets, dopamine could be oxidized by CoOOH to an anthracene derivative. The anthracene derivative could then spontaneously be polymerized into fluorescent polydopamine nanoparticles. Based on this, we designed a new platform to detect GSH. The detection principle was shown in Scheme.1. In the presence of GSH, CoOOH was decomposed to Co$^{2+}$. The reaction equation was as follows:

$$\text{CoOOH} + 2\text{GSH} + 2\text{H}^+ \rightarrow \text{Co}^{2+} + 2\text{GS-SH} + 2\text{H}_2\text{O}$$

Therefore, the fluorescent polydopamine nanoparticles were not synthesized because CoOOH was decomposed so that the oxidation for dopamine cannot be achieved. Conversely, when there was no GSH, CoOOH nanosheets were retained in solution and dopamine would be oxidized to quinone. Then we obtained fluorescent PDA by self-polymerization of quinone. Accordingly, the detection of GSH was achieved by observing the decrease of the fluorescence signal of fluorescent polydopamine particles.

Preferred position for Scheme 1

*Characterizing CoOOH and fluorescent polydopamine particles*

Three characterization methods including transmission electron microscope (TEM), energy dispersive X-ray spectrometer (EDS) and UV-vis absorption spectra were used to characterize as-synthesized CoOOH nanosheets. As shown in Fig.1A, the TEM result certified that the newly prepared CoOOH presented a hexagonal morphology. The O and Co elements were found in CoOOH nanosheets from EDS analysis (Fig.S1). Also, we evaluated
the stability of CoOOH nanosheets in water over seven days (Fig. S2). It could be seen from the TEM images that CoOOH still maintained a hexagonal morphology, which proved that CoOOH was stable. Furthermore, the optical performance of CoOOH was ensured by UV–vis absorption. As seen in Fig. 1B, the absorbance spectrum displayed a peak centered at 410 nm. These results displayed the successful synthesis of CoOOH nanosheets.31–32 In Fig. 1C, it was affirmed that the fluorescent PDA nanoparticles were successfully prepared. When dopamine was mixed with CoOOH (blue line) we could see a remarkable fluorescence signal, while no obvious fluorescence signal was generated when there was only CoOOH or dopamine. The obtained fluorescent PDA particles had irregular shape and different size of about 10–50 nm according to TEM image from Fig. 1D because of the stacking conditions of oligomers and different oligomeric units.33–34 In Fig. S3A, the excitation wavelength of fluorescent PDA particles was 390 nm and the maximum emission wavelength was 490 nm. From Fig. S3B, we could find the emission intensity showed an increasing trend between 360 nm and 390 nm and then began to decrease in the range of 390–410 nm. When the excitation wavelength was constantly changing, the position of the emission peak hardly changed. This might be related to the mild acidic reaction conditions.34 Moreover, we also tested the change in fluorescence value of fluorescent polydopamine particles over seven days. In Fig. S4, the intensity of the fluorescent polydopamine particles remained unchanged, illustrating the fluorescent polydopamine particles were stable.

Preferred position of Fig. 1

Feasibility analysis

At first, we used the changes of the fluorescence value to verify the feasibility of the proposed sensing strategy (Fig. 2). When GSH was not present (red line), the synthesized fluorescent PDA nanoparticles have strong fluorescence at 490 nm, while when GSH was existent in the system (black line), the fluorescence intensity of PDA was significantly reduced, thus demonstrating that GSH could reduce CoOOH to Co²⁺ and inhibit the production of fluorescent PDA nanoparticles. In addition, we also tested the UV–vis absorption spectrum to demonstrate the feasibility of this principle (Fig. S5).
When GSH was present (green line), CoOOH was reduced and could not continue to oxidize dopamine. The absorption spectrum was similar to the same concentration of dopamine solution (red line) and the peak at 410 nm of CoOOH (black line) was disappeared. On the contrary, when GSH was absent (blue line), dopamine was oxidized by CoOOH, and the absorbance of ultraviolet absorption spectrum at 400 nm became stronger, indicating that the successful synthesis of fluorescent polydopamine particles. Meanwhile, in Fig.S6, it was proved that the fluorescence of the polydopamine couldn't be influenced by GSH. While the fluorescent polydopamine particles were mixed with GSH, the fluorescence did not decrease, indicating that the decrease in fluorescence intensity was caused by the decrease of the synthesized fluorescent particles rather than the quenching of GSH.

Preferred position for Fig. 2

Optimization of sensing conditions

We optimized the experimental conditions including HCl concentration, CoOOH concentration and synthesis time of PDA nanoparticles (Fig.S7). The maximal signal could be obtained when 6 mM HCl and 45 ug mL\(^{-1}\) CoOOH were present. The purpose of adding hydrochloric acid after the formation of the fluorescent PDA nanoparticles is to adjust the pH of the solution to about 2 to lower the polymerization rate of the quinone. As shown in Fig. S7A, when the concentration of HCl was increased to 6 mM, the pH of the solution was about 2, and the fluorescence intensity of the PDA nanoparticles was the highest. Therefore, 6 mM HCl was selected as the optimum condition in the subsequent experiments. As shown in Fig.S7B and S7C, it was found that the fluorescence intensity of PDA nanoparticles increased with increasing CoOOH from 7.5 to 45 ug mL\(^{-1}\), but as the concentration of CoOOH continued to increase, the fluorescence intensity decreased gradually, which may be caused by the quenching effect of excess CoOOH and the formation of large PDA nanoparticles. Meanwhile, we also optimized the reaction time between CoOOH and dopamine and when the reaction reached 40 min the signal achieved the highest level (Fig. S7D). At last, we optimized
the reaction time between GSH and CoOOH (Fig. S8). Once the time reached 20 min, the signal reached a steady state and did not change again after that. So we chose 20 min as the reaction time between GSH and CoOOH.

**The detection of GSH**

Under the optimized conditions, the working curve was collected. Different concentration of GSH was added into the system and then reacted for 40 min (Fig.3A). As the concentration of GSH increased, the fluorescence intensity gradually decreased. When the GSH concentration exceeded 300 μM, the fluorescence does not change and reached the platform. Fluorescence decreased values ($F_0 - F$) correlated linearly with the GSH concentrations between 10 and 100 μM (Fig.3B), and the detection limit was 1.93 μM (according to 3σ rule). These results illustrated that the work had highly sensitive and provided a fast means for GSH sensing compared with other developed detection platforms (Table S1).

Preferred position for Fig. 3

**Selectivity analysis**

To evaluate the selectivity of the method before applied in a real sample, we used a variety of different components as interferences (the concentrations of these interferences were listed in Table S2). It could be seen from Fig.4 that only when the GSH (300 μM) was added, an obvious increase of $F_0/F$ was observed, and when other interference components were added to the system, there was no obvious increases. It was worth noting that when cysteine and vitamin C were in a high concentration, they were able to reduce CoOOH into Co$^{2+}$ and cause the fluorescence intensity ratio increase.$^{35,36}$ However, GSH concentration in human blood was much higher than these interferences,$^{37,38}$ thus demonstrating that the proposed method had a desirable selectivity for GSH.

Preferred position for Fig. 4
**GSH detection in human blood**

GSH was tested in blood using the assays we developed to demonstrate the suitability of this protocol. As shown in Table 1, the recovery obtained after adding different amounts of GSH to the blood was between 98.4% and 103% with relative standard deviation from 3.8% to 5.5%. From the result, we could see the PDA system can analyze GSH in real samples.

Preferred position for Table 1

**Conclusions**

In summary, a new platform has been developed to monitor GSH levels. CoOOH could oxidize dopamine to fluorescent polydopamine particles. Once GSH existed in the system, CoOOH was reduced to Co$^{2+}$, and dopamine could not continue to be oxidized to fluorescent PDA particles. In addition, the probe we constructed enabled fast and sensitive detection of GSH. We also found that this probe had a good performance in GSH detection in real sample. This reveals its potential value to apply in biological analysis.

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**Supporting Information**

This material is available free of charge on the Web at http://www.jsac.or.jp/analsci/.

**References**
1. Lu, S. Mol. Aspects Med., 2009, 30, 42.
2. (a) Townsend, D. M.; Tew, K. D.; Tapiero, H. Biomed. Pharmacoother., 2003, 57, 145. (b) Estrela, J. M.; Ortega, A.; Obrador, E. Crit. Rev. Clin. Lab. Sci., 2006, 43, 143.
3. U. Sivasankaran, S. Jesny, A. R. Jose and K. G. Kumar. Anal. Sci., 2017, 33, 281-285.
4. L.G. Chandrasena, L.D.R. De Silva, K.I. De Silva, P. Dissanayaka, H. Peiris. Southeast Asian J. Trop. Med. Publ. Health, 2008, 39, 731–736.
5. J.Q. Huang, J.C. Zhou, Y.Y. Wu, F.Z. Ren, X.G. Lei. Free Radic. Biol. Med., 2018, 127, 108–115.
6. S.J. Chinta, J.K. Andersen. Free Radic. Biol. Med., 2006, 41, 1442–1448.
7. E.L. Bettermann, T.J. Hartman, K.A. Easley, E.P. Ferranti, D.P. Jones, A.A. Quyyumi, V. Vaccarino, T.R. Ziegler, J.A. Alvarez. J. Nutr., 2018, 148, 245–253.
8. A.K. Sakhi, K.M. Russnes, S. Smeland, R. Blomhoff, T.E. Gundersen. J. Chromatogr. A, 2006, 1104, 179–189.
9. G.Y. Shi, J.X. Lu, F. Xu, W.L. Sun, L.T. Jin, K. Yamamoto, S.G. Tao, J.Y. Jin. Anal. Chim. Acta, 1999, 391, 307–313.
10. R. Rellan-Alvarez, L.E. Hernandez, J. Abadia, A. Alvarez-Fernandez. Anal. Biochem., 2006, 356, 254–264.
11. J. Mendoza, T. Garrido, R. Riveros, J. Parada. Phytochem. Anal., 2009, 20, 114–119.
12. Q.Y. Liu, J. Bao, M. Yang, X.J. Wang, S.Y. Lan, C.J. Hou, Y.Z. Wang, H.B. Fa. Sensor. Actuator. B Chem., 2018, 274, 433–440.
13. H.P. Peng, M.L. Jian, Z.N. Huang, W.J. Wang, H.H. Deng, W.H. Wu, A.L. Liu, X.H. Xia, W. Chen. Biosens. Bioelectron., 2018, 105, 71–76.
14. (a) Chen, X.; Zhou, Y.; Peng, X.; Yoon, J. Chem. Soc. Rev. 2010, 39, 2120. (b) Sudeep, P. K.; Joseph, S. T. S.; Thomas, K. G. J. Am. Chem. Soc., 2005, 127, 6516. (c) Banerjee, S.; Kar, S.; Perez, J. M.; Santra, S. J. Phys. Chem. C, 2009, 113, 9659.
15. (a) Ahn, Y. H.; Lee, J. S.; Chang, Y. T. J. Am. Chem. Soc., 2007, 129, 4510. (b) Yi, L.; Li, H.; Sun, L.; Liu, L.; Zhang, C.; Xi, Z. Angew. Chem. Int. Ed., 2009, 48, 4034. (c) Shao, N.; Jin, J.; Wang, H.; Zheng, J.; Yang, R.; Chan, W.; Abliz, Z. J. Am. Chem. Soc., 2010, 132, 725.
16. J. K. Jaiswal, H. Mattoussi, J. M. Mauro and S. M. Simon. Nat. Biotechnol., 2003, 21, 47–
51. I. L. Medintz, H. T. Uyeda, E. R. Goldman and H. Mattoussi. Nat. Mater., 2005, 4, 435–446.

18. X. Michalet, F. F. Pinaud, L. A. Bentolila, J. M. Tsay, S. Doose, J. J. Li, G. Sundaresan, A. M. Wu, S. S. Gambhir and S. Weiss. Science, 2005, 307, 538–544.

19. N. L. Rosi and C. A. Mirkin. Chem. Rev., 2005, 105, 1547–1562.

20. X. Sun, Y. Yang, M. Guo, S. Ma, M. Zheng and J. He. Anal. Sci., 2017, 33, 761–767.

21. D. Liu, X. Pan, W. Mu, C. Li and X. Han. Anal. Sci., 2019, 35, 367–370.

22. Y. Tsuchido, A. Yamasawa, T. Hashimoto and T. Hayashita. Anal. Sci., 2018, 34, 1125–1130.

23. M. J. Ruedas-Rama, J. D. Walters, A. Orte and E. A. H. Hall. Anal. Chim. Acta, 2012, 751, 1–23.

24. O. S. Wolfbeis. Chem. Soc. Rev., 2015, 44, 4743–4768.

25. C. Dai, C. X. Yang and X. P. Yan. Anal. Chem., 2015, 87, 11455–11459.

26. Y. Zhang, J. M. Liu and X. P. Yan. Anal. Chem., 2013, 85, 228–234.

27. T. T. Chen, Y. H. Hu, Y. Cen, X. Chu and Y. Lu. J. Am. Chem. Soc., 2013, 135, 11595–11602.

28. Y. Cen, Y. M. Wu, X. J. Kong, S. Wu, R. Q. Yu and X. Chu. Anal. Chem., 2014, 86, 7119–7127.

29. C. Ma, T. Bian, S. Yang, C. H. Liu, T. R. Zhang, J. F. Yang, Y. H. Li, J. S. Li, R. H. Yang and W. H. Tan. Anal. Chem., 2014, 86, 6508–6515.

30. A. Reisch and A. S. Klymchenko. Small, 2016, 12, 1968–1992.

31. Y. Yang, Y. Cen, W. J. Deng, R. Q. Yu, T. T. Chen and X. Chu. Anal. Methods, 2016, 8, 7199–7203.

32. Y. Cen, J. Tang, X. J. Kong, S. Wu, J. Yuan, R. Q. Yu and X. Chu. Nanoscale, 2015, 7, 13951–13957.

33. W. Zheng, H. Fan, L. Wang and Z. Jin. Langmuir, 2015, 31, 11671–11677.

34. X. J. Kong, S. Wu, T. T. Chen, R. Q. Yu and X. Chu. Nanoscale, 2016, 8, 15604–15610.

35. D. G. He, X. X. Yang, X. X. He, K. M. Wang, X. Yang, X. He and Z. Zou. Chem. Commun., 2015, 51, 14764–14767.
36. W. Y. Zhai, C. X. Wang, P. Yu, Y. X. Wang and L. Q. Mao. *Anal. Chem.*, 2014, 86, 12206–12213.

37. Y. H. Wang, K. Jiang, J. L. Zhu, L. Zhang and H. W. Lin. *Chem. Commun.*, 2015, 51, 12748–12751.

38. L. El-Khairy, P. M. Ueland, H. Refsum, I. M. Graham and S. E. Volllst. *Circulation*, 2001, 103, 2544–2549.
Table 1 GSH detection in blood samples

| Sample | Measured (uM) | Added (uM) | Found (uM) | RSD(n=3) | Recovery(%) |
|--------|---------------|------------|------------|----------|-------------|
| 1      | 25            | 41.2       | 4.1%       | 103      |             |
| 2      | 15            | 50         | 66.4       | 5.5%     | 102.2       |
| 3      | 100           | 113.2      | 3.8%       | 98.4     |             |
Figure captions

Scheme 1 Principle of the fluorescent polydopamine particle-based strategy for GSH detecting.

Fig. 1  (A) TEM image of the prepared CoOOH. Scale bars: 100 nm. (B) UV-vis absorption spectrum of the CoOOH nanosheet (red line) and CoCl₂ (black line). (C) Fluorescence emission spectra of 1.25 mM dopamine (red line), 45 µg mL⁻¹ CoOOH (black line) and 45 µg mL⁻¹ CoOOH + 1.25 mM dopamine (blue line). Iconography: photographs of 45 µg mL⁻¹ CoOOH (tube a), 1.25 mM dopamine (tube b) and the mixture of 1.25 mM dopamine and 45 µg mL⁻¹ CoOOH (tube c). (D) TEM image of the obtained fluorescent polydopamine particles. Scale bars: 0.2 µm.

Fig. 2  Fluorescence emission spectrum of fluorescent polydopamine particles with 300 µM GSH (black line) and without GSH (red line). Iconography: photographs of the prepared fluorescent PDA particles without GSH (tube a) and with 300 µM GSH (tube b).

Fig. 3 (A) The responses of the fluorescent polydopamine particles with diverse concentrations of GSH (0–350 µM). (B) Relationship between (F₀-F) and C_{GSH}. Error bars came from three repetitive experiments.

Fig. 4  F₀/F values in response to GSH and interferents. (F₀: the fluorescence value with no GSH; F: the fluorescence value with GSH or other interference species present). Error bars came from three repetitive experiments.
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