Fluorescent Disulfide-functional Coordination Polymers for Sensitive Detection of Hydrogen Peroxide

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A new type of fluorescent coordination polymer (NCP_{Cd}) based on disulfide carboxylate ligand was prepared by using one-pot synthesis for sensitive detection of reactive oxygen species (ROS). With the reaction between NCP_{Cd} and ROS, the morphology of the NCP_{Cd} was transformed from nanorods to hexagon particles, then broken into nano-fragments. Meanwhile, the fluorescence of NCP_{Cd} (at 421 nm) was quenched accordingly. For designing the highly sensitive probe for ROS, Rhodamine 6G (R6G) was doped in NCP_{Cd}. In the presence of ROS, the fluorescence of NCP_{Cd} moiety at 421 nm was quenched, but the R6G moiety was released from the broken nanorods and the fluorescence at 555 nm from R6G moiety was recovered. The R6G doped NCP_{Cd} (NCP_{Cd}-R) can be used as a highly sensitive and selective probe for hydrogen peroxide (H₂O₂) with detection limit of 12.4 nM. Moreover, the NCP_{Cd}-R was further extended to the glucose sensing combined with glucose oxidase (GOx) to oxidate glucose and generate H₂O₂, demonstrating the potential for practical applications.

Keywords Coordination polymers, reactive oxygen species (ROS), disulfide carboxylate ligand, fluorescent detection, sensitive detection

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Introduction

Reactive oxygen species (ROS), such as hydrogen peroxide (H₂O₂), superoxide (O₂^{•−}), hydroxyl radical (•OH) and singlet oxygen (¹O₂), play important roles in health and disease related processes.^{1–4} The ROS are produced endogenously through the mitochondrial respiration process, or exogenously by exposure to deleterious conditions including infectious agents and UV light.^{5,6} The excessive production of ROS usually results in diseases (*e.g.*, cancer, arthritis, arteriosclerosis). Moreover, the presence of ROS in atmospheric aerosols can also cause to oxidative stress in the human lung.^{7,8} In the past decades, great efforts have been devoted to detect ROS for understanding the biological roles and the molecular mechanisms of these ROS.^{9,10} Due to the very low concentration (nanomolar or picomolar) of ROS in biological and environmental systems, high sensitivity is generally required during ROS detection.

Probes based on nanomaterials have been used effectively for detecting ROS owing to their high sensitivity, good solubility and facile surface functionalization for specific targeting.^{11–13} Among them, the nanoscale coordination polymers (NCPs), constructed from metal connectors and bridging ligands, have shown their advantages as sensors, which include their structural and chemical diversity, tunable chemical compositions and

biodegradability.^{14–16}

Herein, we designed and prepared a type of NCP for sensitive detection of ROS employing Cd²⁺ as metal center, disulfide carboxylate derivative (2,2'-dithiodibenzoic acid, dtba) as ligand and 1,10-phenanthroline (phen) as co-ligand. As shown in Fig. 1, the fluorescence of the prepared nanoprobe (NCP_{Cd}) can be quenched by ROS. In the presence of ROS, the morphology of the NCP_{Cd} was changed from nanorods to hexagon particles accompanied by the decrease of the fluorescence intensity. Then, the hexagon particles were further broken into nano-fragments due to the oxidation of ROS, and the fluorescence intensity of the nanoprobe was further quenched. We found the thiol-compounds, such as glutathione (GSH) and cysteine (Cys), can also quench the fluorescence of NCP_{Cd}, while the morphology of the NCP_{Cd} was not transformed from nanorods to the final nano-fragments. We suppose the transformation of the morphology of the NCP_{Cd} was due to the breaking of the disulfide bond caused by the oxidation of ROS.^{17,18} Furthermore, the Rhodamine 6G (R6G) doped NCP_{Cd} (NCP_{Cd}-R) exhibits good sensing ability toward ROS. Without ROS, the emission at 421 nm from NCP_{Cd} moiety can be observed, but the emission at 555 nm from R6G moiety was quenched. In the presence of ROS, the fluorescence of NCP_{Cd} moiety at 421 nm was quenched, but the R6G moiety was released from the broken NCP_{Cd}-R and the fluorescence at 555 nm of R6G moiety was recovered. The NCP_{Cd}-R shows high selectivity and sensitivity toward ROS, and can be used as a potential ROS probe.

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Fig. 1 Schematic illustration of fluorescent coordination polymers based on disulfide carboxylate ligand for ROS sensing.

Fig. 2 Schematic overview of redox-based disulfide modification. (A) The structures of ligand dtba and co-ligand for NCP_{Cd} . (B) The disulfide redox species and their interrelationship. (C) The reaction of disulfide with ROS.

Experimental

Reagents and materials

$\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ (98%), 2,2'-dithiodibenzoic acid (96%, dtba), 1,10-phenanthroline (96%, phen), glutathione (GSH) and cysteine (Cys) were purchased from Alfa Aesar. Rhodamine 6G (95%, R6G) and glucose oxidase (GOx) were purchased from Sigma-Aldrich (USA). Hydrogen peroxide (H_2O_2 , 30%) and glucose were purchased from Nanjing Chemical Reagent Co., Ltd. (Nanjing, China). All aqueous solutions were prepared from deionized water (18 M cm^{-1} , PURELAB Classic, PALL, USA). Unless otherwise stated, all chemical materials were purchased from commercial sources and used without further purification.

Apparatus and measurements

The morphology of the NCPs was characterized by transmission electron microscopy (TEM, JEM-200CX, Japan). X-ray diffraction patterns were obtained on an X-ray powder diffractometer (XRD, X'TRA, Cu $K\alpha$ radiation, Switzerland). Fourier transform infrared (FTIR) spectra were collected on a Nicolet 6700 FTIR spectrometer (Thermo Scientific, USA). Fluorescence spectra were recorded on a RF-5301PC spectrophotometer (Shimadzu, Japan).

Synthesis of NCP_{Cd}

The mixture of dtba (0.0926 g, 0.3 mmol), phen (0.0198 g, 0.1 mmol) and $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ (0.0770 g, 0.1 mmol) was added into 10 mL NaOH solution (0.1 mM), and sealed in a 30-mL

vial. The mixture was reacted at 160°C for 30 h. The product (NCP_{Cd}) was washed with water and ethanol three times each.

Synthesis of $\text{NCP}_{\text{Cd-R}}$

The mixture of R6G (0.0100 g, 0.02 mmol), dtba (0.1852 g, 0.6 mmol), phen (0.0396 g, 0.2 mmol) and $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ (0.1540 g, 0.2 mmol) was added into 25 mL NaOH solution (0.1 mM), and sealed in a 30-mL vial. The mixture was reacted at 160°C for 30 h. The product ($\text{NCP}_{\text{Cd-R}}$) was washed with water and ethanol three times each.

Fluorescent ROS sensing

In a typical measurement, NCP_{Cd} (or $\text{NCP}_{\text{Cd-R}}$, $\sim 10 \mu\text{g mL}^{-1}$) was suspended in 10 mM PBS buffer (pH 7.4), then H_2O_2 with different concentrations (from 1 nM to 1 μM) was added into the NCP_{Cd} suspension. After allowing the mixture to react for 6 min at room temperature, the fluorescence spectra of the mixture were detected.

Fluorescent glucose sensing

Briefly, $\text{NCP}_{\text{Cd-R}}$ ($\sim 10 \mu\text{g mL}^{-1}$) was suspended in 10 mM PBS buffer (pH 6.8) containing $50 \mu\text{g mL}^{-1}$ GOx. Then, different concentrations of glucose were incubated with the mixture at 37°C for 30 min. The fluorescence intensities of the reaction solution were measured.

Results and Discussion

The NCP_{Cd} nanorods were successfully synthesized by

Fig. 3 The morphology of the NCP_{Cd} before and after reacting with ROS (H_2O_2). (A1 and A2) The NCP_{Cd} nanorods. (B1 and B2) The NCP_{Cd} after reacting with H_2O_2 (100 nM). (C1 and C2) The NCP_{Cd} after reacting with H_2O_2 (1 μM).

hydrothermal method by using dtba as ligand and phen as co-ligand (Fig. 2A). The dtba contains a disulfide ($-\text{S}-\text{S}-$) moiety, which can be oxidized by ROS and converted to sulfinic acid ($-\text{SO}_2\text{H}$) or sulfonic acid ($-\text{SO}_3\text{H}$), and also can be reduced by thiol-reducing agents (Fig. 2B).^{18–20} Therefore, in the presence of ROS, the disulfide groups in NCP_{Cd} nanorods can be cracked (Fig. 2C) and the morphology of the NCP_{Cd} was transformed from nanorods to the final nano-fragments.

The morphology of the NCP_{Cd} was characterized by transmission electron microscopy (TEM) (Figs. 3A1 and 3A2). Before the reaction with ROS, the morphology of the NCP_{Cd} was nanorods. The powder X-ray diffraction (PXRD) study reveals that the NCP_{Cd} was not well crystallized (Fig. S1, Supporting Information). After the NCP_{Cd} nanorods reacted with H_2O_2 , an interesting change of the morphology of the NCP_{Cd} occurred. In the presence of a low concentration of H_2O_2 (100 nM), the nanorods were changed to hexagon particles with diameter of 100–200 nm (Fig. 3B1). Figure 3B2 shows that the hexagon particles were in a crystalline state, monitored by high-resolution TEM. However, the structure of the hexagon particles was hard to confirm, because the $-\text{SO}_2\text{H}$ or $-\text{SO}_3\text{H}$ generated from the reaction between H_2O_2 and disulfide, and the particle size was too small for single-crystal X-ray diffraction. Moreover, if more H_2O_2 was presented, the hexagon particles further reacted with H_2O_2 and broke into nano-fragments (Figs. 3C1 and 3C2). Figure S2 shows the morphology changes during the reaction between hexagon particles and H_2O_2 with different concentrations from 100 nM to 1 μM . We suppose the morphology change was due to the cleavage of $-\text{S}-\text{S}-$ after oxidation by H_2O_2 . FT-IR spectra confirmed the reaction between disulfide and H_2O_2 . As shown in Fig. S3 (Supporting Information), the peak intensity of $\nu_{(\text{S}-\text{S})}$ around 852 cm^{-1} was decreased, while the peak intensity of $\nu_{(\text{S}-\text{O})}$ around 910 cm^{-1} was increased. Furthermore, the generation of the peak $\nu_{(\text{OH})}$ located around 3330 cm^{-1} indicated the existence of $-\text{SO}_2\text{H}$ or $-\text{SO}_3\text{H}$ in NCP_{Cd} after reacting with H_2O_2 .^{21,22}

The fluorescence property of NCP_{Cd} nanorods was investigated in PBS buffer (pH 7.4) at room temperature. Figure 4A shows the excitation and emission spectra of the NCP_{Cd} nanorods. The NCP_{Cd} displays an emission peak at 421 nm with the excitation

at 400 nm that can be attributed to the intra-ligand $\pi^*-\pi$ transitions.¹⁶ Among the ROS, H_2O_2 is relatively stable and was thus selected as the analyte for investigating the ROS sensing ability of NCP_{Cd} . The NCP_{Cd} can quickly react with H_2O_2 within 10 min and the emission peak at 421 nm was accordingly quenched (Fig. 4B). Various concentrations of H_2O_2 (from 5 nM to 1000 nM) were investigated to interact with NCP_{Cd} (Fig. 4C). A plot of the fluorescence quenching intensity (I_0 is the fluorescence intensity of NCP_{Cd} at the beginning of the reaction with H_2O_2 ; I is the fluorescence intensity of NCP_{Cd} after reacting with H_2O_2) as a function of the H_2O_2 concentration gives a linear calibration curve from 50 to 120 nM (Fig. 4D).

Furthermore, we found the thiol-compounds can also quench the fluorescence of NCP_{Cd} . But, the morphology of the NCP_{Cd} was not transformed from nanorods to hexagon particles or nano-fragments, which can be induced by ROS (Fig. S4, Supporting Information). It might be because the thiol-compounds tend to be adsorbed on the surface of NCP_{Cd} nanorods, where there are Cd^{2+} ions not fully coordinated. Therefore, there is little chance for thiol-compounds to reduce the disulfide and break the NCP_{Cd} nanorods.

For developing a fluorescent probe with high selectivity towards ROS, the R6G doped NCP_{Cd} ($\text{NCP}_{\text{Cd}}\text{-R}$) was prepared by one-pot synthesis. Figure S5 (Supporting Information) gives the bright-field photographs of $\text{NCP}_{\text{Cd}}\text{-R}$ and NCP_{Cd} . The color of $\text{NCP}_{\text{Cd}}\text{-R}$ was pink because of the doped R6G, while the NCP_{Cd} was white powder. In the $\text{NCP}_{\text{Cd}}\text{-R}$, the fluorescence intensity of R6G (at 555 nm) was quenched because the metal cations (Cd^{2+}) of NCPs have intrinsic fluorescence quenching ability.^{23–25} However, the fluorescence of $\text{NCP}_{\text{Cd}}\text{-R}$ at 421 nm was not affected by the doped R6G (Fig. 5A). Furthermore, photobleaching experiments for $\text{NCP}_{\text{Cd}}\text{-R}$ and NCP_{Cd} were investigated. According to Fig. S6, the fluorescence intensities of $\text{NCP}_{\text{Cd}}\text{-R}$ and NCP_{Cd} at 421 nm decrease slowly with UV irradiation within 60 min. This indicates that the $\text{NCP}_{\text{Cd}}\text{-R}$ and NCP_{Cd} are suitable as fluorescent probes for long-time observations.

The morphology of $\text{NCP}_{\text{Cd}}\text{-R}$ was also nanorod similar as NCP_{Cd} (Fig. 5B1). The $\text{NCP}_{\text{Cd}}\text{-R}$ nanorods with shorter length can be obtained simply by ultrasonication (Fig. 5B2). These

Fig. 4 Fluorescence property of NCP_{Cd}. (A) Excitation and emission spectra of the NCP_{Cd}. (B) Fluorescence of the NCP_{Cd} ($\sim 10 \mu\text{g mL}^{-1}$ in PBS, pH 7.4) quenched by H₂O₂ (1 μM , freshly diluted from 30% H₂O₂ before experiment) with different reaction time. (C) Fluorescence of the NCP_{Cd} ($\sim 10 \mu\text{g mL}^{-1}$ in PBS, pH 7.4) quenched by H₂O₂ with different concentrations (the reaction time was 6 min). (D) Plot of the fluorescence intensity ($I_0 - I$) of NCP_{Cd} at 421 nm as a function of the concentration of H₂O₂ (5–1000 nM). Inset: linear correlation between the fluorescence quenching intensity and H₂O₂ concentration (10–120 nM). Error bars indicate s.d. ($n = 3$).

Fig. 5 NCP_{Cd}-R for ROS sensing. (A) Schematic illustration of ROS sensing by NCP_{Cd}-R. (B) TEM images including: (B1) the morphology of NCP_{Cd}-R; (B2) the morphology of NCP_{Cd}-R broken by ultrasonication; (B3) the morphology of NCP_{Cd}-R after reacting with H₂O₂ (1 μM).

small nanorods were well dispersed in PBS buffer (pH 7.4). After reacting with H₂O₂, the nanorods were broken into nano-fragments (Fig. 5B3). Meanwhile, the emission peak at 421 nm

was quenched, and the R6G was released followed by the increase of the emission peak at 555 nm (Fig. 6A). The NCP_{Cd}-R shows good selectivity for ROS. As shown in Fig. 6B,

Fig. 6 ROS sensing by NCP_{Cd}-R. (A) Fluorescence of the NCP_{Cd}-R ($\sim 10 \mu\text{g mL}^{-1}$ in PBS, pH 7.4) before and after reacting with H₂O₂ (1 μM). The emission peak at 421 nm was excited by 400 nm and the emission peak at 555 nm was excited by 520 nm. (B) Relative fluorescence intensity observed upon reaction of NCP_{Cd}-R with ROS, thiol-compounds and other anions (or biomolecules)²⁶ (1 μM). (C and D) Plot of the fluorescence intensity ($I_{R6G} - I_{0,R6G}$) of NCP_{Cd}-R at 555 nm as a function of the concentration of H₂O₂ (20 – 100 nM) (C) and glucose (glc, 50 – 800 nM) (D). Error bars indicate s.d. ($n = 3$).

Table 1 Comparison of NCP_{Cd}-R nanorods with some of the recently reported nano-sensors for ROS (H₂O₂) sensing

Name	Nanomaterial supporter	Ratiometric sensing	Detection limit	Reference
NCP _{Cd} -R	Coordination polymer	No	12.4 nM	This work
FNFM	Gold nanocluster	No	500 nM	27
Fc@MSN-F _{DNA} /PTAD	Silica nanoparticle	No	2.4 nM	28
CNWD	CeO ₂ nanowire	No	0.64 μM	29
CYD1-UCNPs	Upconverting nanoparticle	Yes	80 nM	30
MnO ₂ -modified UCNPs	MnO ₂ nanosheet, and upconversion nanoparticle	No	0.9 μM	31
PMT-F127 micelle	Polymeric micelle	Yes	0.95 μM	32
CuNCs	Cu nanocluster	No	0.2 μM	33
Single plasmonic nanoprobe	Single Au nanoparticle	No	10 μM	34
Eu(III)-doped GdVO ₄ nanoparticles	GdVO ₄ nanocrystal	No	1.6 μM	35

the fluorescence of NCP_{Cd}-R detected at 421 and 555 nm can be selectively quenched or recovered in the presence of H₂O₂. Even the thiol-compounds (such as GSH and Cys) can quench the emission peak at 421 nm, but these compounds cannot lead to the recovery of the emission peak at 555 nm. It is because the thiol-compounds cannot break the NCP_{Cd}-R nanorods into nano-fragments and the R6G cannot release from the NCP_{Cd}-R. Therefore, the NCP_{Cd}-R can be used as a fluorescent probe for selectively sensing ROS. According to the fluorescence intensity of R6G, a good linear relationship for ROS (including H₂O₂, •OH, ClO₂⁻, and O₂⁻) can be obtained (Fig. 6C and Fig. S7). The detection limit for H₂O₂ (prepared by diluting 30% H₂O₂ directly) was 12.4 nM, calculated according to $3S_0/S$, where S_0 is the standard deviation of the blank ($n = 11$) and S is the slope

of the calibration curve. As a demonstration, the NCP_{Cd}-R shows good H₂O₂-detecting ability compared with the recently reported nano-sensors (including single Au nanoparticle, upconversion nanoparticles, polymeric nanoprobe, etc.) (Table 1).

The sensitive response of NCP_{Cd}-R toward H₂O₂ provides a potential platform to detect substrates involving H₂O₂-generation reactions for biological applications. For example, the GOx can specifically catalyze the oxidation of glucose in the presence of oxygen to form H₂O₂.³⁶ Herein, as a proof-of-concept demonstration, glucose was chosen as the model detective sample. Because of the high substrate specificity of GOx, H₂O₂ can be generated after the addition of glucose to the NCP_{Cd}-R suspension containing GOx. Then, the fluorescence intensity of

R6G was increased due to the reaction of H_2O_2 and $\text{NCP}_{\text{Cd-R}}$. As shown in Fig. 6D, good linear relationship of $(I'_{\text{R6G}} - I'_{0,\text{R6G}})$ (where I' and I'_0 are the peak fluorescence intensities in the presence and absence of the target, respectively) *versus* glucose was obtained in a range of 50 – 800 nM. Therefore, the $\text{NCP}_{\text{Cd-R}}$ can be potentially used as a glucose biosensor based on the reaction of GOx and glucose.

Conclusions

In conclusion, a fluorescent coordination polymer ($\text{NCP}_{\text{Cd-R}}$) based on disulfide carboxylate ligand was prepared *via* one-pot synthesis. The $\text{NCP}_{\text{Cd-R}}$ nanorods can be broken by ROS, meanwhile the fluorescence of NCP_{Cd} moiety (at 421 nm) was quenched and the fluorescence of the released R6G moiety (at 555 nm) was recovered. Even the thiol-compounds can also quench the fluorescence of NCP_{Cd} moiety, but it cannot break the $\text{NCP}_{\text{Cd-R}}$ nanorods into nano-fragments and R6G cannot be released. Therefore, the thiol-compounds cannot make the fluorescence of R6G “turn-on”. The $\text{NCP}_{\text{Cd-R}}$ probe shows high selectivity and sensitivity towards H_2O_2 . Furthermore, the $\text{NCP}_{\text{Cd-R}}$ probe provided an alternative platform as a glucose sensor by detecting H_2O_2 , which is produced from the GOx-catalyzed oxidation of glucose.

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Supporting Information

Figures S1 – S7 [PXRD, TEM images, FT-IR spectra of NCP_{Cd} , and photobleaching experiment]. This material is available free of charge on the Web at <http://www.jsac.or.jp/analsci/>.

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