



An optical sensing composite for cysteine detection using up-conversion nanoparticles and a rhodamine-derived chemosensor: Construction, characterization, photophysical feature and sensing performance



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ABSTRACT

In this paper, we reported an optical sensing composite for cysteine detection. A chemosensor derived from rhodamine 6G was synthesized and characterized. To minimize its photobleaching, up-conversion nanocrystals β - $\text{NaYF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ were prepared and modified with α -cyclodextrin, serving as excitation host. Under 980 nm laser excitation, emission of these up-conversion nanocrystals overlapped well with the absorption of our chemosensor. Energy transfer between them was analyzed and confirmed by emission decay analysis. Job's analysis suggested that the complexation equilibrium between our chemosensor and cysteine was a simple one with binding stoichiometry of 1:1. A sensing system was constructed with up-conversion nanocrystals (modified with α -cyclodextrin) and this chemosensor. Emission "turn-on" effect was observed only for cysteine but immune to other competing amino acids and thiols, showing a good selectivity.

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1. Introduction

Cysteine (CYS) is an important biological thiol and sulfide source in human body. Its disorder generally causes a series of impairments such as slow growth, liver damage, skin lesions and even Alzheimer's disease [1–3]. CYS recognition and quantification thus have been considered as an important task for health and medical care. Among the various techniques for CYS detection, optical sensing is usually recommended owing to its advantages of instant response, non-destructive character, simple instrumentation and operation procedure [4–6]. Hybrid structures are usually adopted since they combine virtues of each component, offering multiple and improved functions [7]. For a typical optical sensing system, there are generally two components: chemosensor and its supporting substrate [8–10]. Supporting substrate generally has good mechanical strength and stability to support its cargo. Chemosensor indicates the existence and quantification of analyte by giving sensing signal.

Some precursive efforts have reported optical sensing systems for CYS detection. Their chemosensors, however, are usually excited by UV light which leads to chemosensor photobleaching and even background light interference [7–10]. As a consequence, novel strategies should be explored aiming at improved photostability and low

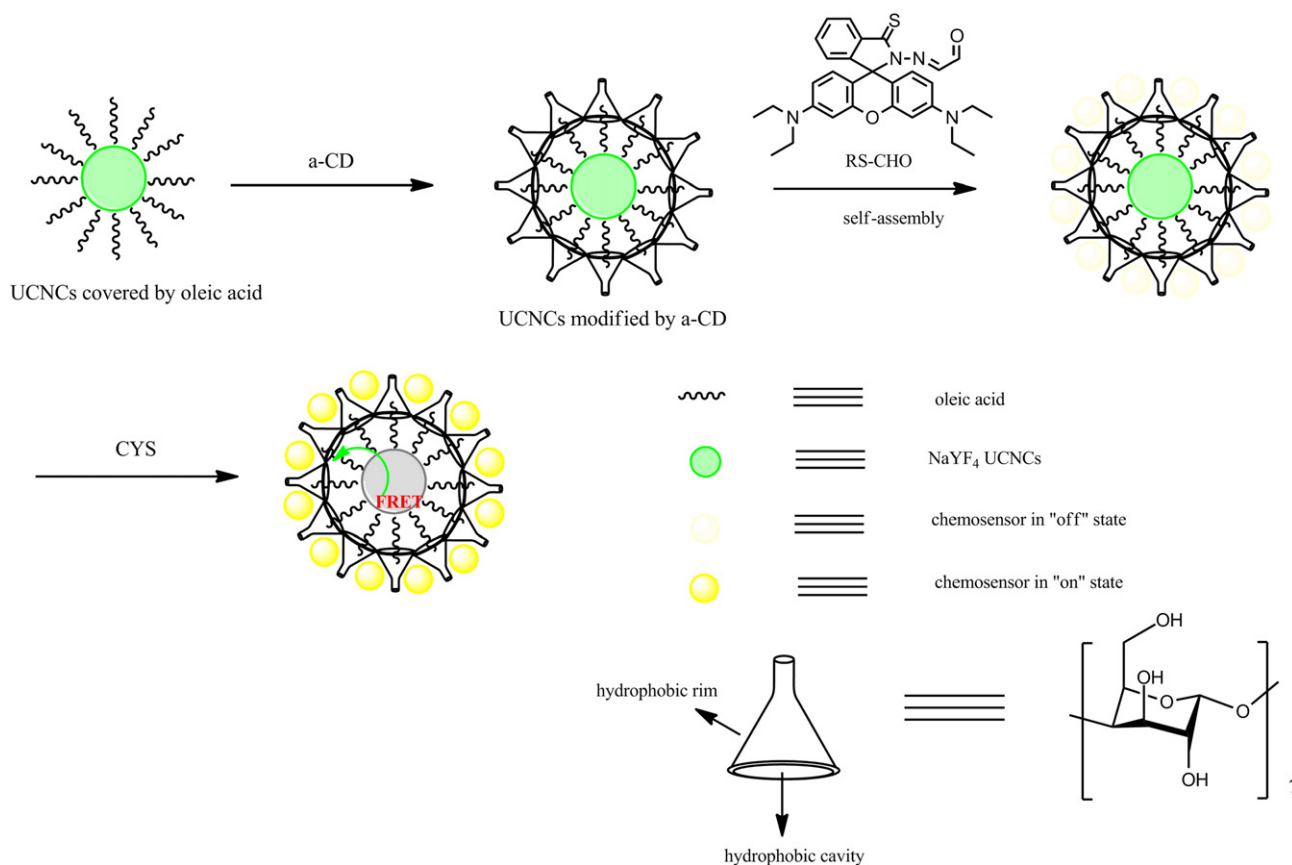
background light interference. Fortunately, up-conversion nanocrystals (UCNCs) have been proved as a promising excitation host for chemosensors. They harvest near-IR radiation and transfer energy indirectly to chemosensors, avoiding photobleaching and background light interference [11,12]. NaYF_4 lattice is a well-known up-conversion host owing to its high up-conversion efficiency and good matching with biological optical window [13]. Its other virtues include long lifetime, low cytotoxicity, good photostability and deep tissue penetration, which makes itself a possible supporting matrix for chemosensors of biological sensing, labeling, imaging and therapy [14].

There is one issue to be solved, though. Most UCNCs are prepared with oleic acid as stabilizing reagent and thus are covered by it [15]. This hydrophobic surface makes them incompatible with hydrophilic biological systems. Thus, proper surface treatment should be carried out on these UCNCs to make them hydrophilic.

In this work, we intend to modify NaYF_4 UCNCs with α -cyclodextrin (α -CD) which has been explored as a phase transfer reagent for nanoparticles [15]. In this case, α -CD offers a hydrophobic rim and a hydrophilic cavity through its self-assembly interaction. Oleic chains on NaYF_4 UCNCs surface are inserted into α -CD hydrophobic cavity with its hydrophilic rim open for suitable cargos such as chemosensors, as depicted by Scheme 1, so that their aqueous dispersibility can be improved [15]. A rhodamine derivative is synthesized and tried as a chemosensor for these NaYF_4 UCNCs, hoping to realize a sensing system of high sensitivity, good selectivity and limited photobleaching.

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Scheme 1. Synthetic route and sensing strategy of UCNCs (modified by α -CD) and RS-CHO.

2. Experimental section

2.1. Information for reagent and apparatus

Starting reagents, including rhodamine B, Lawesson's Reagent, oxalaldehyde and α -cyclodextrin (α -CD), were purchased from Alfares Pharma Corporation and used with no further purifications. Common reagents, including absolute ethanol, POCl₃, anhydrous hydrazine (95 wt.%), acetonitrile, hexane, cyclohexane, NaOH, oleic acid, 1-octadecene, concentrated HCl, rare earth salts and other inorganic salts, were supplied by Yongji Chemical Company (Shanghai, China). Organic solvents were firstly redistilled before usage. Solvent water was deionized.

NMR, MS and elemental analysis were recorded by a Varian INOVA 300 spectrometer, an Agilent 1100 MS series/AXIMA CFR MALDI/TOF MS spectrometer and a Vario Element Analyzer, respectively. IR, UV-vis and fluorescence spectra were recorded by a Bruker Vertex 70 FTIR spectrometer (400–4000 cm⁻¹, KBr pellet technique), a Shimadzu UV-3101PC spectrophotometer and a Hitachi F-4500 fluorescence spectrophotometer, respectively. XRD patterns were measured by a Rigaku D/Max-Ra X-ray diffractometer ($\lambda = 1.5418 \text{ \AA}$). Morphology and energy-dispersive X-ray (EDX) analysis were finished on a Hitachi S-4800 microscope and a JEM-2010 transmission electron microscope, respectively. Emission decay lifetimes were measured by a two-channel TEKTRONIX TDS-3052 oscilloscope, using a tunable laser as excitation source ($\lambda = 980 \text{ nm}$). For photophysical measurement and sensing evaluation, UCNCs were dispersed in phosphate buffer (PBS, pH = 7.0, 5 mg in 10 mL), then our chemosensor was added and shaken for 5 min.

2.2. Synthesis of RS-CHO

(E)-2-((3',6'-bis (diethylamino)-3-thioxospiro [isoindoline-1,9'-xanthen] -2-yl) imino) acetaldehyde (RS-CHO) was synthesized

following a three-step procedure [16]. First, rhodamine B (20 mmol) and CHCl₃ (50 mL) were mixed and cooled to 0°. POCl₃ (20 mL) was dispersed in CHCl₃ (50 mL) and slowly added into rhodamine B solution. This mixture was stirred at room temperature for 30 min and then at 90° for 8 h under N₂ protection. Excess POCl₃ and solvent were removed by rotary evaporation under reduced pressure. Solid product was purified in ethanol/water (V:V = 2:8) to give 2-amino-3',6'-bis(diethylamino)spiro[isoindoline-1,9'-xanthen]-3-one (RB-NH₂). ¹H NMR (CDCl₃), δ (ppm): 1.22 (t, 12H, NCH₂CH₃), 3.26 (q, 8H, NCH₂CH₃), 3.69 (s, 2H, N-NH₂), 6.34 (dd, 2H, xanthen-H), 6.39 (d, 2H, xanthen-H), 6.44 (d, 2H, xanthen-H), 7.17 (dd, 1H, Ar-H), 7.47 (dd, 2H, Ar-H), 8.14 (dd, 1H, Ar-H). ¹³C NMR (CDCl₃), δ (ppm): 12.25, 44.19, 71.45, 94.84, 105.19, 113.39, 127.34, 127.88, 128.32, 130.43, 131.37, 132.52, 140.67, 148.75, 150.35, 158.45. ESI-MS *m/e*: calc. for C₂₈H₃₂N₄O₂, 456.6; found, 456.4 [m]⁺. Anal. Calcd. for C₂₈H₃₂N₄O₂: C, 73.66; H, 7.06; N, 12.27. Found: C, 73.52; H, 7.17; N, 12.19.

Second, RB-NH₂ was reacted with Lawesson's reagent to give 2-amino-3',6'-bis (diethylamino) spiro[isoindoline-1,9'-xanthen]-3-thione (RS-NH₂) [17]. The mixture of RB-NH₂ (10 mmol), Lawesson's reagent (15 mmol) and anhydrous toluene (30 mL) were heated to 110° and kept for 6 h under N₂ protection. Solvent was removed by rotary evaporation under reduced pressure. Crude product was purified on a silica gel column using CH₂Cl₂ as eluent to give RS-NH₂. ¹H NMR (CDCl₃), δ (ppm): 1.21 (t, 12H, NCH₂CH₃), 3.24 (q, 8H, NCH₂CH₃), 3.65 (s, 2H, N-NH₂), 6.34 (dd, 2H, xanthen-H), 6.41 (d, 2H, xanthen-H), 6.48 (d, 2H, xanthen-H), 7.15 (dd, 1H, Ar-H), 7.47 (dd, 2H, Ar-H), 8.15 (dd, 1H, Ar-H). ¹³C NMR (CDCl₃), δ (ppm): 12.47, 44.82, 77.61, 95.28, 105.84, 113.67, 124.95, 127.12, 128.11, 129.69, 131.01, 141.22, 148.93, 150.29, 178.51. ESI-MS *m/e*: calc. for C₂₈H₃₂N₄OS, 472.6; found, 472.5 [m]⁺. Anal. Calcd. for C₂₈H₃₂N₄OS: C, 71.15; H, 6.82; N, 11.85. Found: C, 71.24; H, 6.73; N, 11.94.

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