



Full Length Article

Colloidal $\text{GdVO}_4:\text{Eu}^{3+}@\text{SiO}_2$ nanocrystals for highly selective and sensitive detection of Cu^{2+} ions

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ABSTRACT

Nowadays, in view of health and safety demands, the controlled design of selective and sensitive sensors for Cu^{2+} detection is of considerable importance. Therefore, we construct herein core-shell colloidal $\text{GdVO}_4:\text{Eu}^{3+}@\text{SiO}_2$ nanocrystals (NCs) as optical sensor for the detection of Cu^{2+} , which were synthesized by a facile hydrothermal reaction and encapsulated with a uniform layer of ultrathin silica through a sol-gel strategy. The NCs present strong red emission due to energy transfer from VO_4^{3-} groups to Eu^{3+} when exciting with ultraviolet (UV) light. This intense red emission from Eu^{3+} could be selectively quenched in the presence of Cu^{2+} in comparison to other metal ions and the limit of detection is as low as 80 nM in aqueous solution. It is revealed that the spectral overlap between the emission band of NCs and the absorption of Cu^{2+} accounts for this intriguing luminescence behavior. The detection ability is highly reversible by the addition of ethylenediaminetetraacetic acid (EDTA) with the recovery of almost 100% of the original luminescence. The luminescence quenching and recovery processes can be performed repeatedly with good sensing ability. These remarkable performances allow the colloidal $\text{GdVO}_4:\text{Eu}^{3+}@\text{SiO}_2$ NCs a promising fluorescence chemosensor for detecting Cu^{2+} ions in aqueous solution.

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1. Introduction

Lanthanide-doped inorganic compounds, consisting of a crystalline host doped with small concentrations of trivalent lanthanide ions (Ln^{3+}) in the form of solid solutions, have been the subject of intensive research during the past decades, due to their fascinating optical properties and good photochemical stability, which endow them with great potential applications in the fields of lighting devices, displays, optical fibers, optical amplifiers, solid-state lasers, as well as biotechnological applications [1–6]. Among them, Ln^{3+} ions are almost irreplaceable components for the generation of distinct and intense light emissions from UV to near infrared (NIR) spectral region in inorganic hosts (e.g., phosphates [7,8], vanadates [9–11], molybdates [12–14], tungstates [15,16], fluorides [17–19]). Such unique spectroscopic characteristics mainly arise from their partial filling of the 4f orbitals [20,21]. Among these available inorganic phosphors, micro/nanocrystalline vanadates (e.g., YVO_4 and GdVO_4) with tetragonal structure have emerged as a particularly attractive class of luminescent materials because of their excellent chemical and thermal stability, high emission

efficiencies under UV or NIR excitation, as well as the strong UV absorption of VO_4^{3-} groups followed by efficient energy transfer to Ln^{3+} [22–24]. In particular, GdVO_4 , as the host material, shows higher absorption cross sections and better luminescence performance when compared with other vanadates (e.g., YVO_4) [25,26]. For this reason, Ln^{3+} doped GdVO_4 micro/nanomaterials have been widely used as phosphors for efficient emission of the desired color of light (after doping with Eu^{3+} , Tb^{3+} , Dy^{3+} and Tm^{3+}) [27–29], as upconverters for the conversion of near infrared light to visible light (doped with $\text{Yb}^{3+}/\text{Er}^{3+}$, $\text{Yb}^{3+}/\text{Tm}^{3+}$ and $\text{Yb}^{3+}/\text{Ho}^{3+}$ upconversion pairs) [30,31], and as active laser medium for diode laser-pumped solid-state lasers (doped with Nd^{3+}) [32]. Additionally, $\text{GdVO}_4:\text{Ln}^{3+}$ ($\text{Ln} = \text{Eu}$ or Yb/Er) in the form of nanoparticles can function as drug carriers [33,34], luminescent sensors [25,35], and multifunctional nanoprobes for simultaneous optical and magnetic resonance detection [36–39].

Copper ion (Cu^{2+}) is a transition metal ion essential to human life and human health, which plays a vital role in multiple functions ranging from bone formation and cellular respiration to connective tissue development [40]. However, excess intake of Cu^{2+} can cause serious neurodegenerative diseases known as Wilson disease and Alzheimer's disease [41]. Accordingly, the maximum allowable level of Cu^{2+} in drinking water set by the U.S. Environmental Protection Agency (EPA) is 1.3 ppm ($\sim 20 \mu\text{M}$) [42]. Nevertheless,

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because of the widespread use of Cu^{2+} in modern agriculture and industry, the Cu^{2+} contamination and its subsequent potential toxic effects on humans is still an ongoing challenge. Therefore, it is necessary and of particular interest to develop highly sensitive and selective sensors for the detection of Cu^{2+} in the environment and biological systems. So far, there are quite a few reports on the detection of Cu^{2+} by using fluorescence-based methods due to their unique properties including ease of operation, time-saving, high detection limit and low cost. Most of them are based on fluorescent organic molecules [43–46], which could covalently bind to the Cu^{2+} in the solution and subsequently switch off their fluorescence. Meanwhile, new sensing technologies based on inorganic luminescent nanoparticles for Cu^{2+} detection have attracted a growing interest, with representative ones including functionalized gold nanoparticles [47–50], and QDs (e.g., ZnS, CdTe, and carbon dots) [51,52]. These fluorescence-based approaches open up new avenues in the development of high performance fluorescent sensors for the selective detection Cu^{2+} . Nevertheless, they also suffer from some drawbacks, which have been perplexing their practical applications to some extent. The emission spectra profiles of above-mentioned materials are usually very broad resulting from excitonic processes, which have an adverse effect on their detection sensitivity [53]. Moreover, most of organic molecules are not water-soluble due to the presence of hydrophobic ligands, and complex surface modification to transfer hydrophobic QDs from nonpolar solvent to aqueous solution are generally needed, which restrict their wide applications for the detection of Cu^{2+} in biological systems. In addition, the above mentioned luminescent nanomaterials, including silver nanoparticles, gold nanoparticles, and QDs show size dependent optical properties [54,55], thus demanding stringent control of synthesis process to obtain monodisperse and uniform nanoparticles.

On the other hand, Ln^{3+} -doped inorganic nanoparticles can largely inherit the optical properties of their corresponding bulks, which exhibit sharp emission signals, large Stokes shift, and long fluorescence lifetime due to the intraconfigurational 4f–4f transitions of Ln^{3+} dopants [20]. Recently, Ln^{3+} doped upconverting nanoparticles have been used for the selective detection of Cu^{2+} ions through the fluorescence resonance energy transfer (FRET) between the nanoparticles (energy donor) and organic fluorophore (energy acceptor) [56,57]. Although the sensing of Cu^{2+} using upconversion luminescence refers to the conversion of low-energy NIR photon to two or more high-energy photons, which favors the reinforced light penetration depth in tissue, there are still some daunting disadvantages. For example, the upconversion efficiency is quite low, particular in aqueous solution, owing to the presence of many hydroxyl groups [58], and the attached dye molecules on the surface of nanoparticles are generally characterized by low resistance to photodegradation [59], making them not reusable for long-term detection. In comparison to upconversion luminescence, the down-shifting luminescence (or photoluminescence) of Ln^{3+} doped NCs processes considerably higher luminescent quantum yield and is expected to have promising applications in the areas of sensing and diagnostic technologies. However, little attention has been devoted to the assessment of their potentiality as chemosensors for Cu^{2+} detection. In fact, to the best of our knowledge, only a few recently published works report on the sensing ability of Cu^{2+} using luminescent down-shifting nanoparticles [53,60–62].

In this contribution, we have constructed an effective optical sensor based on the colloidal core-shell $\text{GdVO}_4:\text{Eu}^{3+}@\text{SiO}_2$ NCs for highly sensitive and selective detection of Cu^{2+} in aqueous solution. The rigid amorphous SiO_2 structure can protect the luminescent $\text{GdVO}_4:\text{Eu}^{3+}$ core from the harsh environment and endow the luminescent core with good water dispersibility and biocompatibility. The free hydroxyl groups on the surface of NCs can adsorb various

metal ions, such as Al^{3+} , Ca^{2+} , Cd^{2+} , Cr^{3+} , Fe^{2+} , Mg^{2+} , Mn^{2+} , Ni^{2+} , Pb^{2+} , Zn^{2+} and Cu^{2+} , through the strong electrostatic interaction. In comparison to other common metal ions, direct quenching of the intense red emission of the Eu^{3+} can be selectively induced in the presence of Cu^{2+} even at very low concentration levels. More interestingly, the photoluminescence intensity of NCs can be almost 100% restored by the addition of EDTA.

2. Materials and methods

2.1. Materials

Rare earth nitrate hydrate ($\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, all with 99.99% purity), ammonium hydroxide ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 28–30 wt%) and poly(acrylic acid) (PAA, average Mw \approx 1800) were acquired from Aldrich. Sodium orthovanadate (Na_3VO_4 , 99.9%) and ethylene glycol (EG, 99%) were purchased from Alfa Aesar. Tetraethyl orthosilicate (TEOS, 98%) was used as received from Acros. $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ were supplied by Alfa Aesar. 0.5 mM Al^{3+} , Ca^{2+} , Cd^{2+} , Cr^{3+} , Fe^{2+} , Mg^{2+} , Mn^{2+} , Ni^{2+} , Pb^{2+} , Zn^{2+} and Cu^{2+} aqueous solutions were prepared by dissolving the corresponding salts into distilled water, respectively. EDTA was obtained from Daejung Chemicals & Metals. Ethanol was supplied by SK chemicals. All chemicals were of analytical grade and were used directly without further purification. Distilled water was used throughout the whole experimental process.

2.2. Synthesis of colloidal $\text{GdVO}_4:\text{Eu}^{3+}$ NCs

The crude $\text{GdVO}_4:5\%\text{Eu}^{3+}$ NCs were prepared by a facile hydrothermal method. Appropriate amounts of $\text{Gd}(\text{NO}_3)_3$ and $\text{Eu}(\text{NO}_3)_3$ were added into 25 ml ethylene glycol (EG) to form a clear solution. At the same time, Na_3VO_4 and PAA were dissolved in a mixture of 10 ml EG and 15 ml water. The two precursor solutions were mixed at room temperature under magnetic stirring. The mixed solution was transferred into a Teflon-lined stainless steel autoclave and heated at 120 °C for 12 h. As the autoclave was cooled to room temperature, the resulting suspension was separated by centrifugation, washed with ethanol and distilled water for three times, and redispersed in 40 ml of distilled water for further use and characterization.

2.3. Synthesis of core-shell $\text{GdVO}_4:\text{Eu}^{3+}@\text{SiO}_2$ NCs

The core-shell $\text{GdVO}_4:\text{Eu}^{3+}@\text{SiO}_2$ NCs were prepared by a modified Stöber process. 10 ml of colloidal $\text{GdVO}_4:\text{Eu}^{3+}$ solution was dispersed in 40 ml of ethanol under ultrasonic treatment for 30 min. Then 1 ml of concentrated ammonia and 0.15 ml of TEOS were added to the solution. After stirring at room temperature for 4 h, the resulting NCs were centrifugally separated from the suspension, washed with ethanol and distilled water, and redispersed in distilled water (20 mg/L) for further use.

2.4. Characterization

Powder X-ray diffraction (XRD) analysis of the as-prepared samples were characterized on a Bruker D8 Advance X-ray diffractometer with $\text{Cu K}\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$). Fourier transform infrared spectroscopy (FTIR) spectra were obtained using a Nicolet-IR 200 spectrometer with the KBr pellet technique. UV–vis diffuse reflectance spectra were recorded on a V-670 (JASCO) UV–vis spectrophotometer. Thermogravimetric analysis (TGA) was performed

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