



Review

Modification of silica nanoparticles with fluorescein hydrozide for Cu(II) sensing

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ABSTRACT

Fluorescein hydrozide modified silica nanoparticles (FH-SNPs, 280–550 nm) were prepared by covalently immobilizing a fluorescein hydrozide (FH) derivative containing organosilyl ligands onto the surface of silica nanoparticles. FT-IR, elemental analysis, SEM microscopy and steady-state fluorescence anisotropy were used to characterize the functionalized FH-SNPs. Upon the addition of Cu(II), the spiro-lactam ring of FH moiety on the silica surface was opened and a fluorescent product was formed, exhibiting a selective Cu(II)-amplified fluorescence signal. Under the optimized conditions, the linear range of fluorescence intensity for Cu(II) is 5–80 μM ($R^2 = 0.992$), and the limit detection for Cu(II) is 1.0 μM according to IUPAC definition ($C_{\text{LOD}} = 3.3S_b/m$).

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1. Introduction

Nanoparticle supports for hybrid organic dyes include silica, titania, alumina, and gold, which lead to pigments of smaller particles and an increase efficiency of dye adsorption [1–3]. Silica provides a hydrophilic surface due to the presence of silanol groups, which are weakly acidic and reactive for chemical modification [4,5]. Hybrid pigments composed of silica and organic dyes are promising substrates for chemical sensors [6–9], adsorption [10–12] and catalysis [13,14]. There are mainly two approaches to synthesize modified silica nanoparticles (SNPs). For the “bottom-up” approach, building blocks are allowed to self-organize into nanoparticle systems with functional properties [15–18]; nanoparticles prepared by water-in-oil microemulsion (W/O) are monodispersed, uniform in size, and relatively easy to control the size by varying the water to surfactant molar ratio and dynamic properties of microemulsion [19–21]. On the other hand, the direct modification of a dye to silica involves its modification with aminosilane coupling agent to graft silane chain onto silica surface, and then a functional group reacts with the grafted silane groups [22]. By above methods, the silica offers an optically transparent solid

support to be chemically modified by target-selective molecules, resulting in a boost in the development of optical sensor such as pH, anions, metal ions and neutral molecules [23–26].

In particular, the detection of Cu(II) by SNPs has received considerable attention, since the analytical significance of trace Cu(II) found in both environmental and biological processes [27–29]. Tonellato and his co workers grafted Cu(II) ligands and a fluorescent dye (8-anilinenaphthalensulfonic acid) to the surface of commercially available silica particles, and the operative range of sensors can be tuned either by switching the ligand units or by modification of components ratio [23]. However, it is well known that the detection mechanisms of Cu(II) were usually based on fluorescence quenching because of its paramagnetic properties, which would not satisfactory for the detecting effect [28,30–32]. Therefore, chemosensors exhibiting a Cu(II)-amplified fluorescence signal are always considered to be more attractive and efficient [33,34].

In this work, we selected a fluorescein hydrozide (FH) as an organic moiety, which was grafted onto the surface of silica nanoparticles to obtain FH-SNPs to detect Cu(II). In 30% (v/v) water/CH₃CN (10 mM Tris–HCl, pH = 5.2) buffer media, FH-SNPs displayed a fluorescence enhancement at 560 nm in the presence of Cu(II), and a selective detection of Cu(II) over other metal ions was achieved with the detection limit as 1 μM . Moreover, FH-SNPs could be repeatedly used for Cu(II) sensing after regeneration procedures

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by hydrazine solutions, which facilitated a reproducible dye-grafted fluorescent solid sensor for Cu(II) in water and practical samples.

2. Experimental section

2.1. Reagents

Doubly distilled deionized water was used throughout the experiment. All reagents were purchased from commercial suppliers (Beijing Chemical Reagent Co., China; Acros; Fluka) and used without further purification. The solutions of Cu(II), Fe(III), Co(II), Pb(II), Cd(II), Ag(I), Mn(II), Hg(II), Ca(II), Mg(II), Ba(II), K(I) and Zn(II) were prepared from their nitrate salts. The silica nanoparticles were purchased from Wanjing Co., China. Unless otherwise noted, all reagents and solvents used were analytical grade and without further purification.

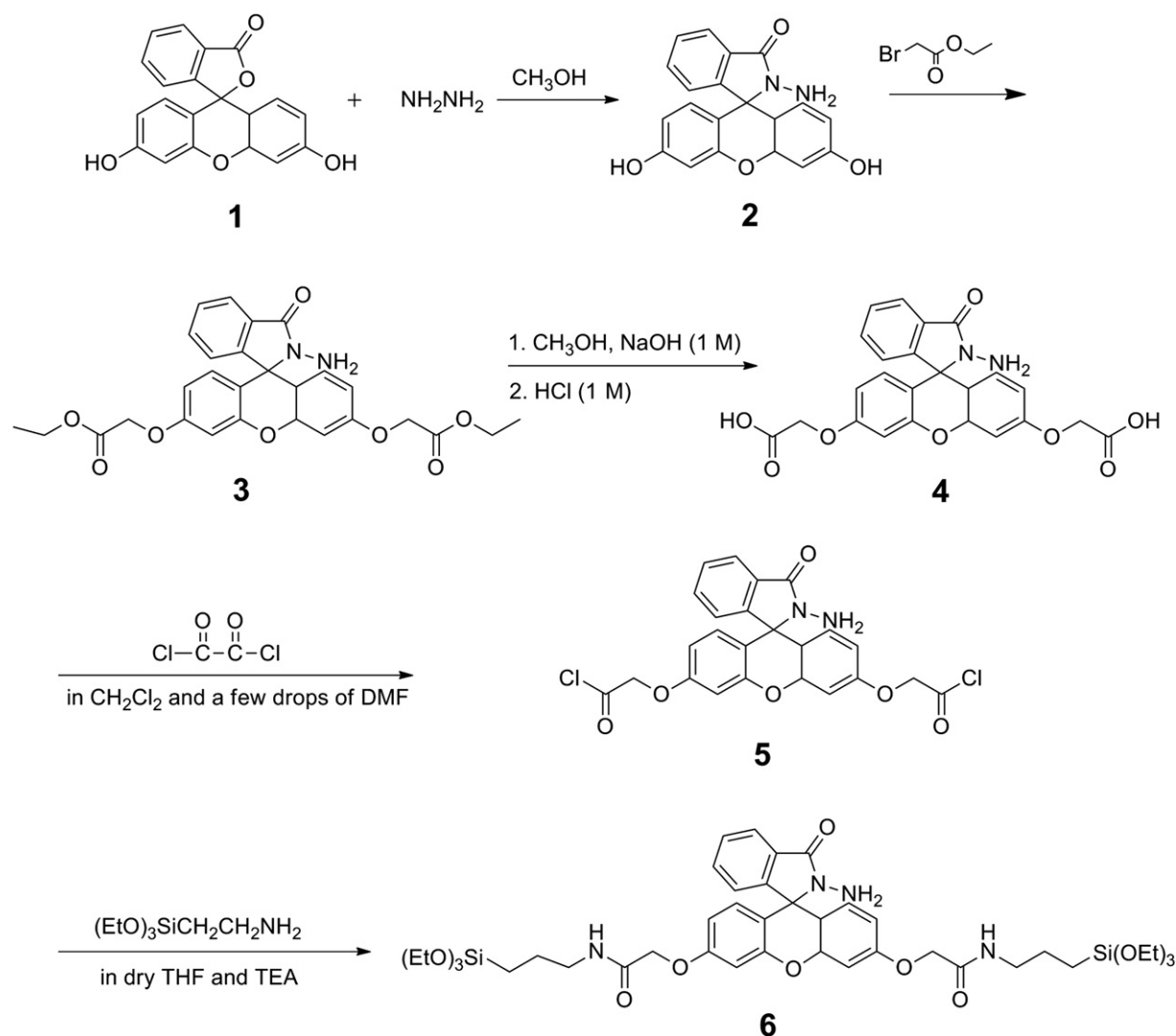
2.2. Apparatus and spectroscopic measurements

Absorption spectra were determined on a JASCO V-550 UV–vis spectrophotometer. Fluorescence spectra measurements were

performed on a JASCO FP-6500 spectrofluorimeter equipped with a xenon discharge lamp, 1 cm quartz cells. NMR spectra were recorded using a JOEL JNM-ECA300 spectrometer operated at 300 MHz. ESI spectra were obtained on an HP 1100 LC-MS spectrometer. Elemental analysis results were gained from Elementar Vario EL (Germany). Scanning electron microscopy (SEM) experiments were performed at JEM 2010. The particle size distributions were constructed with MIOURO-PLUS (50 nm–555 μm) light scattering instrument. Nitrogen adsorption–desorption isotherms were measured with a Micrometric ASAP 2020 adsorption analyzer (Norcross, GA). The specific surface areas of the sample membranes were calculated using the multiple-point Brunauer-Emmett-Teller (BET) method. The degree of modification and the silica support coverage with dyes were estimated by FT-IR spectrophotometer (JASCO FI/IR-6200). All measurements were operated at room temperature (about 298 K).

2.3. Synthesis of fluorescein hydrozide

The synthesis route was shown in Scheme 1. Fluorescein hydrozine ($C_{20}H_{16}N_2O_4$, **2**) was prepared as previously reported [35]. Diethyl fluorescein hydrozine-3,6-diacetate ($C_{28}H_{28}N_2O_8$, **3**)



Scheme 1. Chemical structures and synthesis route of **1–6**.

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