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Fluorescence sensor for Cu(II) based on R6G derivatives modified silicon nanowires

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ABSTRACT

A fluorescence sensor for selective detection of Cu(II) is realized by covalently immobilizing derivatives of rhodamine6G (R6G) on the surface of silicon nanowires (SiNWs). It features the release of R6G from the SiNWs in the presence of Cu(II), which causes a significant enhancement of the fluorescence over other metal ions. The present Cu(II) sensor has good selectivity and sensitivity, and exhibits a linear response in the range of 0.0–7.0 μM Cu(II). Different from conventional Cu(II) sensor with fluorescence quenching, the present sensor based on fluorescence enhancement facilitates the practical application. Especially, the release of the R6G from SiNWs could be utilized as fluorescent labeling for Cu(II) in microenvironment.

1. Introduction

Inorganic nanomaterials have been widely used in biological and environmental fields such as bio-labeling, imaging, drug delivery, separation processes and optical sensing [1–5]. In these applications, the size and the shape of nanomaterials have very important effects on their properties. Recently, much attention has been given to one-dimensional nanomaterials for building various sensors, due to its high activity, high surface-to-volume ratio, easy assembly in an array for the device [6–9] and especial suitability for intracellular detection by inserting it into cell [10]. Among these one-dimensional nanomaterials, SiNW is particularly favorable to be used as building block to fabricate sensor since its easy preparation in large quantity, high stability and biocompatibility [11,12]. Up to now, the study of the SiNWs-based sensor was mainly focused on electric or electrochemical method [13–17]. However, few optical sensors based on SiNWs have been reported [18–20]. Cu(II) is a very important element for hemopoiesis, metabolism and immune system [21]. There are many methods for detection of Cu(II), including electrochemical method [22], atomic absorption spectrometry [23], colorimetric method [24], fluorescence method, etc. However, the electrochemical method and atomic absorption spectrometry usually suffer from low spatial resolution and in some cases require complicated instrumentation, or time consuming procedures that are necessary for sample pretreatment [25]. The colorimetric method is in a simple manner, but its sensitivity is not good enough. The fluorescence detection offers several advantages including its high sensitivity, high-speed spatial analysis [26–29]. Although a variety of fluorescent agents for Cu(II) have been reported, most of them are based on organic molecules in solution, which usually suffer from the water-fast, complicated synthesis and necessary hydrolysis by intracellular esterase when used as the cellular imaging agent. By grafting these organic molecules on surface of one-dimensional (1D) nanomaterials, these organic molecules could be rationally brought into a cell by the 1D nanomaterials and avoid the hydrolysis. Moreover, such configuration could make one to sense the special part of the cell by inserting 1D nanomaterials into the cell [30]. Our previous work showed that the SiNWs-based fluorescence sensor could be used to detect Cu(II) with high sensitivity and specificity [31]. However, the sensor based on fluorescence quenching is inconvenient to detect trace metal ions due to interference from other quenchers. In this paper, the SiNWs were covalently modified with R6G derivatives to form a 'turn-on' fluorescence sensor for Cu(II). When Cu(II) exists, R6G can be released from the SiNWs, which causes a significant enhancement of the fluorescence over other metal ions. Taking into account the biocompatibility of SiNWs, the SiNWs modified with the R6G derivatives could be inserted into a single cell and exhibit a fluorescence response by releasing a fluorophore at specific location where Cu(II) exists. Therefore, the present sensor provides a foundation for the fluorescence marking in a single-cell.

2. Experimental details

2.1. Materials

SiO powder, chloropropyltrimethoxysilane and R6G were purchased from Sigma-Aldrich and used without further purification.

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The organic solvents used in all the experiments were purchased from Lanyi chemical Co., Inc., in Beijing, China and distilled for purification.

2.2. Preparation of SiNWs

SiNWs were prepared by chemical vapor deposition method [32]. SiO powder (Aldrich, 99%) loaded in an alumina boat was placed at the center of a high-temperature tube furnace. The system was vacuumized to 10^{-3} Pa as base pressure. The mixed gas consisting of Ar(95%) and H_2(5%) was introduced into the system as carrier gas. The system pressure was retained at 1×10^4 Pa. The furnace was heated and the temperature was maintained at 1350 °C for 6 h, then the furnace was cooled down to room temperature naturally. The yellow, cotton-like product was obtained in the furnace. As-prepared SiNWs with a diameter 8–10 nm were immersed in a solution of H_2SO_4:H_2O_2 3:1 (v:v) at 90 °C for 1 h and washed with distilled water. Then the SiNWs were immersed in a mixture of H_2O:$NH_3\cdot H_2O$:30%H_2O_2 5:1:1 (v:v:v) for 45 min and washed with distilled water to be neutral. The collected SiNWs were dried under vacuum for 10 h.

2.3. Synthesis of R6G hydrazide

2 g R6G was dissolved in 50 mL ethanol. After 5 mL hydrazine hydrate was added to the solution, the mixture was stirred for 6 h at 80 °C. The mixture was cooled down to the room temperature naturally. The pink product R6G hydrazide was collected by filtering and repeatedly washed by anhydrous alcohol. The product was dried under vacuum. ^{1}HNMR(400 MHz, $CDCl_3$): $\delta=1.34$ (t, 6H), 1.92 (s, 6H), 3.24 (q, 4H), 3.57 (s, 2H), 6.26 (s, 2H), 6.39 (s, 2H), 7.07 (t, 1H), 7.46 (m, 2H), 7.97 (d, 1H).

2.4. Modification of SiNWs

40 mg dried SiNWs were placed in a round-bottom flask, which was connected to a Dean–stark apparatus. 45 mL anhydrous toluene was added into the flask under nitrogen atmosphere. The mixture was heated at 140 °C to remove water. When 30 mL anhydrous toluene was obtained in the Dean–stark, the mixture was cooled down to room temperature naturally and 0.1843 mL (1 mmol) 3-chloropropyltrimethoxysilane was added into the flask. The mixture was stirred at 90 °C for 24 h. The products were defined as Cl-SiNWs. Cl-SiNWs were collected by a micro filter and repeatedly washed by anhydrous toluene, dichloromethane and ethanol. Finally, Cl-SiNWs were dried under vacuum.

30 mg Cl-SiNWs and 5 mg NaOH were placed in a round-bottom flask and 30 mL toluene was added. Then 41 mg(0.1 mmol) R6G hydrazide was dissolved in 15 ml acetonitrile and added into the flask. After the mixture was stirred for 24 h at 110 °C , the product defined as R6G-SiNWs were collected by a micro-filter and repeatedly washed by acetonitrile. The R6G-SiNWs were dried under vacuum.

2.5. Characterization

The structures of sample were characterized using transmission electron microscopy (TEM: JEOL JEM-2100F). A BRUKER-ADVANCEII400 spectrometer was used for NMR with TMS as the internal standard. Surface elemental characterization was performed with a MIQ-156 XPS spectrometer (RIBER, France). The fluorescence properties of the R6G-SiNWs were measured using a fluorescence spectrometer (Hitach 4500, Japan). The R6G-SiNWs were dispersed into HEPES buffer solution of 30% CH_3OH-aqueous at pH 7.0 to form a 20 μg/mL suspending solution. A 150 W Xe lamp was used as the light source and the excitation wavelength was modulated at 521 nm. The way to perform concentration dependent experiments is gradually titrating ions into solution of R6G-SiNWs.

3. Results and discussion

The TEM image of SiNWs before modification was shown in Fig. 1. To characterize the modification of SiNWs, the elements on the surface of the bare SiNWs, Cl-SiNWs and R6G-SiNWs were analyzed by the XPS spectra. Observing from Fig. 2(A), we found that there were few Cl atoms on the surface of the bare SiNWs and lots of Cl atoms on the surface of the Cl-SiNWs, which indicated that the 3-Chloropropyltrimethoxysilane has been connected to the SiNWs. After Cl-SiNWs further reacted with R6G hydrazide, the content of Cl was obviously decreased on the surface of the R6G-SiNWs. It reveals that most of the Cl was replaced by the R6G hydrazide. Furthermore, it can be observed that no N exists on the surface of the SiNWs and Cl-SiNWs, but

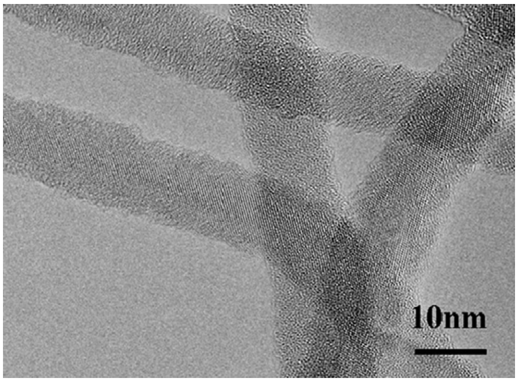

Fig. 1. HRTEM image of SiNWs.

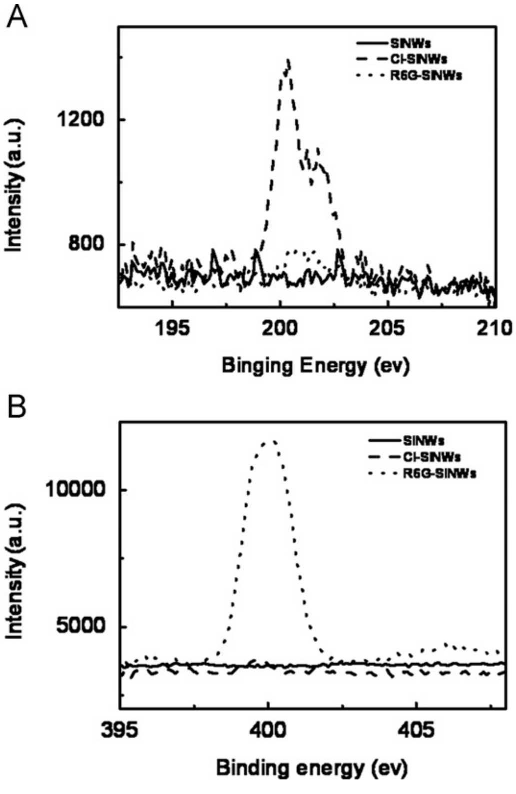

Fig. 2. XPS spectra of SiNWs, Cl-SiNWs and R6G-SiNWs. (A) Cl(2p) (B) N(1s).