



# A reversible colorimetric chemosensor for naked-eye detection of copper ions using poly (aspartic acid) nanofibrous hydrogel



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## ARTICLE INFO

### Article history:

Received 8 June 2015

Received in revised form

20 July 2015

Accepted 23 July 2015

Available online 31 July 2015

### Keywords:

Copper ions

Naked-eye detection

Chemosensor

Poly (aspartic acid)

Nanofibrous hydrogel

Reversibility

## ABSTRACT

A novel, biodegradable colorimetric chemosensor for  $\text{Cu}^{2+}$  ions detection in aqueous water was designed using poly (aspartic acid) nanofibrous hydrogel, based on the strong complexation ability of poly (aspartic acid) nanofibrous hydrogel and the specific color change phenomena of biuret reaction. The poly (aspartic acid) nanofibrous hydrogel sensor exhibited high sensitivity and selectivity toward  $\text{Cu}^{2+}$  ions over other competing ions with a detection limit of 0.01 mg/L. Furthermore, the poly (aspartic acid) nanofibrous hydrogel sensor displayed a sensitive colorimetric response in the presence of  $\text{Cu}^{2+}$  ions according to the pH values it exposed to. The on–off–on color switching behavior upon pH alternation between 14 and 1 illustrated an excellent reversible color change. This low-cost, biodegradable and reversible sensor possessed a promising application for practical  $\text{Cu}^{2+}$  ions detection in real water samples and provided a new insight into the design of colorimetric sensor based on nanofibrous hydrogel.

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## 1. Introduction

Copper is a common transition metal element with high thermo-electric conductivity and it is extensively used in various industries such as alloy [1], electric wires [2] and batteries [3]. Copper is also one of the most important micronutrients required in numerous biological processes, including neurotransmitter synthesis, free radical defense and neutral myelination [4–6]. However, exposure to elevated concentrations of copper ions is dangerous as it can damage brain and other organs. A growing body of evidence suggests that excess dietary copper can cause Wilson's disease [7], Menkes disease [8], Parkinson's disease [9] and Alzheimer's disease [10]. The United States Environmental Protection Agency (US EPA) limits the maximum contaminant levels goals (MCLG) for copper in drinking water to 1.3 mg/L for protection of public health. Due to the toxicity and widespread existence of  $\text{Cu}^{2+}$  ions in wastewater from electroplating, metallurgy, chemical industry, etc., the development of highly sensitive, low cost and

feasible methods to determine  $\text{Cu}^{2+}$  ions in water is of great significance.

During the past decades, several techniques for  $\text{Cu}^{2+}$  ions detection have been developed, including atomic absorption spectroscopy [11], inductively coupled plasma mass spectrometry (ICP-MS) [12], inductively coupled plasma atomic emission spectrometry (ICP-AES) [13] and electrochemical method [14]. Although these methods can provide accurate measurements, the requirement of costly and large precision instruments limits their application in many cases. Therefore, the development of efficient colorimetric sensors is practical and highly desired. Considerable research has been conducted on colorimetric detection, including sensors based on gold or silver nanoparticles [15], DNzyme [16], fluorophores [17], and conjugated polymers [18,19], but most of these methods still suffer from expensive material and complicated preparation process. Additionally, disposal of these used sensors is a troublesome problem since they could cause negative effects on the environment. To solve this problem, poly (aspartic acid) (PASP) that has excellent biocompatibility and biodegradability was employed to design the sensor for  $\text{Cu}^{2+}$  ions detection in this study.

PASP is a kind of poly (amino acids) and falls under the category of polypeptides. Owing to its low cost, simple synthetic technique, excellent biocompatibility and degradability, strong

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metal complexation ability and high water absorption, PASP has extensive potential applications in water treatment, cleaning products, sanitary, agricultural and biomedical fields [20–22]. As a polypeptide, PASP complexed with  $\text{Cu}^{2+}$  ions under alkaline conditions can shift the color of  $\text{Cu}^{2+}$  ions solution from blue to purple, which is commonly termed “biuret reaction”. The well-known biuret reaction is widely recognized as a simple, selective method for proteins and peptides determination [23]. Though the biuret reaction is usually described in the condition of overdose  $\text{Cu}^{2+}$  ions for protein detection,  $\text{Cu}^{2+}$  ions can be detected using overdose proteins via biuret reaction in turn. The limit and the linearity range of protein detection using biuret method are 0.02 mg/mL and 0.5–4.0 mg/mL, respectively [24]. Thus, the biuret method is not available for  $\text{Cu}^{2+}$  ions detection at low concentration because of its less sensibility. Compared to nature proteins, PASP possesses more functional groups in the side chains for heavy ions binding. In this present paper, an enrichment system based on PASP nanofibrous hydrogel (PASP-NH) was developed for  $\text{Cu}^{2+}$  ions detection.

Due to its water-solubility, PASP can hardly be employed for ions enrichment. A super water-absorbent hydrogel without water-solubility can remedy this defect. Traditional bulk hydrogel has a slow response due to its lack of interconnected micro-pores. Recently, we have successfully prepared the microporous PASP-NH via electrospinning. The versatile PASP-NH membrane has numerous interconnected pores and large specific area, which will not only boost the diffusion of analytes into the membrane, but also promote the contact and interaction between analytes and the surface of PASP-NH. The metal ions in aqueous water can be loaded into the PASP-NH assemblies and immobilized onto the surface of PASH-NH via complexation. To explore the potential applications of PASP-NH, this paper devotes to the development of an eco-friendly PASP-NH based copper sensor, and for the first time the naked-eye colorimetric chemosensor based on PASP-NH for  $\text{Cu}^{2+}$  ions sensing in aqueous solution is studied.

## 2. Experimental section

### 2.1. Reagents and apparatus

Aspartic acid and 85% phosphoric acid for PSI synthesis were purchased from Aladdin Co., Shanghai, China. N, N-Dimethylformamide (DMF), ethylenediamine and sodium hydroxide were obtained from Fisher Scientific. The solutions of various metal ions were prepared from  $\text{CaCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{ZnCl}_2$ ,  $\text{SnCl}_2$ ,  $\text{NiCl}_2$ ,  $\text{CuCl}_2$ ,  $\text{AgNO}_3$ ,  $\text{Pb}(\text{NO}_3)_2$ . Distilled water was used throughout all experiments. All chemicals were purchased from commercial suppliers and used as received without further purification.

The morphology of nanofibrous membranes was observed with scanning electron microscope (SEM) (S3000N, Hitachi Ltd., Japan). Absorption spectra were recorded on a UV–Vis spectrophotometer (Cary 5000, Varian, USA) with a 1.0 cm quartz cell.

Fourier transform infrared (FTIR) spectra in attenuated total reflectance mode (ATR) were obtained on an FTIR spectroscopy (Frontier, PerkinElmer, USA). The pH measurements were conducted using a pH meter (Orion 4 Star, Thermo Scientific, USA).

### 2.2. Preparation of PASP-NH

The PASP-NH was prepared as precisely described (Scheme 1) [25]. Firstly, polysuccinimide (PSI), as the intermediate of PASP, was synthesized via polymerization of aspartic acid with 85% phosphoric acid as a catalyst. Then the PSI was dissolved in DMF with concentration of 30 wt% and electrospun into nanofibers. Finally, the PSI nanofibers were crosslinked in 0.3 mol/L ethylenediamine

solution (solvent was water/ethanol (1:1, vol:vol)) and hydrolyzed in 0.1 mol/L NaOH solution to obtain the PASP-NH.

### 2.3. Naked-eye sensing of ions measurements

Solutions of various metal ions ( $\text{Cu}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Pb}^{2+}$ ) were prepared by dissolving predetermined concentration of the corresponding salts in water. For preparation of PASP-NH sensor, the PSI nanofibrous membrane was cut into square strips with a dimension of about 30 mm × 30 mm, and the weight of strips was fixed at 10 mg before crosslinking and hydrolysis. In a typical naked-eye sensing measurement, 500 mL sample solution containing metal ions was added to a 1 L beaker and the strip was immersed into the sample solution with a stirring rate of 200 rpm for 5 min. Then the hydrogel strips were taken out and kept in 1 mL sample solution with 0.1 mL of 1 mol/L NaOH for naked-eye determining. For UV–Vis experiment, the strip was cut into tiny pieces and the solution was diluted to 2 mL. PASP-NH in pure distilled water without metal ions was employed as a baseline. To compare with the PASP-NH, 10 mg PASP powder without crosslinking was added into 2 mL sample solution containing various concentrations of  $\text{Cu}^{2+}$  ions with 0.1 mL of 1 mol/L NaOH directly for UV–Vis detection.

To investigate the effect of pH values on color change of the sensor, sensor strips were immersed into 100 mg/L  $\text{Cu}^{2+}$  ions solution simultaneously for 12 h and then removed from the solution and separately put into 2 mL aqueous solution with pH from 1 to 14. HCl and NaOH were used to adjust the pH values of the aqueous solution.

## 3. Results and discussion

### 3.1. Preparation of PASP-NH

Due to the insolubility, PASP-NH is difficult to be electrospun into nanofibers directly. PSI is the intermediate of PASP and the liner molecular structure endows it with excellent spinnability for electrospinning. Therefore, PSI was employed for the preparation of nanofibers as an intermediated product form. As shown in Scheme 1, PSI nanofibers with a smooth surface and uniform fiber diameter were manufactured through electrospinning of 30 wt% PSI solution. PASP-NH was then obtained through crosslinking and hydrolysis of the PSI nanofibers. The PASP-NH nanofibers were lightly distorted and fused together after crosslinking and hydrolysis process, but they still exhibited nanofibrous geometric characteristics. When immersed in water, the PASP-NH quickly swelled and turned into transparent instantly due to the abundant interconnected micro-pores and small nanofibers diameter. Moreover, the only bonding at nanofibers contact sites endowed PASP-NH membrane flexibility and the structural integrity when swollen.

The  $^1\text{H}$  NMR spectrum of synthetic PSI powder was identified in Fig. 1A. The peak at 5.3 ppm corresponded to the methine protons while the peaks at 2.7 ppm and 3.2 ppm were assigned to the methylene protons [26]. FTIR/ATR spectra of PSI nanofibers and PASP-NH were shown in Fig. 1B. The adjacent bands at  $\sim 1713\text{ cm}^{-1}$  and  $\sim 1795\text{ cm}^{-1}$  assigned to imide rings of PSI were observed in the spectrum of PSI nanofibrous mat. After crosslinking and hydrolysis, the bands corresponding to imide rings of PSI disappeared. At the same time, the N–H stretching at  $\sim 3268\text{ cm}^{-1}$ , C=O stretching at  $\sim 1647\text{ cm}^{-1}$ , and the overlapped band of C=O stretching and N–H bending at  $\sim 1541\text{ cm}^{-1}$  were obtained [27], indicating the amide rings of PSI open and PASP-NH successfully synthesized.

### 3.2. Basic mechanism for visual detection of $\text{Cu}^{2+}$ ions

Scheme 2 explains the sensing mechanism of the PASP-NH based chemosensor. Considering the metals ions will form

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