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A paper-based ferrous ion sensor fabricated from an ion exchange polymeric membrane coated on a silver nanocluster-impregnated filter paper

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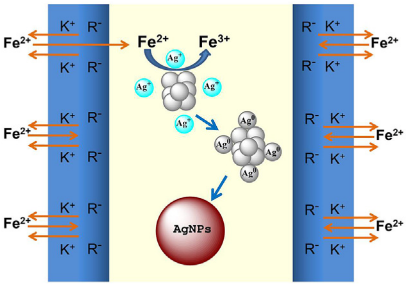
HIGHLIGHTS

- Demonstrate a new type of paper-based colorimetric sensor.
- Use ion exchange polymeric membrane couple with paper-based concept.
- Utilizing of silver nanoclusters as a selective chromogenic material impregnated on the paper substrate.
- Highly selective colorimetric sensor for Fe^{2+} and can be observed by naked eye.

GRAPHICAL ABSTRACT



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ABSTRACT

A paper-based colorimetric sensor was fabricated using polymethylacrylic acid-templated silver nanoclusters (AgNCs) as a sensing probe for the detection of Fe^{2+} and employing an ion exchange polymeric membrane as a coating layer. AgNCs were impregnated on a cellulose filter paper. The AgNC-impregnated filter paper was then lacquered with a hydrophobic membrane of polyvinyl chloride plasticized with *o*-NPOE incorporating a hydrophobic cation exchanger. Due to the ion exchange phenomenon at the membrane surface, Fe^{2+} was extracted into the paper layer, and the bound Ag^+ on the AgNCs was reduced by Fe^{2+}. The growth of the cluster could be observed by measuring the increase in the silver nanoparticle (AgNP) plasmon band. The maximum plasmon band on the paper at 447 nm increased as a linear function of the increasing Fe^{2+} concentration. The proposed sensor was highly selective to Fe^{2+} over Fe^{3+} and other cations. The proposed sensor was optimized and could be used to detect Fe^{2+} solution concentrations as low as 50 μM, with a wide working linear concentration range of 0.2–1.0 mM. The sensor was applied to determine Fe^{2+} in iron supplement tablet samples with satisfactory results.

1. Introduction

Paper-based sensors have been introduced in several applications in analytical chemistry due to the excellent physical and chemical properties of paper [1]. Paper composition has a majority

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of cellulose, which is a hydrophilic material. Paper can provide excellent properties such as flexibility, high specific stiffness [2], lightness [3], a high surface-to volume ratio [1], a porous structure, a soft texture, compatibility with biological samples [4], and chemical and biological inertness [5]. It can be used to produce disposable sensors with low analysis cost, suitable for onsite measurements. Several paper-based sensor platforms have placed hydrophobic materials on some areas to control the water diffusion zone [6]. Moreover, different types of paper-based devices such as paper-based microfluidic sensors [7], paper strips [8], and paper-based inkjet-printed sensors [9] have been fabricated for use in both chemical and biological applications.

Colorimetric paper-based sensors are the most prevalent, as such devices offer a bright, high-contrast, colorless background for color change readings [10]. Basically, when a target analyte interacts with sensing compounds on the paper, a color change is observed. Several sensing materials have been introduced into paper-based colorimetric sensors, such as silver nanoparticles (AgNPs) modified with homocysteine and dithiothreitol for the sensing of Cu^{2+} [11]. Ceria nanoparticles have been demonstrated as paper-based chromogenic probes in bioanalysis for the detection of H_2O_2 or glucose [12]. In addition, organic dyes can be immobilized on paper-based colorimetric sensors. Eight pyridylazo derivatives combined with array technology-based pattern-recognition were proposed for the detection of eight heavy metal ions at concentrations as low as 50 μM [13].

PVC plasticized with DOS or *o*-NPOE has been used as a polymer matrix to fabricate ion selective membranes [14] and bulk optodes due to its high hydrophobicity and good physical and mechanical properties for fabricating thin membranes [15]. An ion selective membrane comprises a hydrophobic ionophore and a hydrophobic ion exchanger dissolved in the polymer matrix. A hydrophobic chromoionophore is also added in the case of bulk optodes. At the interface between the sample solution and the membrane, primary ions are extracted into the membrane by an ion exchange process and complex with the ionophore inside the membrane. This phenomenon creates a potential change at the membrane interface, and the membrane potential against reference electrodes can be measured [16]. From this principle, the ion exchange membrane limits the species to be extracted into the membrane phase. Therefore, in this work we are interested in the introduction of an ion exchange membrane for the fabrication of paper-based colorimetric sensors.

Nanomaterials have been introduced into the fabrication of chemical sensors due to special properties that are not found in their bulk materials [17]. Several types of chemical sensors such as electrochemical sensors [18], fluorescence sensors [19] and colorimetric sensors [20] using nanomaterials as sensing probes have recently been demonstrated. Among nanomaterials used in the fabrication of chemical sensors, nanostructures of noble metals such as gold and silver seem to be most popular materials. Silver nanostructures can be divided into two major groups depending on their size: silver nanoparticles (AgNPs) and silver nanoclusters (AgNCs) [21]. The size of AgNCs is approximately 2 nm [22], and sizes larger than this are classified as AgNPs. Most colorimetric sensors have been based on the measurement of the plasmon resonance phenomenon in AgNPs [23]. However, the recent discovery of AgNCs has attracted chemists' attention because the size of AgNCs is between the size of silver atoms and silver nanoparticles, resulting in discrete electronic levels [24]. This characteristic allows the transition of an electron upon excitation with a suitable light source. In addition, the optical phenomenon changing from light absorption to resonance with the light source (plasmon) when changing from AgNCs to AgNPs [25] can be monitored and used as a transducer.

In our previous report [26], we proposed a selective colorimetric sensor to detect ferrous ions based on polymethylacrylic acid-templated silver nanoclusters. In the presence of Fe^{2+}, un-reacted Ag^{+} in the AgNC solution could be reduced to Ag^{0} and deposit on the AgNCs. Therefore, the increasing particle size and the color changes could be observed visually. On the other hand, other studied metal ions did not alter the color of the AgNCs.

In this work, we demonstrated a proof of concept that hydrophilic materials can be used as a selective sensing probe with a hydrophobic ion exchange membrane by using paper as an interface material. In this paper, we describe the utilization of water-soluble AgNCs as a selective chromogenic material impregnated in the paper substrate. A plasticized PVC membrane with a hydrophobic cation exchanger was then lacquered on the filter paper. The proposed sensor was used as a selective sensor for the detection of Fe^{2+}. In the presence of Fe^{2+} in solution, Fe^{2+} ions can be extracted into the paper layer by the ion exchange process to reduce Ag^{+} remaining in the AgNCs to Ag^{0}, which then deposits on the AgNCs. The color change based on the size increase from AgNCs to AgNPs can be observed and monitored.

2. Experimental

2.1. Chemicals and materials

All reagents were of analytical grade and used without further purification. High molecular weight poly(vinylchloride) (PVC), potassium tetrakis (*p*-chlorophenyl)borate (KT*p*ClPB), 2-nitrophenyl octyl ether (*o*-NPOE) and tetrahydrofuran (THF) were obtained from Fluka. Silver nitrate was purchased from BDH. Poly(-methacrylic acid) sodium salt was purchased from Sigma-Aldrich. Ferrous ammonium sulfate, sodium hydroxide, sodium acetate, and sodium hydroxide were obtained from Carlo Erba. Glacial acetic acid was obtained from QRec. Ferric nitrate nonahydrate, lead(II) nitrate, nickel nitrate hexahydrate and zinc nitrate hexahydrate were purchased from Fluka. Ultrapure water (18.2 MΩ cm) was obtained from a Millipore water purification system. Whatman No.1 filter paper was obtained from Cole-Parmer (Vernon Hills, IL). The silver nanoclusters were synthesized and characterized according to a previously published procedure [26].

2.2. Instrumentation

Absorption spectra were recorded using a Shimadzu UV-3101PC UV-VIS-NIR spectrophotometer. Absorption spectra of Fe^{2+}-phenanthroline complexes were recorded using an Agilent HP 8453 UV–Vis spectrophotometer. The morphology of the paper surface was imaged using a Hitachi S-4800 scanning electron microscope (SEM) combined with an energy dispersive spectrometer using an acceleration voltage of 3 kV and a working distance of 3.8 mm in a high vacuum chamber. An inductively coupled plasma optical emission spectrometer (ICP-OES, Optima 2100 DV, USA) was used to determine total Fe in supplement samples. The pH levels of solutions were measured using an UB-10 Ultra Basic pH meter (Denver Instrument).

2.3. Preparation of the paper-based sensor

A filter paper was cut to 1 × 1 cm. Then, the paper was immersed in a 6.0 mM AgNC solution for 10 min, after which the paper was removed from the solution and dried in an oven at 80 °C for 5 min, thereby obtaining the AgNC-impregnated paper. The ion exchange membrane was prepared by dissolving 0.0013 g of KT*p*ClPB, 0.07 g of *o*-NPOE and 0.03 g of PVC in THF (3 mL). Each AgNC-impregnated paper was dipped into the polymer solution for