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Research Paper

Gold nanoclusters immobilized paper for visual detection of zinc in whole blood and cells by coupling hydride generation with headspace solid phase extraction

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ABSTRACT

A novel visual detection method was developed for the determination of zinc (Zn) in whole blood and cells using gold nanoclusters (AuNCs) immobilized paper. The detection of Zn was based on a headspace-solid phase extraction (HS-SPE), visible fluorescence from the AuNCs coated paper was quenched by ZnH_2 generated from hydride generation (HG). The potential mechanism was investigated by using X-ray photoelectron spectroscopy (XPS) and Density Functional Theory (DFT). The selectivity was significantly increased because the zinc hydride was effectively separated from sample matrices by hydride generation. A limit of detection (LOD) of 3 $\mu g\,L^{-1}$ Zn^{2+} and a relative standard deviation (RSD, n = 7) of 2% at a concentration of 50 $\mu g\,L^{-1}$ of Zn^{2+} were obtained when using a commercial fluorescence spectrophotometer as the detector. In visual detection, as low as 20 $\mu g\,L^{-1}$ of Zn^{2+} in biological samples can be easily discriminated from the blank with the naked eye. The proposed method retains several unique advantages, including straightforward, rapid, affordable and equipment-free for visual detection.

1. Introduction

Zinc (Zn) is an essential trace element of great importance for animals and human [1]. It is a cofactor in more than 200 important enzymes and has a structural role in numerous of Zn finger proteins [2]. Decency of zinc in human beings may lead to several diseases such as delayed wound healing, retardation of growth, decrease in the immunological defense, skin lesions and infertility [3]. Zn may enter the human body via the environmental food chain, ambient air or drinking water [4]. In this regard, the determination of trace zinc in biological samples attracts a growing interest [5,6].

Hydride generation (HG) atomic spectrometry (AS) is one of the most widely used methods for zinc analysis [7,8]. However, there remains a number of serious impediments for Zn detection, including require expensive and bulky atomic spectrometric instruments, need high energy consumption, and cannot be accomplished at home or in the field [9]. Fluorescence assays, hence, have attracted the attention of analytical scientists owing to the advantages of simple, sensitivity and economy [10,11]. Owing to its ultra-small size, biocompatibility and highly fluorescent properties, gold nanoclusters (AuNCs) has become an attractive field in fluorescent assays [12–14]. Recently, the nanomaterials immobilized paper analytical device (PAD) has drawn much attention in analytical because of its low cost, simplicity, rapidness, disposable, and can be used in visual detection with the naked eye [15–17]. Quantum dots, golden nanoparticles and other materials coated papers have been successfully applied to the determination of Se, Cu and some molecular compounds like catechol and glucose [18–23]. Krull et al. have presented a paper-based solid phase assay for transduction of nucleic acid hybridization by using immobilized quantum dots (QDs) as donors in fluorescence resonance energy transfer (FRET) [24,25]. But there have few works utilize AuNCs for PAD assay. This may be due to the major shortcoming of serious interferences from coexist-

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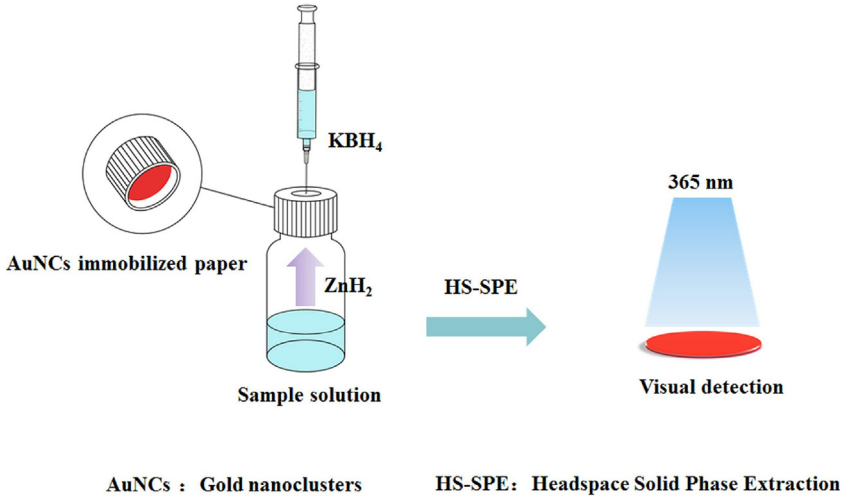

Scheme 1. Schematic diagram of the experimental setup.

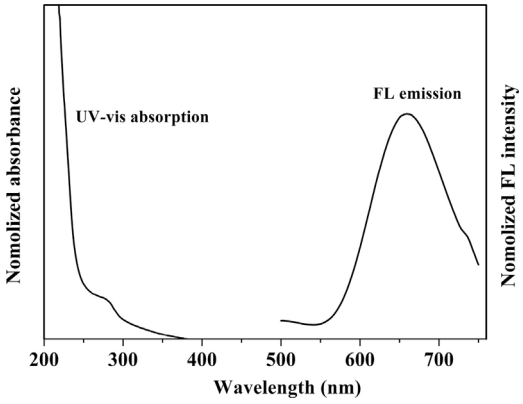

Fig. 1. The UV–Vis absorption spectra and the fluorescence emission spectra of AuNCs.

ing ions (like Fe^{3+}, Hg^{2+}, Cu^{2+}) when the AuNCs-based paper assay methods was used for determination of analyte ions in liquid phase [26–29].

In this work, a novel visual method based on AuNCs based PAD assay with headspace-solid phase extraction (HS-SPE) was developed for detection of zinc in biological samples. In the proposed method, a gas–solid reaction between the paper supported AuNCs and the ZnH_2 generated by HG occurred to quench the fluorescence of the AuNCs. Owing to the advantage of efficient matrix separation from HG, the interferences from sample matrices were eliminated (such as Hg^{2+}, Cu^{2+} and Fe^{3+}), which can significantly and rapidly quench the fluorescence of AuNCs.

2. Experimental

2.1. Chemicals and materials

Reagents used in this work were of at least analytical grade. High purity deionized water (DIW, 18.2 MΩ cm resistivity) produced by a water purification system (Chengdu Ultrapure Technology Co., Ltd., Chengdu, China) was used throughout this work. 1000 mg L^{-1} of standard stock solutions of Zn^{2+}, Hg^{2+}, Mg^{2+}, Ca^{2+}, Ag^{+}, Fe^{3+}, Ni^{2+}, Sr^{2+}, Cu^{2+}, Cd^{2+}, Ba^{2+}, Co^{3+}, Na^{+}, K^{+}, As^{3+} and Pb^{2+} were purchased from the National Research Center for Standard Materials of China. BSA, $HAuCl_4$ from Aladdin Reagent Co. (Shanghai, China) were used to prepare AuNCs. HCl, KBH_4 and NaOH were purchased from Kelong Reagent Factory (Chengdu, China). Diethylpyrocarbonate (DEPC) and *N*-ethylmaleimide were purchased from Aladin (Shanghai, China).

2.2. Instrumentation

The fluorescence spectra were performed on a commercial F-7000 fluorescence spectrophotometer (Hitachi, Japan) equipped with a solid sensing cell was used to measure fluorescence quenching of the AuNCs. The absorption spectra were acquired on a UV–vis spectrophotometer (lambda 950, PerkinElmer, USA). High-resolution transmission electron microscopy (HRTEM) images of the QDs were obtained with a transmission electron microscope at an accelerating voltage of 200 kV (HRTEM, Tecnai F20, FEI). A Quanta 250 (FEI Instrument Co., USA) scanning electron microscope (SEM) was used here to collect scanning electron microscope images. Atomic force microscope (AFM, Bruker-Multimode8, German) and X-ray photoelectron spectroscopy (XPS, PHI-5000 Versa Probe, ULVAC-PHI) were employed for the characterization of AuNCs. Fluorescence imaging was carried out with a gel image analysis system (Shanghai Jiapeng Instrument Factory, F-2) equipped with a 365 nm reflected UV source. A pH meter (PHS-25, Shanghai, China) was used to measure the pH of the aqueous solutions. A RCT B S25 magnetic stirrer (IKA, Germany) was used synthesized AuNCs.

2.3. Synthesis of BSA–AuNCs

BSA–AuNCs was synthesized in aqueous solution using a simple and green synthetic method reported previously with a little change [30]. Aqueous $HAuCl_4$ solution (5 mL, 10 mM, 37 °C) was added to BSA solution (5 mL, 50 mg mL^{-1}, 37 °C) and then kept stirring. After two minutes, NaOH solution (0.5 mL, 1 M) was added in the solution and the mixture reacted at 37 °C for 12 h. The color of the solution changed from light yellow to light brown, finally to deep brown. The AuNCs then kept at 4 °C prior to use.

2.4. Preparation of the paper devices

All the conditions for the preparation of gold nanoparticles should be consistent to obtain a better reproducibility. A chromatography paper (Whatman, UK) cut to a diameter of 2 cm was immersed in AuNCs solution (3 mL/15 paper sheets) 30 min and dried in an oven at 40 °C for 30 min. Finally, the papers doped with AuNCs were then sealed in plastic bags and kept at room temperature to use.

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