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Performance of electrokinetic stacking enhanced paper-based analytical device with smartphone for fast detection of fluorescent whitening agent

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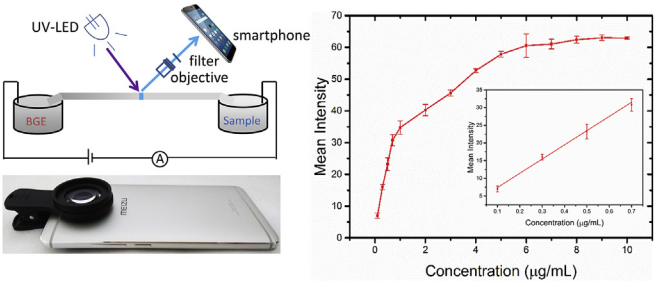
HIGHLIGHTS

- The sensitivity of aportable PAD for fluorescent whitening agent (FWA) was 160 times enhanced by electrokinetic stacking.
- A LOD comparable to the fluorescent spectrophotometer was achieved with smartphone fluorescent imaging detection.
- Fast determination of FWA in napkin was successfully demonstrated with high recovery rate and reasonable reproducibility.

GRAPHICAL ABSTRACT



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ABSTRACT

Quantification is a fundamental aspect of performance of an analytical system. Paper-based analytical device (PAD) as an on-site detection platform has drawn wide attention mainly due to its portability and cost effectiveness. In this work, a portable and low-cost PAD for online preconcentration and sensitive determination of fluorescent whitening agent (FWA) was demonstrated, which was consisted of ultra violet light-emitting diode (UV LED), macro-focusing lens, smartphone and miniaturized DC voltage source. Taking a widely used FWA component VBL as the analyte, the performance of the PAD enhanced with electrokinetic stacking (ES) and fluorescence imaging detection was systematically investigated. With ES, the sensitivity of the PAD system was 160-fold enhanced, and a limit of detection (LOD) of 0.06 μg mL^{-1} was achieved. The dynamic range was 0.1–10.0 μg mL^{-1} (linear in 0.1–0.7 μg mL^{-1}, $R^2 = 0.99$). With manual operation, the relative standard deviation (RSD) of intra-day and inter-day were all below 15%. Eventually, VBL from different napkin samples and toilet paper was determined with average recovery rates in the range of 90%–95% (RSD = 8.0%–12.0%). This work shows that with ES, the sensitivity of PAD can be greatly improved, and a LOD close to a desktop fluorescent spectrophotometer can be achieved as demonstrated by the detection of FWA component.

1. Introduction

Since microfluidic paper-based analytical device (PAD) was introduced by Whitesides and co-workers in 2007 [1], PAD continues to develop in many fields, for instance, environmental

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monitoring [2,3], medical diagnostic [4–7], food quality control [8] and security [9]. The major advantages of PAD include simplicity, cost effectiveness, easy fabrication, flexibility and on-site detection [10]. Major detection methods so far introduced in PAD include colorimetric method [4,7,11], electrochemistry [12,13], chemiluminescence [14] and fluorescence [3,15]. Among these detection methods, fluorescence detection exhibits substantially high sensitivity [16]. Crooks and co-workers achieved LOD of 9.3 μg mL^{-1} for BSA by fluorescence imager on a three-dimensional (3-D) paper microfluidic device [16]. Desktop fluorescent detection system is normally bulky and expensive, and not suitable for on-site analysis. On the other hand, smartphone as a detection means in PAD is portable and cheap with advanced imaging functions [17,18]. However, poor sensitivity is a limit for its wider application in the determination of low concentration analytes in PAD [19]. Some methods have been proposed to improve the sensitivity of PAD, for instance, chemical or biological signal amplification [15,20,21], electrokinetic stacking (ES) [22], evaporative concentration [23]. ES is an important signal enhancement method in capillary and chip electrophoresis system [24]. Up to now, three modes of ES have been introduced in PAD. They are ion concentration polarization (ICP) [25–28], isotachophoresis (ITP) [29], field-amplified sample stacking (FASS) [30–32]. Sinton et al. [25] used ICP to concentrate and detect FITC-BSA by inverted fluorescence microscope in a PAD, and limit of detection of 0.13 μg mL^{-1} was achieved. FASS is a simple yet effective approach that only requires the conductivity difference between background electrolyte (BGE) and sample solutions [32,33]. We have demonstrated signal enhancement of 1000-fold for fluorescein dye and DNA on a PAD with FASS [30]. Although ES is very effective for sensitivity enhancement of PAD, the quantitative performance still needs to be further investigated.

Fluorescent whitening agent (FWA) is a type of chemical that absorbs ultraviolet light (290–400 nm) and emits visible blue light (400–480 nm), hence can be used to increase the visual brightness and whiteness. It is widely used in daily commodities such as in napkin and cloth [34,35], and its potential harmfulness to health is still controversial [36,37]. Conventionally, FWA is determined by high-performance liquid chromatography (HPLC), ultra-high performance liquid chromatography tandem mass spectrometry (UPLC-MS), UV absorption and fluorescence spectrophotometry [34,35,38,39]. These methods require expensive and bulky instruments, and are not suitable for on-site fast detection.

In this paper, taking the fluorescent whitening agent (FWA) as the detection target, the quantitative performance of a portable PAD enhanced with ES was systematically investigated. The ultra violet light emitting diode (UV LED) was used to excite the fluorescence, and the camera of a smartphone was used for fluorescent imaging. We showed here that with this simple PAD system, a LOD comparable to that of a desktop fluorescence spectrophotometer was achieved, and determination of FWA in napkin samples was demonstrated with high recovery rate and reasonable reproducibility.

2. Experimental

2.1. Chemicals and materials

Tris (hydroxymethyl) aminomethane (Tris), hydroxyethyl cellulose (HEC), polyvinyl pyrrolidone (PVP), hydrochloric acid (HCl) and ethanol were purchased from Laibo Technology Co. Ltd (Shenyang, China). Fluorescent whitening agent 85 (VBL) was obtained from Qingshan Chemical Industry Co. Ltd (Shanxi, China). The stock VBL solutions were prepared in brown centrifuge tube and stored at 4 °C. Deionized water was used throughout the experiments. Glass fiber paper substrate was obtained from Kejia Environmental product Co. Ltd., Dezhou, China. The paper substrate was cut into strips (35 mm × 2.5 mm) by a dedicated cutter (No. 8061, Deli Stationery, Ningbo, China). Platinum wires of 0.5 mm diameters were used as the electrodes.

2.2. Instruments

The PAD system was schematically shown in Fig. 1a. A small size voltage converter (300 V DC, GRB12300D, ESSO Latham Electronic Technology Co., Ltd., Shenzhen, China) was supplied by 5 V portable Li battery. The UV LED (365–370 nm, Xin Huakai Photoelectric Co. Ltd., Shenzhen, China) was used for the excitation light source. A working distance between the paper channel and the image acquisition system of about 6 cm was necessary for placing the LED illumination. However, the image acquired directly with the smartphone camera (M1 Note, Meizu, China) was not clear enough due to poor focusing. In this work, either a stereomicroscope (ZTX-3E-3C, Huaguang Precision Instrument Co., LTD., Ningbo, China) or a clip lens with 12.5 × (50 RMB from Mai Pu Luo Technology Co., Ltd., Shenzhen, China) could be used for better focusing. A long-pass filter (400–700 nm) was placed in the light path to reduce the background. The filter and smartphone could be either installed on the tube adapter to the eyepiece of the stereomicroscope (Fig. S1b, SI), or be adapted directly to the clip lens as shown in Fig. 1b. The system was covered by a light proof cloth to avoid interference from ambient light. Multimeter (MT-1232, ProsKit, Taiwan) was used for monitoring the working current. A desktop

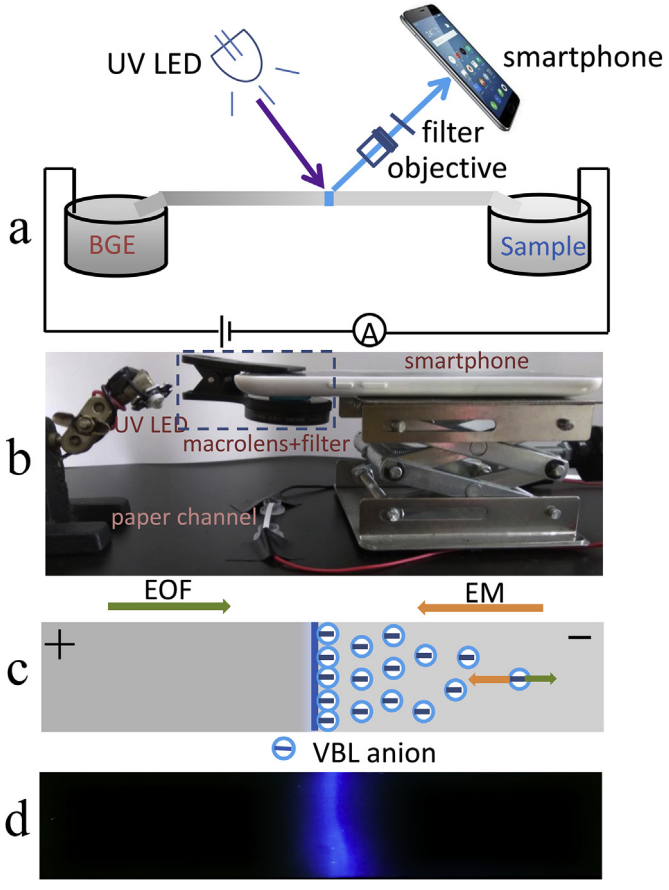

Fig. 1. (a) Schematic of the set-up of the PAD. (b) The picture of the PAD with the lens. (c) Principle of electrokinetic stacking of VBL anion. EM was electromigration and EOF was electroosmotic flow. (d) Typical fluorescent image of the stacking band on the PAD.