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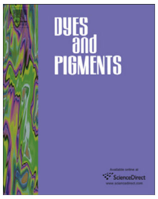

Sensitive determination of Sudan dyes in foodstuffs by Mn–ZnS quantum dots

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ABSTRACT

A novel luminescence sensing system has been designed for Sudan dyes detection based on the quenched fluorescence (FL) of oleic acid-functionalized Mn–ZnS quantum dots (QDs). The Sudan dyes could quench the fluorescence signal of Mn–ZnS QDs due to the so-called inner filter effect. Herein, it was demonstrated that this facile methodology could offer a rapid, reliable and selective detection of Sudan dyes, and the detection limits of Sudan I, II, III, and IV were 24.6, 32.7, 2.1, and 3.2 ng/mL, respectively. In this work, Sudan dyes were mainly detected in hot chili sauce, sausage, egg and tomato sauce, and Sudan I was chosen as spiked substance owning to its wide use as a coloring matter among Sudan dyes in many industrial and daily products. Furthermore, the recoveries of Sudan I from the standard fortified blank samples were in a range of 93.0–107.0%, and the relative standard deviations (RSDs) were lower than 2.8% ($n = 3$).

1. Introduction

Sudan dyes [1–3] (Sudan I, II, III, and IV) are phenyl-azoic derivatives with an orange–red appearance and extensively using as color waxes, oils, petroleum, solvents, and polishes [4]. Sudan I [5,6], one of the most frequently used Sudan dyes, has also been adopted for coloring various foodstuffs, such as particular brands of curry powder and chili powder. Owning to their azoic structure (Scheme 1), Sudan dyes have evident toxic effect to human's organs [7,8]. Such as the aniline which produced during the Sudan dyes metabolic processes, could attack the hepatocytes and lead to toxic hepatic disease [9]. Moreover, the nerve system would be also destroyed by long-term intaking of aniline [10]. So, they posed an increased risk of cancer for humans and were classified as category 3 carcinogens by the IARC (International Agency for Research on Cancer) [11]. Due to this fact, the European Union and other countries have prohibited the use of Sudan dyes in various processed foods since 1995. China has also enacted the laws to forbid adding Sudan I into food such as red chili power, chili sauce, cream, tomato, ketchup [12]. Up to now, no national and international food regulation act has permitted the use of these colorings as food additives [13]. Unfortunately, a variety of foodstuffs contaminated with Sudan dyes (particularly Sudan I) have been detected throughout Europe and Asia. In April 2003, that Sudan I was detected in hot chili and hot chili products from India engendered fears in the EU [14]. And two years later, in March 2005, similar food panic happened in China as well as in the EU again [15]. For this reason, accurate and reliable methods for the determination of Sudan dyes in foodstuff are required for the assurance of consumer healthiness.

There have been several methods to detect the presence of Sudan dyes [16–18]. The most commonly used method was high performance liquid chromatography (HPLC) [19–21], which included various detector systems, such as UV, atmospheric pressure chemical ionization-mass spectrum (APCI-MS), diode array detection electrospray ionization mass spectrum (DAD-ESI-MS), electrospray ionization mass spectrum/mass spectrum (ESI-MS/MS) [22,23], and so on. Besides, many other methods have been developed, for example, capillary electrophoresis [24,25], which was approved by the European Commission to separate and detect Sudan I, II, III and IV, plasmon resonance light scattering [18], enzyme-linked immunosorbent assay [26–28] and electrochemical

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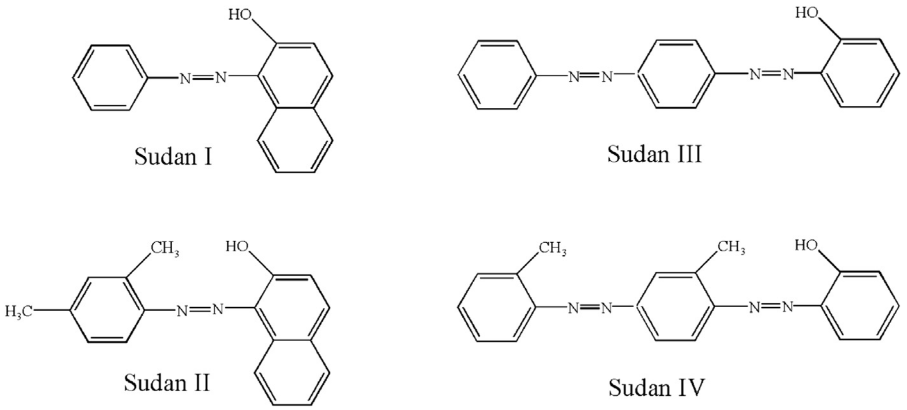


Scheme 1. Chemical structures of Sudan I, II, III, and IV.

method [29–31]. Although these methods were quantitative, they took a long time, needed large sample volumes, generated large amounts of waste, and required bulky and expensive instruments. Therefore, a simple, rapid and sensitive method to detect Sudan dyes in foodstuffs is highly desirable.

In this work, a new luminescence sensing system has been designed for Sudan dyes detection based on the quenched fluorescence signal of oleic acid-functionalized Mn–ZnS QDs, which was owing to the so-called inner filter effect. The experimental strategy was inspired by the phenomena and the detailed approach was depicted in Scheme 2. The salient advantages of the present work were as follows. Firstly, it was the first time to apply Mn–ZnS QDs luminescence sensing system to detect Sudan dyes. Secondly, no complex process and expensive instruments except fluorescence spectrophotometer were needed. What's more, the interferences from some hydrophilic chemicals such as salts were avoided due to the detection progress conveying in cyclohexane system. Besides, the method was so simple, rapid and less sample needed. Finally, the method developed here showed high selectivity toward Sudan dyes detection, which could be attributed to the maximum fluorescence emission of Mn–ZnS QDs at 580 nm, and very little chemicals showed interferes at this wavelength.

2. Experimental section

2.1. Chemicals

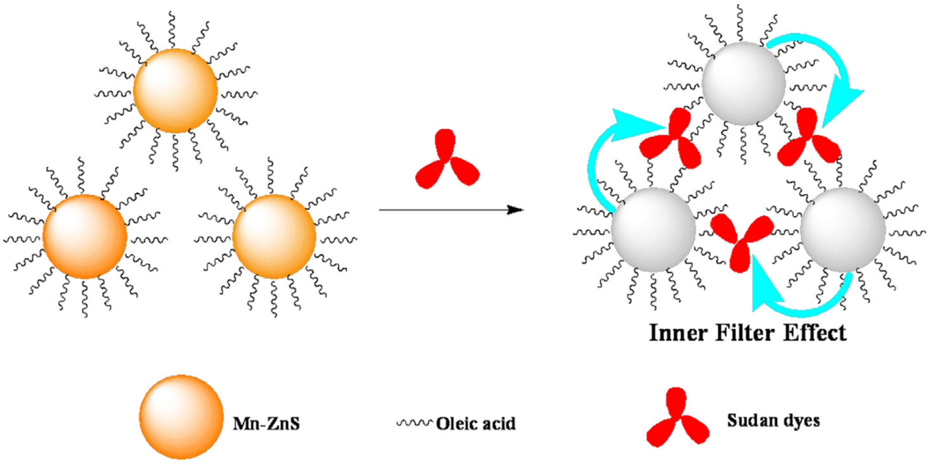
In brief, $ZnCl_2$, $MnCl_2$, NaOH and $Na_2S \cdot 9H_2O$ were purchased from Tianjin Guangfu Chemical Reagents Co. Ltd (Tianjin, China). Oleic acid was obtained from Xilong Chemical Co. Ltd (Guangdong, China). Ethanol and cyclohexane were purchased from Rionlon Chemical Reagents Co. Ltd (Tianjin, China). Sudan I, II, III, and IV were all commercially available from Aladin Reagents Co. Ltd (Shanghai, China). Sodium chloride, sodium acetate, sodium benzoate, sodium citrate, acetic acid, ethanol, sucrose, ascorbic acid, urea, L-Glu, L-Cys, L-Tyr and L-Lys were analytical reagent grade and used as received without further purification. Milli-Q deionized water (18.2 MΩ cm) was used during all the experiments.

2.2. Instrumentation

X-ray diffraction (XRD) measurements were performed on a X'Pertpro Philips X-ray powder diffractometer with Cu Kα radiation ($\lambda = 1.54056$ Å) at a scanning rate of 10°/min in the 2θ range from 15 to 80°. The morphology and diameter of Mn–ZnS QDs nanoparticles were confirmed by transmission electron microscopy (TEM) (Tecnai G^2 F30, Netherland). All luminescence spectra were surveyed on an RF-5301PC fluorescence (FL) spectrophotometer using 5/5 nm slit width, and equipped with a 1-cm quartz cell (Shimadzu, Kyoto, Japan). The ultraviolet–visible (UV–Vis) absorption spectra were acquired on a TU-1901 UV–Vis Spectrophotometer with a 1-cm quartz cell (Beijing Purkinje General Instrument Co., Ltd., Beijing, China).

2.3. Synthesis of Mn–ZnS QDs

The Mn–ZnS QDs stabilized by oleic acid were prepared according to the reference with slight modifications [32]. Briefly, 1.2 g



Scheme 2. Schematic illustration of the Sudan dyes detection mechanism using the Mn–ZnS QDs.