Carbohydrate Polymers 200 (2018) 560–566

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Luminescent, stabilized and environmentally friendly $[EuW_{10}O_{36}]^{9-}$-Chitosan films for sensitive detection of hydrogen peroxide

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ARTICLE INFO

Keywords:
Chitosan (CS)
Europium-containing polyoxometalates (Eu-POM)
Films
Hydrogen peroxide (H_2O_2)
Sensitive detection
High specificity

ABSTRACT

Fabrications and applications of luminescent films have been an interesting and important challenge within the realm of academia and industry. Herein, a novel fluorescence-based strategy for the H_2O_2 detection has been developed by fabrication of stabilized, thin, transparent, and luminescent films composed of europium-containing polyoxometalates (Eu-POM) and environmentally friendly chitosan (CS) via a facile solution casting approach. In comparison with pure Eu-POM, enhanced fluorescent properties are obtained from the as-prepared Eu-POM/CS films in terms of prolonged fluorescence lifetime and a remarkable fluorescent quenching effect in the presence of hydrogen peroxide (H_2O_2). The fluorescence intensity of Eu-POM/CS films exhibits a linear correlation in response to the H_2O_2 concentration over a wide range of 1.1–66 μM, with a detection limit of 0.11 μM. Furthermore, the fluorescent films display a high detection selectivity which are capable of differentiating hydrogen peroxide (H_2O_2) from the interfering species, such as sugars, L-amino acids, and other metabolites. All these advances towards the development of Eu-POM/CS films open up new applications for luminescent films, but most importantly, they can help in the far-reaching technological implementations of a simple, cost-effective method for the detection of H_2O_2 in many fields.

1. Introduction

Hydrogen peroxide (H_2O_2), as a reactive oxygen species (ROS), involves in various biological processes as byproduct and plays an important role in assessment of human health hazards. For instance, H_2O_2 is the product of leukocyte and erythrocyte metabolism in human plasma (Sagi & Fluhr, 2001). Moreover, H_2O_2 is also an indispensable intermediate for activated phagocytes in inflammatory process (Bolwell, 1999). In addition, the H_2O_2 concentration in the human body is directly related on the oxidative stress on account of the mediating diverse physical responses. Therefore, it is known as one of the major parameters that indicates progressive neurodegenerative diseases in human body, such as Alzheimer's (Barnham, Masters, & Bush, 2004), cancer (Ohshima, Tatemichi, & Sawa, 2003) and Parkinson's (Matet, Heuzey, Pollet, Ajji, & Averous, 2013). The detection of H_2O_2 has attracted broad interest over past several decades given the far-ranging impacts of H_2O_2 on human health and disease. Numerous methods have been exploited for monitoring H_2O_2 including spectrophotometry (Chen, Hai, Chen, & Wang, 2014), chemiluminescence (Lan, Li, & Zhang, 2008), electrochemistry (Lin, Yan, & Li, 2014) and fluorometry (Shen & Xia, 2014). Despite the numerous advantages, there has several drawbacks which those well-established methods suffer from. In detail, spectrophotometry and chemiluminescence approaches are not capable of analyzing colored samples. The electrochemistry method relies strictly on the cleanness of the electrodes, which could be easily contaminated by the proteins in blood. Therefore, a robust method to detect H_2O_2 would be highly desirable and has always been a major topic of interest in relevant communities. In recently years, fluorescence spectroscopy has received a great deal of attention for the detection of chemical and biological due to its rapid response, simple technical implementation and low-cost. Chang's group applied the ratiometric fluorescent approach based on Ratio-Peroxyfluor-1 (RPF1) to the detection of hydrogen peroxide (Albers, Okreglak, & Chang, 2006). Zhang et al. constructed functionalized fluorescent gold nanoclusters based on the model functional template for the detection of hydrogen peroxide, which was utilized to detect H_2O_2 in living cells (Wen et al., 2011). More recently, Chu and colleagues synthesized up-conversion nanoparticles (UCNPs) modified by the manganese dioxide (MnO_2)

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https://doi.org/10.1016/j.carbpol.2018.08.038
Received 9 April 2018; Received in revised form 10 August 2018; Accepted 10 August 2018
Available online 11 August 2018

nanosheets as a rapid turn-on fluorescent sensor for the detection of hydrogen peroxide and glucose (Yuan et al., 2015). Nevertheless, synthetic methods of these applied material are usually complicated, and their bio-stability are also low. As an emerging field, there has been a continuous innovations about luminescent films in support of easy fabrication, controllable shape and size (He & Hu, 2004), admirable chemical stability (Ma, Zeng, Zheng, & Wu, 2011), which allows real-time detection of substrate (Lü, Gao, Ding, Jiang, & Fang, 2006) in recent years. However, synthesis of luminescent films faces enormous with superior properties encouters many difficulties. For instance, the synthesis processes of these applied material are usually complicated, and their bio-stabilities are also low. It is extremely difficult to apply luminescent films in aqueous solution, since most of them are constructed from the organic small molecule luminophores with an intrinsic hydrophobicity (Li, Gao, Shi, & Ma, 2013). Thus far, however, luminescent films haven't been able to make its way to a sufficiently mature material and is still described as emerging. To this end, it is imperative to prepare environmentally benign and stable luminescent films for detecting H_2O_2 based on fluorescence quenching.

Chitosan (CS) is the second most abundant natural biopolymers in the world, which is mainly obtained from the hard outer skeleton of shellfish including shrimps and crab. It has controllable mechanical properties, and excellent biocompatability and biodegradability, which allows widespread applications in controlled drug-release (Fang, Gao, Wang, Lian, & Zhao, 2010; Wang, Ma, & Su, 2005) and enzyme immobilization (He, He, & Shen, 2018), *etc*. In recent years, enormous works using chitosan films have been emerging as compelling materials in detecting various chemical or biomolecules. Wang's group reported that AchE-PB/GCE films composed of chitosan enzyme membrane and prussian blue/glassy carbon electrode (PB/GCE) were used to identify organophosphorus (OP) pesticides (Sun & Wang, 2010). Ding et al. designed and manufactured electrospun nanofibrous PEI-chitosan films via a one-step electrospinning/netting method. In particular, such films were evidently sensitive to formaldehyde vapor at room temperature (Wang et al., 2014). From detection point of view, it is promising to apply the chitosan in the detection of H_2O_2. Primarily, however, such studies are still in its infancy.

In this respect, we report herein a fabricated luminescent and long-term stabilized films made by the encapsulation of europium-containing polyoxometalates (Eu-POM) in the chitosan (CS) (Scheme 1), aiming to explore their applications in the identification of H_2O_2. Comparisons made of fluorescent properties between the pure Eu-POM with the as-prepared Eu-POM/CS films suggest the excellent fluorescent features of as-prepared Eu-POM/CS films. Their fluorescent intensity at 622 nm decreased gradually with respect to the increment of H_2O_2 concentration and the detection limit of H_2O_2 is determined to be 0.11 μM. Notably, Eu-POM/CS films demonstrate favorable specificity towards H_2O_2 in serum compared to other compounds. These findings indicate that Eu-POM/CS films are highly sensitive and selective to detection of H_2O_2, which provides a promising approach to consider such films as excellent candidates for the detection of H_2O_2 and identification of biologically-relevant matter for diagnostic applications.

2. Experimental section

2.1. Materials

Europium nitrate hexahydrate (99%), sodium tungstate dehydrate (99%), L-Histidine (98%), L-Lysine (98%), L-Leucine (98%), L-Phenylalanine (99%), D-(+)-Fructose (99%), D-(+)-Galactose (99%), D-(+)-Sucrose (99%) D-(+)-Glucose and urea (98%) were obtained from J&K Chemical Technology, China. 1-Bromododecane (98%), imidazole (99%), acrylonitrile (99%) isopropanol (99%), chitosan (with a deacetylation degree of ≥ 95%) and dopamine hydrochloride (98%) were purchased from Aladdin Chemistry Co., Ltd. of China. L-Methionine (98%), L-Tryptophan (99%), L-Threonine (99%), L-Valine (99%) and L-Isoleucine (98.5%) were bought from Chemical &Technology (Shanghai) Co., Ltd. of China. Calcium chloride, potassium chloride, magnesium chloride, sodium chloride, hydrogen peroxide (30%), methanol, sodium hydroxide, chloroform and glacial acetic acid were obtained from Sinopharm Chemical Reagent Co., Ltd. Benzophenone was obtained from Shanghai Shifeng Biological Technology Co., Ltd. of China. All the reagents are utilized without further purification. The water used was triply distilled and its specific conductance is 1.2 mS cm^{-1}.

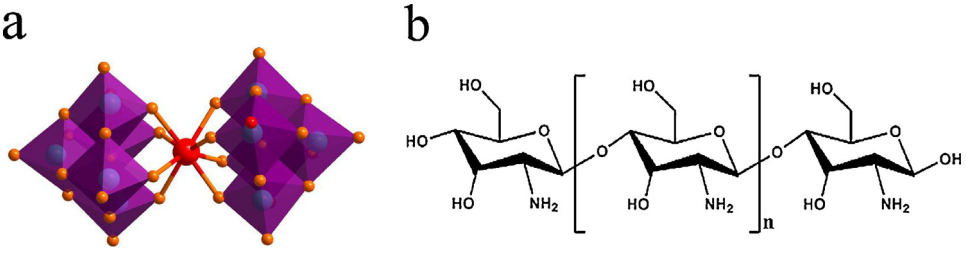
2.2. Synthesis of Eu-POM and $[C_{12}$-2-$C_{12}im]Br_2$

Eu-POM was synthesized according to the published literature (Sugeta & Yamase, 1993).

$[C_{12}$-2-$C_{12}im]Br_2$ was prepared based on the previous works (Ao, Xu, Zhu, & Bai, 2008). The synthesis method is divided into the five parts as follows:

(1) 0.15 mol of imidazole and 0.24 mol of acrylonitrile were mixed in methanol (16 ml). The mixture was stirred for 8 h at 55–60 °C under nitrogen, followed by distillation at reduced pressure to remove the remained methanol and acrylonitrile.
(2) 0.12 mol of 1-bromododecane was added into 20 ml of isopropanol. Then mixture solution was refluxed at 65 °C for 24 h under nitrogen.
(3) The residue was dissolved in the chloroform (35 ml), then the aqueous sodium hydroxide (60 ml, 15%, w/w) was added. The mixed solution was stirred at 25–30 °C for 3 h.
(4) Chloroform layer was washed with deionized water for several times after aqueous layer was eliminated. The mixture was introduced into the 20 ml of isopropanol which was evaporated under vacuum for 2 h at 50 °C. Then the solution was followed by dropwise injecting 0.05 mol of 1, 2-dibromoethane, with continuous stirring under nitrogen at 65 °C for 24 h.
(5) The product was recrystallized five times in acetone and dried under vacuum atmosphere for 48 h after removal of isopropanol.

The chemical structure of $[C_{12}$-2-$C_{12}im]Br_2$ was confirmed by ^{1}HNMR (300 MHz, $CDCl_3$,δ/ppm):10.32(s, 2 H), 8.82(s, 2 H), 7.21(s, 2 H), 5.31(t, 4 H), 4.16(t, 4 H), 1.92(m, 4 H), 1.30(m, 36 H), 0.88(t, 6 H).



Scheme 1. The schematic of chemical structures of Eu-POM (a) and CS (b).