



Fe₃O₄ and metal–organic framework MIL-101(Fe) composites catalyze luminol chemiluminescence for sensitively sensing hydrogen peroxide and glucose



Xue Qian Tang^a, Yi Dan Zhang^a, Zhong Wei Jiang^a, Dong Mei Wang^a, Cheng Zhi Huang^{a,b,*}, Yuan Fang Li^{a,*}

^a Key Laboratory of Luminescent and Real-Time Analytical Chemistry (Southwest University), Ministry of Education, College of Chemistry and Chemical Engineering, Southwest University, 400715, Chongqing, PR China

^b College of Pharmaceutical Sciences, Southwest University, 400715, Chongqing, PR China

ARTICLE INFO

Keywords:

Fe₃O₄/MIL-101(Fe)
Chemiluminescence
H₂O₂
Glucose

ABSTRACT

In this work, Fe₃O₄ and metal–organic framework MIL-101(Fe) composites (Fe₃O₄/MIL-101(Fe)) was demonstrated to possess excellent catalytic property to directly catalyze luminol chemiluminescence without extra oxidants. We utilized Fe₃O₄/MIL-101(Fe) to develop an ultra-sensitive quantitative analytical method for H₂O₂ and glucose. The possible mechanism of the chemiluminescence reaction had been investigated. Under optimal conditions, the relative chemiluminescence intensity was linearly proportional to the logarithm of H₂O₂ concentration in the range of 5–150 nM with a limit of detection of 3.7 nM (signal-to-noise ratio = 3), and glucose could be linearly detected in the range from 5 to 100 nM and the detection limit was 4.9 nM (signal-to-noise ratio = 3). Furthermore, the present approach was successfully applied to quantitative determination of H₂O₂ in medical disinfectant and glucose in human serum samples.

1. Introduction

Metal-organic frameworks (MOFs) are a class of crystalline inorganic–organic hybrid materials with well-defined porous structure and large specific surface area [1]. Over a period of time, MOFs were utilized in catalysis by virtue of open metal sites, unsaturated metal centres and catalytically active organic linkers [2,3]. Recently, a great deal of research efforts was put on the combination of MOFs with other distinct materials, which enable to prepare novel composite materials with sophisticated architectures and superior properties [4]. Especially, the incorporation of MOFs and the materials with intrinsic enzyme mimetic activity, such as metal-oxide nanoparticles [5,6], graphene oxide (GO) [7,8], carbon dots [9] and quantum dots [10–12], was extensively explored, and the prepared composite materials possessed more excellent catalytic activity, which further strengthen the presence of MOFs in catalysis field and broaden the application scope. Also, it was reported that Fe₃O₄ nanoparticles own intrinsic peroxidase-like activity, and was used to develop an immunoassay [13]. According to the above mentioned idea, we can hypothesize that the win-win cooperation of MOFs and Fe₃O₄ would benefit us with a satisfied functional composite, Fe₃O₄/MOFs, which display higher catalytic property

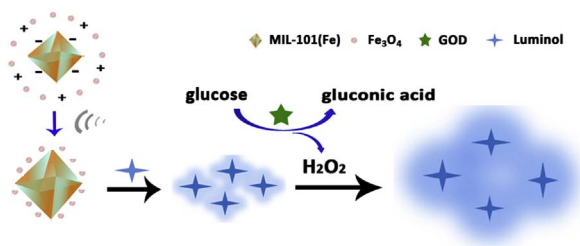
by means of synergistic effect.

The obtained hybrid material with high activity was commonly used in catalyzing various kinds of organic reactions. For example, Fe₃O₄@MIL-100(Fe) core–shell magnetic microspheres catalyzed the Claisen–Schmidt condensation reaction [14] and Fe₃O₄/MIL-101(Fe) catalyzed the dimerization reaction of o-phenylenediamine [15]. Nevertheless, the application in chemiluminescence of Fe₃O₄/MOFs as catalyst has not been reported yet. As a powerful technique in analytical fields, chemiluminescence (CL) is an attractive topic by means of low limit of detection, large calibration ranges, no excitation light source, simple instruments and easy operation [16], and CL has been widely utilized in chemical sensing and biological analyses [17–19]. However, due to the poor efficiency of the classical CL systems for transforming the chemical energy into light signal [18], it is necessary to further enhance the efficiency to obtain intense emission for quantitative analysis. Hence, we attempt to apply Fe₃O₄/MOFs to the field of CL for increase transformation ratio and enhance detection sensitivity, which is meaningful and achievable.

In our work, we prepared Fe₃O₄/MIL-101(Fe) by ultrasound-assisted electrostatic self-assembly technology, which the catalyst preparation procedure is simple and the catalysts contain no toxic

* Corresponding author.

E-mail addresses: chengzhi@swu.edu.cn (C. Zhi Huang), liyf@swu.edu.cn (Y. Fang Li).



Scheme 1. Schematic illustration of the preparation process for the $\text{Fe}_3\text{O}_4/\text{MIL-101(Fe)}$ and CL method for H_2O_2 and glucose detection.

materials (Scheme 1). The prepared $\text{Fe}_3\text{O}_4/\text{MIL-101(Fe)}$ had been proven that the catalytic activity of $\text{Fe}_3\text{O}_4/\text{MIL-101(Fe)}$ was higher than Fe_3O_4 or MIL-101(Fe) to catalyze luminol CL and obviously increase the sensitivity of CL measurement of H_2O_2 and glucose. Moreover, there is no need extra oxidant in the CL reaction of luminol, so our method is more environmentally friendly. Functional integration of inexpensive magnetic nanoparticles with ferric materials makes $\text{Fe}_3\text{O}_4/\text{MIL-101(Fe)}$ a sustainable, environmentally friendly and economic catalyst. Based on the mentioned above, we constructed a sensitive and environmental CL sensor for quantitative determination of H_2O_2 and glucose.

2. Experimental

2.1. Materials and chemicals

The ligand terephthalic acid (H_2BDC) and glucose were obtained from Aladdin Chemistry Co. Ltd (Shanghai, China). H_2O_2 was purchased from Chongqing Chuandong Chemical (group) Co. Ltd (Chongqing, China). Luminol (5-amino-2,3-dihydrophthalazine-1,4-dione) was obtained from Aladdin Chemistry Co. Ltd (Shanghai, China). A 0.01 M stock solution of luminol was prepared by dissolving 0.1770 g of luminol in 100 mL of 0.1 M NaOH solution and storing it in a dark place for at least seven days. Working solutions of luminol were prepared by diluting the stock solution with 0.05 M $\text{K}_2\text{HPO}_4\text{-KOH}$ buffer solutions. The glucose oxidase (GOD) solution was prepared by dissolving 1.0 mg GOD in 1.0 mL phosphate buffer (pH 7.4). Working solutions of H_2O_2 were prepared fresh daily by dilution of 30% (v/v) H_2O_2 . H_2O_2 medical disinfectant as real sample was purchased from Beibei Tong Jun Ge Big Pharmacy (Chongqing Tong Jun Ge Co. Ltd), which was produced by Hebei Jianning Co. Ltd. Clinical serum samples were collected and processed by the school hospital of southwest university. Unless other indicated, all reagents and solvents used were of analytical grade and used without further purification. Millipore Milli-Q water (18 M Ω cm) was used in all experiments.

2.2. Apparatus

The CL spectra of this system were obtained using a computerized BPCL ultra weak luminescence analyzer (Institute of Biophysics, Chinese Academy of Sciences, Beijing, China) with high-energy cutoff filters of various wavelengths from 230 to 640 nm, and the high potential of the photomultiplier tube was set to -850 V for H_2O_2 detection and -900 V for glucose detection. The morphology of the MOFs was characterized by an S-4800 scanning electron microscope (SEM) (Hitachi, Japan). Transmission electron microscopic (TEM) characterization was performed on an FEI Tecnai G2 F20 TEM instrument (FEI, America). Powder X-ray diffraction (XPRD) patterns were collected on a XD-3 X-ray diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) in the range of $2\text{--}70^\circ$ at a scan rate of $2.0^\circ \text{ min}^{-1}$ (Purkinje, China). Magnetization measurement was carried out with MPMS (SQUID) XL-7 magnetometer. Analysis of the X-ray photoelectron spectroscopy (XPS) was performed on Thermo ESCALAB 250Xi. Electron spin resonance (ESR) spectra were performed on a JES-FA200 X-band ESR

spectrometer (JEOL, Japan). The absorption spectra were recorded with a Hitachi UV-3010 spectrophotometer (Tokyo, Japan). The dynamic laser light scattering (ZEN3600, Malvern) was performed to characterize the zeta potential of materials.

2.3. Fabrication of $\text{Fe}_3\text{O}_4/\text{MIL-101(Fe)}$

The MIL-101(Fe) and Fe_3O_4 were synthesized based on previous reports [20,21]. The hybrid $\text{Fe}_3\text{O}_4/\text{MIL-101(Fe)}$ was prepared according to our previous work with some modification [15]. 25 mg of MIL-101(Fe) and 10 mg Fe_3O_4 were respectively suspended in 7.5 mL deionized water, and 1 mM NaOH solution was added dropwise into Fe_3O_4 solution until the pH was adjusted to 8 approximately, which could make the surface charge of Fe_3O_4 nanoparticles to positive. The two solutions were treated by ultrasonic for 10 min until homogeneous, and then mixed them together, the $\text{Fe}_3\text{O}_4/\text{MIL-101(Fe)}$ was obtained after 20 min. The as-synthesized samples were separated by magnet and washed with deionized water for three times. Finally, the magnetic hybrid $\text{Fe}_3\text{O}_4/\text{MIL-101(Fe)}$ was dried at 60°C in a vacuum oven for further use.

2.4. Chemiluminescence measurements

2.4.1. H_2O_2 detection using $\text{Fe}_3\text{O}_4/\text{MIL-101(Fe)}$

The dynamic CL profiles were achieved by a static system consists of a quartz cuvette and the BPCL luminescence analyzer. In a typical experiment, the analyzer was run for at least 30 min before measurement. H_2O_2 detection was realized as follows: under the optimize experimental conditions, 50 μL of $\text{Fe}_3\text{O}_4/\text{MIL-101(Fe)}$ and 100 μL of H_2O were premixed in the cuvette, and 100 μL diluted water as blank or 100 μL of different concentrations of H_2O_2 . Then 250 μL of luminol was quickly injected by a microliter syringe. The CL signal kinetics (intensity versus times) was recorded soon after mixing of the solutions with a 0.1 s interval. The relative CL intensity, which stands for the difference between the CL intensity of sample and blank, was used for quantitative determination.

2.4.2. Glucose detection using GOD and $\text{Fe}_3\text{O}_4/\text{MIL-101(Fe)}$

Glucose detection was carried out as follows: 100 μL of glucose of different concentrations or 100 μL of H_2O as blank, 100 μL of 1 mg/mL GOD and 800 μL of H_2O were incubated at 37°C for 30 min, then 100 μL of the above glucose reaction solution was added into the mixture solution of 50 μL $\text{Fe}_3\text{O}_4/\text{MIL-101(Fe)}$ and 100 μL H_2O . Finally, under the optimize experimental conditions, 250 μL of luminol was quickly injected, and the CL signal was recorded.

2.5. Sample preparation

The sample solution of H_2O_2 disinfection was prepared simply by diluting with deionized water. The standard addition method was carried out by spiking different concentrations of H_2O_2 to sample solution. Serum samples of three healthy adults were treated by spin dialysis at 12,000 rpm for 45 min, and then the upper serum were diluted with deionized water before determination. The final concentration of glucose in the serum was obtained by calculation, namely dilute times multiplied by diluted concentration. The diluted concentration is calculated directly via linear equation.

3. Results and discussion

3.1. Characterization of $\text{Fe}_3\text{O}_4/\text{MIL-101(Fe)}$

MIL-101(Fe), a Fe^{3+} -based MOF with molecular formula $\text{Fe}_3\text{OH}(\text{H}_2\text{O})_2\text{O}[(\text{BDC})]_3$, is made from inexpensive and biocompatible Fe^{3+} and terephthalic acid (BDC). It can be considered as Fe^{3+} -oxide clusters linked together in three dimensions by BDC linkers, which resulted in

Download English Version:

<https://daneshyari.com/en/article/7676950>

Download Persian Version:

<https://daneshyari.com/article/7676950>

[Daneshyari.com](https://daneshyari.com)