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A novel photoelectrochemical sensor for bilirubin based on porous transparent TiO_2 and molecularly imprinted polypyrrole

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ABSTRACT

Transparent photocatalytic surfaces are of ever increasing importance for the enhancement of the photocatalytic efficiency. Here, the porous transparent TiO_2 (PTT) was conveniently fabricated on the glass substrate by a sol-gel process, and a novel photoelectrochemical sensing platform with excellent photochemical catalysis and molecular recognition capabilities was established for bilirubin detection based on the modification of molecularly imprinted polypyrrole (MIPPy) onto PTT surface by the molecular imprinting technique. The performance of the fabricated sensor was evaluated and the results indicated that the sensor exhibited high sensitivity in bilirubin detection, with a linear range from 0.03 to 28 μM and a limit of detection of 0.001 μM. Moreover, the sensor exhibited outstanding selectivity while used in coexisting systems containing various interferents with high concentration. The practical application of the sensor was also realized in the selective detection of bilirubin in real samples. The favorable performance of the developed bilirubin sensor can be mainly attributed to the high transparency and photoelectric activity of PTT and selective recognition and excellent conductivity of MIPPy.

1. Introduction

Bilirubin, a common metabolite of hemoglobin, is normally conjugated with albumin to form a water-soluble complex and excreted from hepatocytes into bile mainly as bilirubin glucuronides [1]. Extra free bilirubin in body can cause disorders in the metabolism of bilirubin and evoke various diseases [2]. Therefore, detection and quantification of bilirubin is vitally important for the diagnoses, monitoring, prevention and treatments of the associated diseases. In the past years, some analytical methods have been developed for bilirubin detection, including UV-vis spectroscopy [3], electrochemical assay [4–6], Point-of-care testing [7], high-performance liquid chromatographic (HPLC) [8], electrochemiluminescence [9], piezoelectricity [10] and photoelectrochemical sensor [11]. Among them, photoelectrochemical analytical technique based on electron transfer among analyte, photoactive species and electrode with photoirradiation is the most attractive and promising method due to its high sensitivity, low background signal, low cost and easy miniaturization of detection devices [12,13]. The photoelectrochemical analysis exhibits the properties of both optical methods and electrochemical sensors by coupling photoirradiation with electrochemical detection [14–16], and its performance mainly depends on the electrode material, especially the selection and fabrication of sensing materials. Recently, Fe_3O_4/HAP/MIPPy nanoparticles with high selectivity have been used for the photoelectrochemical detection of bilirubin in our report [11]. However, the developed sensor still does not meet the growing demand for more convenient and sensitive detection of bilirubin due to the complicated fabrication and poor transparency of electrode. Thus, the further development of simple, facile and cost-efficient methods with high sensitivity for bilirubin detection is urgently demanded.

TiO_2 is an ever growing research field due to its remarkable photocatalytic activity, structural rigidity, chemical stability, excellent biocompatibility and relatively low price [17]. It is well-known that the properties and performance of TiO_2 partly depend on its crystallinity and morphology [18]. Currently, PTT has attracted considerable scientific interest in such fields as solar energy conversion, electrochromic device, antireflection coating and self-cleaning applications due to its large surface to volume ratio, high transparency and enhanced photoactivity [19–22].

Molecular imprinting technique, the design and construction of mimetic receptor system with predetermined recognition for

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target molecule, has been proposed and developed rapidly [23]. Recently, MIPPy with excellent selectivity, high conductivity and stability has been used to fabricate sensors, which were used for the selective detection of organisms [24–27]. Although MIPPy showed favorable selectivity and conductivity in photoelectrochemical sensing, the electrodes based on MIPPy usually possessed a poor transparency, which would significantly affect its sensing performance. Hence, the development of photoelectrochemical sensor based on modified electrode with excellent transparency, photoactivity, selectivity and conductivity was still highly desired until now.

In this work, selective MIPPy and transparent PTT were employed as sensing film and photochemical catalyst, respectively. A novel photoelectrochemical sensor with excellent transparency and photoactivity has been developed for bilirubin detection based on the immobilization of PTT onto indium tin oxide (ITO) glass and modification of MIPPy film on PTT. The constructed photoelectrochemical sensor with high sensitivity, selectivity and stability shows excellent performance for the detection of bilirubin.

2. Experimental

2.1. Materials and apparatus

ITO glass was obtained from Shenzhen Jianshengda Technology Co. Ltd. Titanium tetraisopropoxide (TTIP) and polyethylene glycol (PEG, average molecular weight 1000) were purchased from Sigma-Aldrich. Pyrrole monomer was obtained from Merck and distilled before use. Bilirbuin, biliverdin, cholesterol, testosterone and human serum albumin (HSA) were purchased from Shanghai Aladdin Chemical Co., China. All other chemicals were of analytical grade and used without further purification. Deionized (DI) water (resistivity of 18 MΩ cm) was obtained from a Millipore Milli-Q Water System (Millipore Inc.), and was used throughout the experiments. Bilirubin solution was prepared according to the method described in our previous study [10].

UV-vis transmission spectra were recorded by an UV/Vis spectrophotometer (UV-1601, Shimadzu, Japan). Scanning electron micrograph (SEM) was carried out on a Hitachi S-520 scanning electron microscope (Hitachi Ltd., Tokyo, Japan) working at 20 kV. Infrared (IR) spectra were recorded on Nicolet 200SXV FTIR spectrometer using a KBr wafer. X-ray diffraction (XRD) was performed on a Rigaku D/MAX-RC X-ray diffractometer using Cu Kα radiation. Raman spectra were recorded on a Raman spectrometer (InVia, Renishaw Co., UK). A 320W low-pressure mercury lamp (Philips, 254 nm) was used as UV irradiation source. The electrochemical experiments were carried out on CHI660c workstation (CH Instrument, USA).

2.2. Fabrication of the bilirubin photoelectrochemical sensor

The PTT was modified onto ITO-coated glass electrodes by dip-coating method. Specifically, TTIP (12 mmol) was added dropwise into a solution of 20 mL ethanol and 1 mL HCl, and then vigorously stirred for an hour at room temperature. Subsequently, DI water (2.2 mL) and PEG (0.7 g) were dropped into the mixture under continuous stirring. After reaction for 5 h, the resultant sol-gel solution was deposited on the ITO glass washed with ethanol and DI water by dip coating at a constant withdrawal rate of 1 mm s^{-1}. After coating, the modified electrode was placed in relative humidity of 45% for 24 h, and followed by 24 h at 60 °C and a final calcination in air at 400 °C for 2 h. Thus, the ITO/glass electrode modified by PTT layer with ca. 0.76 μm thickness was prepared.

The MIPPy/PTT/ITO/glass electrode was prepared via the surface molecular imprinting technique. The obtained PTT/ITO/glass electrode was firstly dispersed into 100 mL dioxygen-free aqueous solution. Subsequently, 10.0 mL solution containing 0.05 mmol bilirubin and 0.25 mmol pyrrole was introduced into the solution, followed by ultrasonic irradiation for 6 h at nitrogen atmosphere. After that, the electrode was washed with 1% ammonia aqueous solution for several times to remove template molecules, resulting in the formation of MIPPy/PTT/ITO/glass electrode. Thus, the bilirubin sensor was fabricated. Fig. 1 shows the schematic illustration for detection mechanism of the bilirubin photoelectrochemical sensor. For comparison, the non-imprinted PPy-modified electrode was prepared using the same procedure without template molecules, and denoted as PPy/PTT/ITO/glass electrode. The physical area of all electrodes was 1.0 × 2.5 cm^2, and the effective working area was 1.0 × 2.0 cm^2 when applied for the photoelectrochemical experiments.

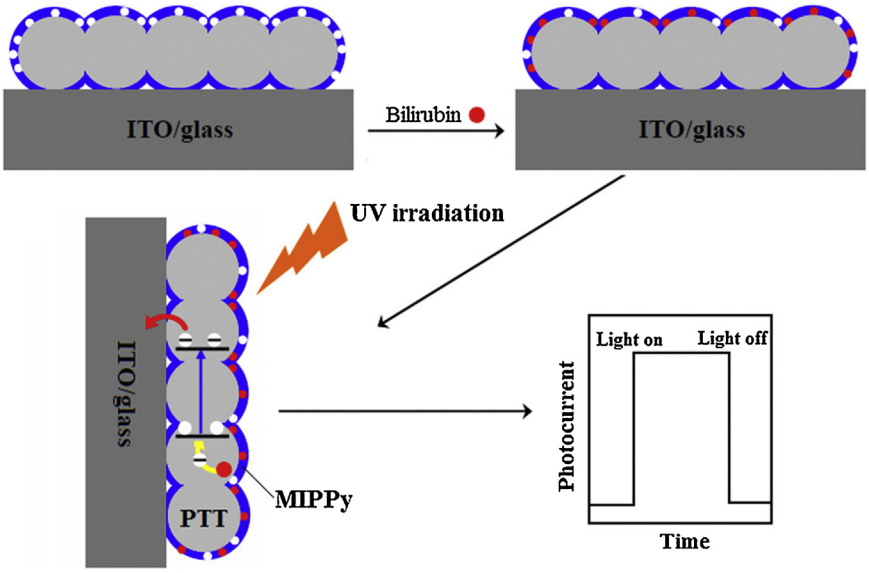

Fig. 1. Schematic illustration for detection mechanism of the bilirubin photoelectrochemical sensor.