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Selective and visible-light-driven profenofos sensing with calixarene receptors on TiO_2 nanotube film electrodes

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ABSTRACT

Highly selective and sensitive determination of profenofos (PFF) is achieved by fast and convenient visible-light-driven photoelectrochemical (PEC) sensor with a low detection limit of 1 nM (S/N = 3). The sensor is fabricated on highly ordered and vertically aligned TiO_2 nanotubes (NTs) employing p-tert-butylcalix[4] arene (CA) as recognition element and visible-light sensitizer. It shows excellent selectivity towards PFF, and 100-fold excess of coexistent interferences only causes minor changes of the photocurrent of PFF. Mechanism study suggests that this high selectivity may be attributed to the specific binding ability of CA to PFF, and it is further confirmed by molecular docking calculations. The best binding mode between CA and PFF is also proposed.

1. Introduction

Profenofos (PFF) is a highly active organophosphorous pesticide widely used for efficient control of insect pests, which can induce significant inhibitory effects on acetylcholinesterase (AChE) activity, as well as instability of erythrocyte membrane [1]. Long-term exposure to PFF-polluted water will do great harm to people's health. Therefore, development of sensitive and selective analytical methods for convenient and fast determination of PFF is of great significance. Previous techniques established for PFF detection include the conventional liquid chromatography [2] and high performance liquid chromatography [3]. While with distinct advantages, these methods also suffer from its own limitations such as usage of large and expensive instruments. Therefore, more simple, accurate, and low-cost PFF detection would be desirable [4]. Photoelectrochemical (PEC) sensor represents a newly appeared but promising analysis technique, which has attracted substantial research attention for its desirable analytical performances, attributed to its different forms of energy for excitation (light) and detection (current) [5–7]. Utilizing the photocatalytic oxidation of PFF on functionalized photocatalyst surface to generate photocurrent under a constant bias potential, PFF can be conveniently quantified by PEC method.

In this paper, supramolecular receptor *p*-tert-butylcalix[4]arene (CA) with cavity diameter of 5.4 Å is employed as recognition element owing to its potential selective binding ability to PFF [8,9] in view of the molecular structure and hydrophobicity of PFF, and a selective and sensitive PEC sensor for PFF is fabricated on highly ordered and vertically aligned TiO_2 nanotubes (NTs). As known, TiO_2 NTs is a promising platform for fabricating PEC sensors because of its high photocatalytic efficiency, large surface area and photochemical stability [10]. Meanwhile, by forming coordination bonds between phenolic hydroxyls of CA and Ti atoms on TiO_2 NTs surface, UV–vis absorption of TiO_2 NTs can be widened to visible region [11]. This will enable the establishment of visible-light-driven PEC sensor, and improve the sensor's stability. Mechanism of the recognition performance is also discussed from both experimental results and molecular docking calculations. To the best of our knowledge, it is for the first time that a selective PEC sensor is fabricated for direct PFF determination in multicomponent water samples.

2. Experimental

2.1. Materials and apparatus

All chemicals are commercially available as analytical reagent grade and used as received unless otherwise stated.

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A 200 W LA-410UV-3 lamp (Hayashi, Japan) is used as visible-light source with a central wavelength of 475 nm. All electrochemical and PEC measurements are performed on CHI 660c electrochemical workstation (CHI Co., USA) in a conventional three electrode cell comprised of platinum wire auxiliary, saturated calomel reference and modified TiO_2 NTs electrode. Before each measurement, the electrode is incubated in PFF containing solution for 10 min. All the photocurrents are recorded at a constant potential of 0 V (versus SCE) in 0.1 M PBS (pH = 6.98) containing 0.1 M ascorbic acid (AA) unless otherwise stated.

UV–vis diffuse reflectance spectra (DRS) are measured on ultraviolet visible spectroscopy of diffuse reflectance (AvaLight-DHS, Avantes). Raman spectra are recorded using Raman microscope (inVia, Renishaw). The contact angles are measured with an Easy Drop contact angle meter (FM40MK2, Krüss) at room temperature and ambient humidity. Field emission scanning electron microscope (S-4800,Hitachi) are used to characterize the electrodes morphology.

2.2. Fabrication of profenofos PEC sensor

CA is synthesized according to the literature [12] and characterized. TiO_2 NTs are fabricated on Ti substrate (4.0×1.0 cm^2) by anodic oxidation [13]. TiO_2 NTs are then refluxed in 200 mL toluene solution containing 0.3 mmol of CA under protection of N_2 for 48 h. The as-prepared CA@TiO_2 NTs is rinsed with hot toluene and dried with N_2. Before use, the CA@TiO_2 NTs electrode is sealed to 0.25 cm^2 with insulating glue.

2.3. Molecular docking calculation

Full geometry optimization of the pesticides substrates is performed applying the DFT-B3LYP method and 6–31 + G basis set [14]. The structure of CA is obtained from Cambridge Crystallographic Data Centre (deposition numbers: CCDC 819522-819527). The optimized small molecules are put in a $30 \times 30 \times 30$ points grid box with rigid spacing 0.375 Å and their docking calculation with CA are performed by AutoDock 4.2 [15].

3. Results and discussion

3.1. Fabrication and characterization of profenofos PEC sensor

The structure of CA@TiO_2 NTs is shown in Fig. 1A. CA is covalently grafted on TiO_2 NTs (diameter of about 50 nm in Fig. 1E) by forming coordination bonds between the hydroxyl groups of CA and surface Ti atoms, which restricts CA as “cone” conformation [11]. The successful graft of CA is first characterized by Raman spectra. Three distinct peaks at around 1301, 1448, 1601 cm^{-1} (Fig. 1B(b)) can be assigned to the skeletal vibration of CA, which cannot be found for TiO_2 NTs (Fig. 1B(a)). UV–vis DRS spectrum (Fig. 1C) of CA@TiO_2 NTs further confirms that CA isn't physically absorbed, but covalently bound on TiO_2 NTs surface. The absorption edge of CA@TiO_2 NTs shifts to nearly 550 nm attributed to the CA–Ti ligand to metal charge transfer (LMCT) originated from the coordination bonds between CA and TiO_2 NTs. It is consistent with the literature [11]. Besides, AC impedance of CA@TiO_2 NTs increases evidently compared to that of TiO_2 NTs (Fig. 1D) owing to the increased mass transfer resistance for $[Fe(CN)_6]^{3-/4-}$ resulted from the layer of grafted CA. The hydrophilic surface of TiO_2 NTs also changes to hydrophobic after binding with CA (Fig. 1E) due to the exposure of hydrophobic parts of CA, such as aromatics and butyl groups (Fig. 1A). However, graft of CA doesn't change the TiO_2 NTs morphology (inset of Fig. 1E).

3.2. Highly sensitive and visible-light-driven performance of profenofos PEC sensor

The PEC sensor is then established using CA@TiO_2 NTs. The photocurrent of TiO_2 NTs is negligible under visible-light irradiation (Fig. 2A(a)), but increases significantly after grafted of CA (Fig. 2A(b)). This confirms that CA plays an important role in visible-light sensitization of TiO_2 NTs. The photocurrent (Fig. 2A(c)) can be further amplified by adding an optimized amount of ascorbic acid (AA) as electron donor [16]. Afterwards, photocurrent of CA@TiO_2 NTs in the presence of PFF is recorded. It is found that the photocurrent is enhanced evidently after addition of PFF (Fig. 2A(d)). Owing to the fact

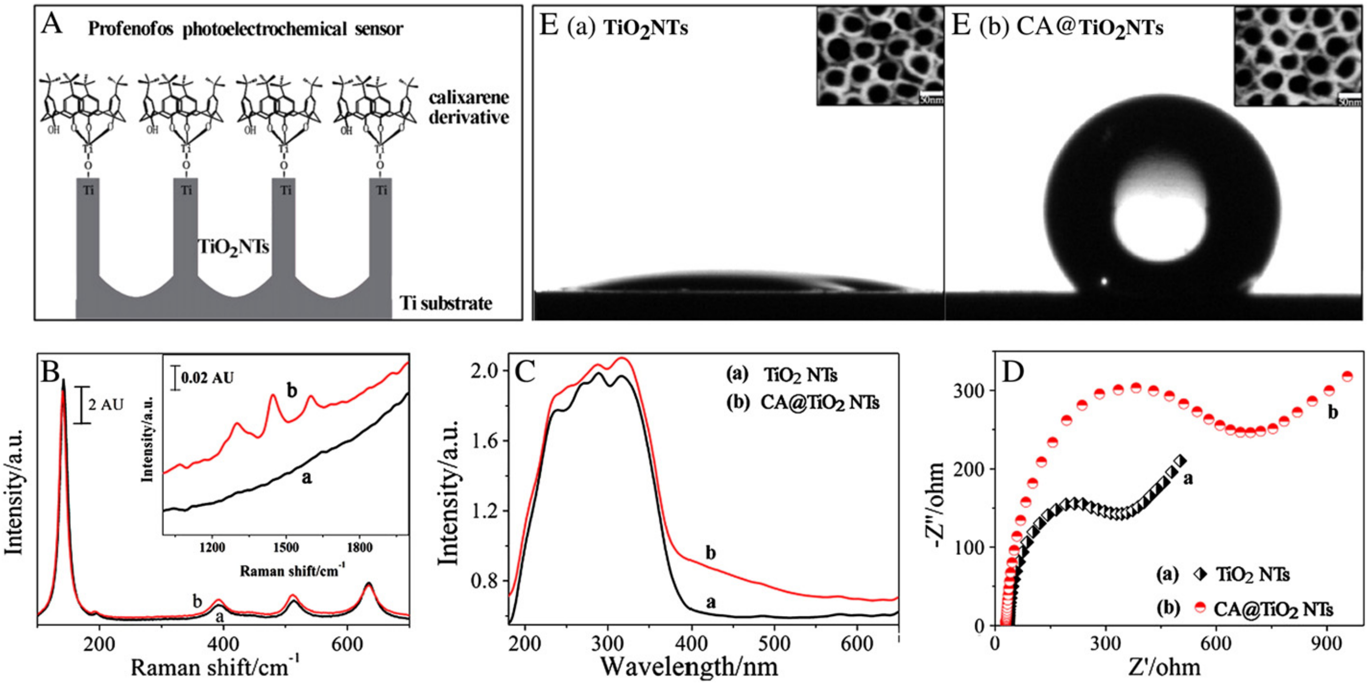

Fig. 1. A: Scheme of CA@TiO_2 NTs; B: Raman spectra, C: UV–vis DRS absorption, D: AC impedance and E: Contact angle of (a) TiO_2 NTs and (b) CA@TiO_2 NTs (inset: SEM image of TiO_2 NTs and CA@TiO_2 NTs). The AC impedance is measured in 5 mM $Fe(CN)_6^{3-/4-}$ and 0.1 M KCl solution at open circuit potential with a frequency range of 1–10^5 Hz and signal amplitude of 5 mV.