Analytica Chimica Acta 766 (2013) 47–52

Contents lists available at SciVerse ScienceDirect

Analytica Chimica Acta

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

A derivative photoelectrochemical sensing platform for 4-nitrophenolate contained organophosphates pesticide based on carboxylated perylene sensitized nano-TiO_2

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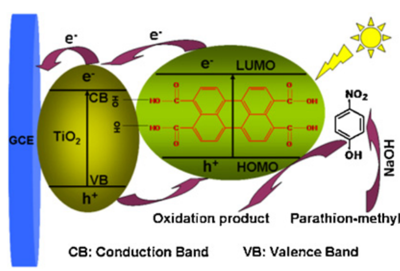
HIGHLIGHTS

- A novel enzymeless photoelectrochemical sensor for 4-nitrophenolate contained OPs.
- Sensors have performances of rapid response, good sensitivity and selectivity.
- PTCA as sensitizer can form ultra-stable thin film and is economic as well.
- The strategy extends the application of PTCA for photoelectrochemical sensor.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 17 October 2012
Received in revised form 17 December 2012
Accepted 20 December 2012
Available online 2 January 2013

Keywords:
Photoelectrochemistry
Sensor
Heterojunction
Nano-titania
Carboxylated perylene

ABSTRACT

A novel visible light sensitized photoelectrochemical sensing platform was constructed based on the perylene-3,4,9,10-tetracarboxylic acid/titanium dioxide (PTCA/TiO_2) heterojunction as the photoelectric beacon. PTCA was synthesized via facile steps of hydrolysis and neutralization reaction, and then the PTCA/TiO_2 heterojunction was easily prepared by coating PTCA on nano-TiO_2 surface. The resulting photoelectric beacon was characterized by transmission electron microscope, scanning electron microscopy, X-ray diffractometry, FTIR spectroscopy, and ultraviolet and visible spectrophotometer. Using parathion-methyl as a model, after a simple hydrolyzation process, p-nitrophenol as the hydrolysate of parathion-methyl could be obtained, the fabricated derivative photoelectrochemical sensor showed good performances with a rapid response, instrument simple and portable, low detection limit (0.08 nmol L^{-1}) at a signal-to-noise ratio of 3, and good selectivity against other pesticides and possible interferences. It had been successfully applied to the detection of parathion-methyl in green vegetables and the results agreed well with that by GC–MS. This strategy not only extends the application of PTCA, but also presents a simple, economic and novel methodology for photoelectrochemical sensing.

1. Introduction

Organophosphates (OPs) are the most toxic species commonly found in both pesticides and chemical-warfare agents whose rapid and severe effects on human and animal health lie in their ability to block the action of acetylcholinesterase (AChE), a critical central-nervous-system enzyme [1,2]. Parathion-methyl (PM) is one kind of OPs that is very toxic, with an LD_{50} of 3 mg kg^{-1} in rats, and may be responsible for more deaths among agricultural field workers than any other pesticide [3]. This creates a demand for the development of accurate, sensitive, rapid, easy-to-use and portable method to detect the high toxic PM.

Over the past two decades, extensive researches for PM analysis have been developed, such as LC–MS or LC–EC [4–6],

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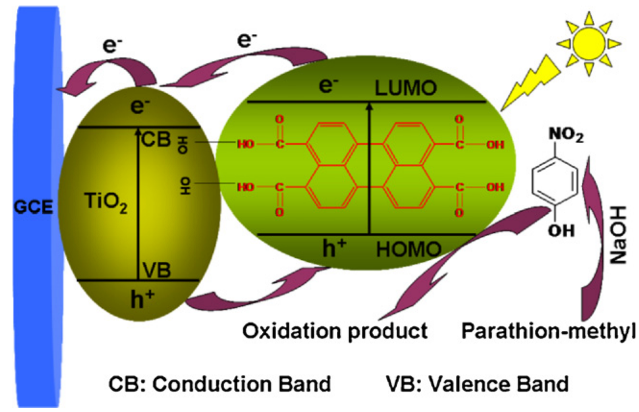
http://dx.doi.org/10.1016/j.aca.2012.12.038

electrochemical sensor [7,8] or enzyme-based electrochemical biosensor [9–12], fluorescence biosensor [13–15], and molecular imprinted technique (MIT)-based electrochemical sensors [16–19]. In general, each of these methods suffers from at least one undesirable limitation, such as limited selectivity, low sensitivity, operational complexity, lack of portability, or the difficulties of real-time monitoring. Recently, great progresses have been made in applying nanomaterial-based electrochemical sensors/biosensors [20,21] or fluorescent chemosensors [22] development for pesticides, which were well known as two kinds of convenient and simple means of chemical detection. But most of them are still enzyme-based biosensors [12,14,15] or MIT-based sensors for PM [18,19]. Enzyme-based biosensors for the detection of OPs can be categorized into two general classes on the basis of the enzyme employed-acetylcholinesterase (AChE) or organophosphorus hydrolase (OPH) and the later have distinct advantages over AChE-based systems [23]. But neither of them has good specificity to PM, let alone the good stability of the sensors. At this point, MIT-based sensors have excellent specificity but suffer from tedious preparation. Consequently, the development of simple, rapid, economic, selective and sensitive method to detect PM is still a challenge.

Photoelectrochemical measurement is potentially as sensitive as electrochemiluminescence (ECL) owing to the complete separation of excitation source (light) and detection signal (photocurrent). It has attracted considerable interests as a newly developed and promising analytical technique [24–35]. Moreover, the utilization of electronic detection makes the photoelectrochemical instruments simpler and low-cost compared with those of the conventional optical methods. During the recent decades, the fascinating inorganic semiconductor titanium dioxide (TiO_2) has attracted extensive attention in the photocatalytic and photoelectrochemical area due to its nontoxicity, hydrophilicity, cheap availability, stability and against photocorrosion for its suitable flat band potential in addition to its easy supported on various substrates [36–38]. However, the wide band gap of TiO_2 (~3.2 eV, anatase) only allows it to absorb the ultraviolet light (<387 nm) [36]. In order to extend the photoresponse to the visible region and promote the photoelectric conversion efficiency, many modification methods have been applied, such as dye sensitization, metal ion/nonmetal atoms doping, semiconductor coupling, and noble metal deposition [38]. Among the above methods, organic molecule-based photovoltaic materials and devices are attracting more and more attention for the advantages such as low-cost, light-weight, feasibility for large-scale device manufacturing [39–42]. Thus, considering of the high electron mobility of nanocrystals as well as the possibility of tuning the optical band gap into visible light region by organic materials, the organic–inorganic heterojunction can fabricate a robust photoelectrochemical sensor. Recently, Ju team [29] has developed a photoelectrochemical biosensor for glutathione based on iron–porphyrin-containing sulfonic group on TiO_2 nanoparticles. Considering of the carboxylic-group-containing porphyrins possess a higher solar-energy conversion efficiency than sulfonic-group-containing porphyrins in dye-sensitized solar cells due to their stronger absorption coefficient [43], they further developed the other photoelectrochemical biosensor for cysteine based on carboxylic-group-containing free-base porphyrins functionalized ZnO nanoparticles, which has nearly the same band-gap as TiO_2 [44]. Also, our group have developed two photoelectrochemical sensors for pesticides dichlofenthion and chlorpyrifos based on TiO_2 photocatalysis coupled with electrochemical detection, namely a derivative electrochemical sensor and P3HT sensitized TiO_2, respectively [45,46]. Recently, a novel AChE-functionalized photoelectrochemical biosensor for OPs was developed [47] based on bismuth oxyhalides as the photoelectric beacon, which has the band gap of 1.8 eV and the absorption edge is about 680 nm. Although the limit of detection (LOD) for PM was lowered to 0.16 nM, but its specificity for PM is limited since AChE has the similar response to other OPs and carbamate pesticides [1,14,15]. Since neither AChE nor OPH has good specificity to PM, novel enzymeless photoelectrochemical sensor with better sensitivity and selectivity for PM is our dream. Consequently, our eyes were focused on novel photoelectric beacon with excellent performances.



Scheme 1. Schematic illustration of proposed photoelectrochemical mechanism for parathion-methyl at PTCA/TiO_2 modified GCE.

Perylene-3,4,9,10-tetracarboxylic acid (PTCA, see Fig. S1) with its conjugated polyaromatic core and the two directly attached active carboxyl groups that facilitate surface anchoring by hydrogen bond formation, may be a good candidate to construct a new heterojunction with TiO_2. It can absorb broad visible light and emit from a singlet state with quantum yields near unity [48], which offers both fundamental and practical advantages for uses as a sensitizer since it has large extinction coefficient and high photostability. As the mother dye of PTCA, perylene together with its derivants has been widely explored in organic electronics [49,50] or as fluorescent agents [51–54]. But surprisingly, there is still no report on their application in photoelectrochemical sensing.

Herein, we developed a novel enzymeless derivative photoelectrochemical sensor for PM based on PTCA–TiO_2 heterojunction, considering of the structure differences of PM with the above two pesticides. This novel sensor has more advantages over our previous photoelectrochemical sensors for OPs [45,46] and the newly developed photoelectrochemical sensor for OPs [47], such as it is more sensitive, more economic, and more facile to prepare the photo-sensitizer, together with no loss in the good selectivity and stability. PTCA was synthesized via facile steps of hydrolysis of 3,4,9,10-perylenetetracarboxylic dianhydride (PTCD) and neutralization reaction [53,54], and then the PTCA/TiO_2 heterojunction was easily prepared by coating PTCA on nano-TiO_2 surface. After hydrolysis of PM to p-nitrophenol which has the phenolic hydroxyl as an excellent electron donor [9,55], the fabricated photoelectrochemical sensor was used for the derivative PM (Scheme 1) detection. It had been successfully applied to the detection of PM in green vegetables and the results agreed well with that by GC–MS.

2. Experimental

2.1. Materials and reagents

3,4,9,10-Perylenetetracarboxylic dianhydride (≥99%) (PTCD), TiO_2 nanopowder (anatase, <25 nm, 99.7%), chlorpyrifos, dichlofenthion and parathion-methyl (≥98%) were purchased from Sigma–Aldrich (St. Louis, MO). Parathion-ethyl, fenitrothion and dicapthon (≥98%) were purchased from Aladdin (Shanghai Corp.,