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Binding-induced internal-displacement of signal-on photoelectrochemical response: A glyphosate detection platform based on graphitic carbon nitride

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ABSTRACT

The exploitation and design of sensitive photoelectrochemical sensor with high performance materials is of great significance to expanding approaches for practical evaluation. Herein, a signal-on photoelectrochemical strategy with graphitic carbon nitride decorated Ag^+ based on the binding-induced internal-displacement for glyphosate monitoring was established. The mechanism of this platform has been elaborately explored and the high sensitivity should be ascribed to two aspects. Firstly, graphite-like carbon nitride as visible light-active material possesses fine photocatalytic activity. The pyridine nitrogen units on g-C_3N_4 backbone could absorb Ag^+ through chemical absorption and then photo-generated electrons would be reacted by Ag^+, leading to the inhibition of electrons transfer and decrement of photocurrent. However, binding-induced internal-displacement of chelate effect between Ag^+ and glyphosate, which promoted the constitution of current circuit and signal improvement owing to that Ag^+ was deprived from the carbon nitride nanosheets and photo-induced electrons could transfer to the electrode. Under the optimal conditions, the photocurrent change was proportional to the glyphosate concentration logarithmically with the wide liner range from 1.0×10^{-10} to 1.0×10^{-3} M and a low detection limit of 30 pM. This economical and sensitive sensor system showed fine practicability which could be applied for broader applications.

1. Introduction

As a newly emerged yet promptly developed analytical technique, photoelectrochemical (PEC) sensing has captured much intriguing attention owing to its inexpensive photoelectric devices and rapid high-throughput assay process [1]. Benefiting from employing light as excitation source and photocurrent transduced as detection response, the undesired background signal could be reduced and high sensitivity can be obtained [2]. The general mechanism for PEC sensor is relied upon the reductive property of photoelectrons or oxidative capacity of photo-induced holes [3]. Specifically, it owns pronounced advantages derived from electrochemical method, the use of an electronic readout makes the PEC instrument simple, accurate and easy to miniaturize [4,5]. Up to present, photoactive materials undeniably play a critical role in PEC performance and enormous efforts have been invested in exploring new materials with prominent optoelectronic properties to enhance the photoconversion efficiency [6,7]. Typically, some wide band-gap semiconductor nanostructures of ZnO (3.37 eV) [8], TiO_2 (3.2 eV) [9,10], and SnO_2 (3.6 eV) [11,12] have been utilized as photoactive nanomaterials for the construction of PEC biosensing. Nevertheless, the wide band gap only allows them to absorb the ultraviolet light, which restricts the utilization of visible light, reduces the segregation of electron–hole pairs [13] and kills the biomolecules [14], resulting in the depression of photoelectric response. In light of this, searching and exploring a promising and visible-light-driven photoactive material or organic photosensitizer is still desired for expanding the application of PEC platform in analysis [15]. Recently, polymeric graphitic carbon nitride nanosheets (g-C_3N_4 NSs) have drawn plenty of scientific interest owing to their appropriate bandgap (2.69 eV), excellent chemical stability, metal-free and unique electronic and optical

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properties [16–18]. As an analog of graphite, the g-C_3N_4 NSs polymer possesses the two-dimensional (2D) structure and consists of carbon and nitrogen which are the affluent elements in planet and thus could be produced sustainably and cost effectively [19]. Up to now, g-C_3N_4 NSs have been widely applied for photoelectric devices in PEC biosensor. For instance, a sensitive PEC biosensor for quantitative detection of arecoline based on g-C_3N_4 NSs with the support of carbon nanohorns was proposed [20]. The detection of protein kinase activity based on g-C_3N_4 and the specific-recognition of Phos-tag was developed [15]. In addition, a novel PEC strategy for monitoring Cu^{2+} with AgX/g-C_3N_4 (X = Br, I) hybrid materials was also constructed [21]. Among these PEC biosensors, g-C_3N_4 and its composite have illustrated the fine photoelectric activity.

To date, the evolution of PEC sensing techniques has been promptly developed. Molecular imprinting technique used for urine, pentachlorophenol, etc. monitoring [22,23], the use of exciton plasmon interaction between quantum dots (QDs) and noble metal nanoparticles for PEC biosensor applications [24,25], microfluidic paper-based analytical device equipped with digital multimeter and internal chemiluminescence excitation source was developed for adenosine triphosphate [26], carcinoembryonic antigen [27], DNA hybridization [28] etc. detection, and in situ generated QDs-enhanced TiO_2 for estradiol assay [29] and AgBr-enhanced ZnO nanorod-based aptasensor for Ag^+ detection [30]. Additionally, such proposed methodologies could be crossly utilized and thus provided more and more innovative routes for bio-molecular determination. However, these PEC detection platform still exist some inherent shortcomings such as complex design solutions and high cost, specific attention should further be paid to some new-type PEC sensing strategies which possess simpler instrumentations, higher sensitivity, and more precise scheme.

In this work, a new platform based on the binding-induced internal-displacement was proposed, in which the glass carbon electrode (GCE) was firstly modified with g-C_3N_4 NSs (g-C_3N_4/GCE), and then Ag^+ was self-assembled onto the g-C_3N_4/GCE. Thereupon, Ag^+ could react with photo-induced electrons form the g-C_3N_4 and be reduced to form Ag, depressing the excitation electrons transfer from the g-C_3N_4 to GCE and restraining the photocurrent producing. However, when the electrode of Ag^+/g-C_3N_4/GCE was immersed into the glyphosate solution and dried in air, a relatively larger signal could be obtained under the light irradiation. During this process, Ag^+ could combine with glyphosate through chelation and then was deprived from g-C_3N_4 NSs, causing the binding-induced internal-displacement. After the chelation, a signal-on PEC response could be obtained because of the electrons produced in excited g-C_3N_4 were transferred to GCE and formed the current in circuit. The detailed PEC process was proposed in Scheme 1. On the basis of this thought, an effective and new signal "on" PEC transducer based on Ag^+/g-C_3N_4 compounds for glyphosate monitoring was established. This binding-induced internal-displacement approach provided a vaster foreground in the field of PEC bioanalysis.

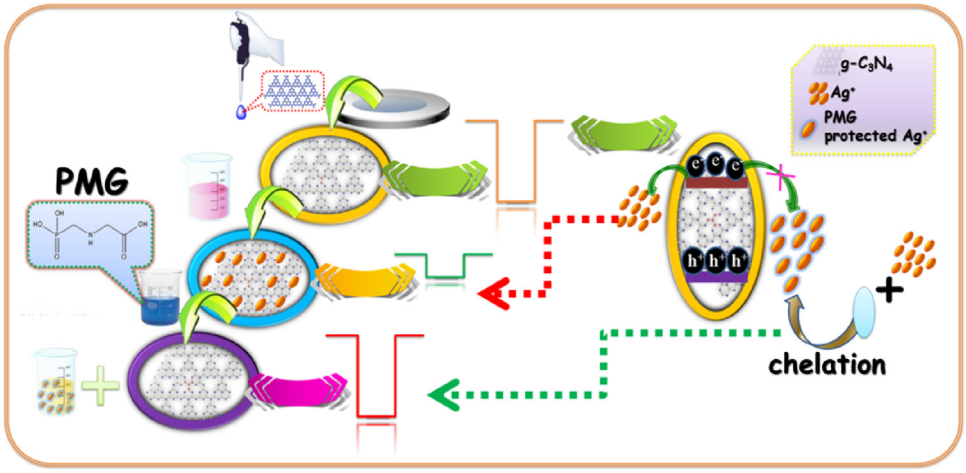
2. Experiment section

2.1. Materials and reagents

Glyphosate (N-(phosphonomethyl)glycine, PMG) was purchased from YuanYe Biological Technology Co., Ltd. (Shanghai, China). Silver nitrate ($AgNO_3$) was obtained from Shenbo Chemical Co., Ltd. (Shanghai, China). Potassium ferricyanide ($K_3Fe(CN)_6$), potassium hexacyanoferrate trihydrate ($K_4Fe(CN)_6{\cdot}3H_2O$) and potassium chloride (KCl) were purchased from Sinopham Chemical Reagent Co., Ltd. (Shanghai, China). The phosphate buffer solution (PBS, 0.1 M) as the supporting electrolyte was prepared by mixing stock solution of 0.1 M NaH_2PO_4 and 0.1 M Na_2HPO_4 to adjust the pH. Other reagents were of analytical reagent grade. The water used for the preparation of the solution was purified utilizing the water purifier (China) purification system.

2.2. Apparatus

The morphologies and sizes of g-C_3N_4 NSs were observed by scanning electron microscopy (SEM, Hitachi S-4800). Electrochemical impedance spectroscopy (EIS), square wave voltammetry (SWV) and photocurrent were measured on an electrochemical workstation (CHI 430) (Shanghai Chenhua Instrument Co., China) with a homemade three-electrode for signal acquisition. A platinum wire, a saturated Ag/AgCl electrode, and the modified GCE (d = 3 mm) were used as counter, reference and working electrode, respectively. The UV–Vis light absorption spectra were obtained from an Agilent Technologies Cary 60 spectrophotometer. The pH adjustments were employed with PHS-3C exact digital pH meter (Shanghai Leici Co. Ltd., China). The composition of g-C_3N_4 was employed by X-ray spectroscopy (XPS, VG 2000) using Al Kα monochromated radiation as the exciting source. The excitation source of homogeneous light (395 nm) was filtered by



Scheme 1. (A) Process of the fabricated PEC sensor construction the mechanization illustration of electrons transfer under the visible light irradiation.