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Sensitive analysis of simazine based on platinum nanoparticles on polyoxometalate/multi-walled carbon nanotubes

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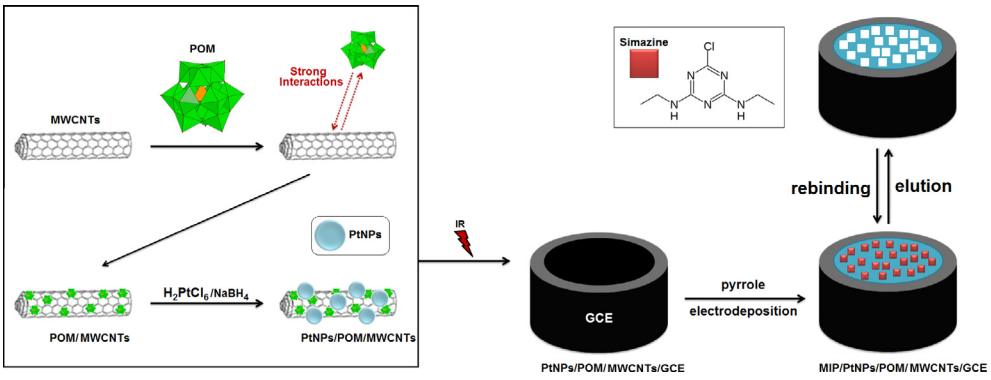
GRAPHICAL ABSTRACT



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ABSTRACT

In this report, a novel molecular imprinted voltammetric sensor based on glassy carbon electrode (GCE) modified with platinum nanoparticles (PtNPs) involved in a polyoxometalate ($H_3PW_{12}O_{40}$, POM) functionalized multi-walled carbon nanotubes (MWCNs) sheets was prepared for the determination of simazine (SIM). The developed surfaces were characterized by using scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) method. SIM imprinted GCE was prepared via electropolymerization process of 100 mM pyrrole as monomer in the presence of 0.1 M acetate buffer (pH 4.0) containing 25 mM SIM. The linearity range and the detection limit of the developed method were calculated as 1.0×10^{-10}–5.0×10^{-9} M and 2.0×10^{-11} M, respectively. In addition, the voltammetric sensor was applied to wastewater samples. The stability and reproducibility of the voltammetric sensor were also reported.

1. Introduction

Triazines are frequently utilized in herbicides at low level. SIM [2-chloro-4, 6-bis(ethylamino)-1,3,5-triazine] is one of the most important herbicides. SIM is stable in neutral medium and weakly alkaline media, but decomposed by UV irradiation [1]. Recently,

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some analytical methods have been developed for the determination of SIM. These are gas chromatography, electron capture detector and high performance liquid chromatography [2,3]. However, the expensive equipments and materials are needed in these methods. In addition, there are many extraction steps during analysis. These problems can be solved by electrochemical methods. Hence, the development of selective and sensitive molecular imprinted electrochemical sensors is required.

Especially, various nanomaterials such as graphene/graphene oxide (GO), carbon nanotubes and nanoparticles such as silver, gold, platinum can been used for the development of sensitive method [4–8]. In addition, significant progress has been performed in the production of carbon-supported materials with suitable cost [9]. Nevertheless, some important problems such as low catalytic performance for analysis sometimes occur. Hence, in order to increase this performance, the novel hybrid nanomaterials such as gold nanoparticles involved in p-aminothiophenol functionalized multi-walled carbon nanotubes, Fe@Au nanoparticles involved in 2-aminoethanethiol functionalized multi-walled carbon nanotubes and graphene oxide/silver nanoparticles [10–12]. In addition, during the last two decades, interests have focused on nano-scaled materials and their use in analytical chemistry because of their specific physico-chemical properties for a wide range of applications including electronics, optics, catalysis and biological sensors. Particularly, metallic nanoparticles such as silver, gold, palladium and platinum have been used extensively due to their unique properties which significantly differ from those presented by the bulk materials [13,14]. Some of their unique properties are sensitive interface roughness, catalytic and conductive properties, mass transport enhancement and larger specific surface area. The nanoparticles can also increase the rate of electrochemical reaction [15]. POMs consist of d-block transitional metal oxide nanosized and have important photocatalytic effects because of the redox properties.

The formation of molecular imprinted polymer is the one of the most effective method in development of sensitive method. The technique is based on polymerization which is formed around the analyte molecule. Due to such a polymerization, the technique forms specific cavities related to target molecule [16–20].

The SIM imprinted voltammetric sensor was firstly developed in this study and applied to wastewater samples. The preparation and characterization of nanocomposites such as POM/MWCNs, PtNPs/POM/MWCNs were firstly performed. After that, GCE surfaces were modified with these nanomaterials by using infrared heat lamp. SIM imprinted surfaces was performed by cyclic voltammetry (CV) of 100 mM pyrrole monomer in the presence of 0.1 M acetate buffer (pH 4.0) containing 25 mM SIM at PtNPs/POM/MWCNs modified GCE (PtNPs/POM/MWCNs/GCE) (20 cycles). The developed system is ultra-sensitive, rapid, and easy and might be preferred to published methods. In addition, the system provides a novel method for the ultra-sensitive determination of SIM in wastewater samples.

2. Experimental

2.1. Materials

SIM, atrazine (ATR) and prometryn (PRO) were obtained from Sigma–Aldrich. The stock solutions of SIM (1.0 mM) were prepared by 0.1 M acetate buffer (pH 4.0). The MWCNTs of 30–40 nm in diameter and 1.0–5.0 μm in length; purity: ⩾95% were purchased from Sigma–Aldrich. $H_3PW_{12}O_{40}$ (POM), pyrrole, chloroplatinic acid (H_2PtCl_6), acetic acid, acetonitrile (MeCN), isopropyl alcohol (IPA) and activated carbon were purchased from Sigma–Aldrich (USA).

2.2. Instrumentation

Differential pulse voltammograms (DPV) and cyclic voltammograms were obtained by IviumStat (U.S) equipped with C3 cell stand. Electrochemical impedance spectroscopic experiments were performed with IVIUMSTAT & IVIUMSTAT.XR: Electrochemical Interface & Impedance Analyser. PHI 5000 Versa Probe (Φ ULVAC-PHI, Inc., Japan/USA) was used for XPS analysis with monochromatized Al Kα radiation (1486.6 eV) as an X-ray anode operated at 50 W. The morphology of PtNPs/POM/MWCNTs was investigated by using the JEOL 2100 HRTEM (Japan) with an accelerating voltage of 200 keV. A drop of sample solution was deposited on a polymeric grid and dried at room temperature under an argon gas stream. SEM images were obtained using the ZEISS EVO 50 analytic microscope (Germany) at 30 kV acceleration voltage. A Rigaku Mini X-ray diffractometer was used for X-ray diffraction measurements.

2.3. Synthesis of POM/MWCNTs and PtNPs/POM/MWCNTs

The MWCNTs was dissolved in ethanol at a concentration of 2 mg mL^{-1} with the ultrasonic agitation for 1 h. The $H_3PW_{12}O_{40}$ (1 mL, 1 mM) was dissolved in ultra-pure water. The prepared The $H_3PW_{12}O_{40}$ was reduced by using a ultra-violet (UV) light source. The MWCNTs suspension was well mixed with the reduced POM at a 1:1 volume ratio for 2 h (POM/MWCNTs). H_2PtCl_6 solution (1 mM) was added to the POM/MWCNTs solution (0.4 mg mL^{-1}) at a 1:1 volume ratio in a quartz bottle. The solution was sonicated to form a homogeneous suspension. The prepared solution was stirred under the UV light for 40 min (the low pressure lamps are used because they emit most of the radiant energy in the germicidal wavelength at 253.7 nm, irradiation flux: 10 Wm^{-2}). After stirring, PtNPs/POM/MWCNTs nanomaterial was formed [21].

2.4. Procedure for the electrode preparation

GCE was cleaned according to our previous reports [22,23]. GCE was cleaned and prepared by polishing it to a mirror-like finish with fine wet emery paper (grain size 4000). The electrodes were polished successively in 0.1 μm and 0.05 μm alumina slurries (Baikowski Int. Corp., U.S) on microcloth pads (Buehler, Lake Bluff, IL, U.S). The electrodes were sonicated first in ultra pure water two times and in 50:50 (v/v) IPA + MeCN solution purified over activated carbon. After removal of trace alumina from the surface by rinsing with water and a brief cleaning in an ultrasonic bath (Bandelin RK 100, Germany) with water and then with IPA + MeCN mixture purified over the activated carbon, they were rinsed with MeCN to remove any physisorbed or unreacted materials from the electrode surface.

After that, MWCNTs, POM/MWCNTs, PtNPs/POM/MWCNTs suspensions of 15 μL were dropped onto the clean GCE. Then, the solvent was evaporated by an infrared lamp.

2.5. Preparation of SIM imprinted voltammetric sensor

The schematic preparation of the SIM imprinted surface is shown in Scheme 1. The SIM imprinted surface on PtNPs/POM/MWCNTs/GCE (**MIP/PtNPs/POM/MWCNTs/GCE**) was constructed by using CV for 20 cycles in the presence of 100 mM pyrrole in 0.1 M acetate buffer (pH 4.0) containing 25 mM SIM at a scan rate of 100 mV s^{-1} between 0.0 V and +1.1 V. The SIM non-imprinted surface (NIP) was performed under the same experimental conditions without SIM for a control experiment.