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A highly sensitive photoelectrochemical detection of perfluorooctanic acid with molecularly imprined polymer-functionalized nanoarchitectured hybrid of AgI–BiOI composite

Jingming Gong *, Tian Fang, Dinghua Peng, Aimin Li, Lizhi Zhang

Key Laboratory of Pe sticide & Chemical Biology of Ministry of Education, Institute of Environmental Chemistry, College of Chemistry, Central China Normal University, Wuhan 430079, PR China

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ABSTRACT

A rapid and ultrasensitive signal-off photoelectrochemical sensor has been developed under visible-light irradiation, for the detection of perfluorooctanoic acid (PFOA), especially low level PFOA present in environment, whereby a novel nanostructured probe made of molecularly imprinted polymer (MIP) modified AgI nanoparticles–BiOI nanoflake arrays (AgI–BiOINFs) is designed as the photoactive electrode (denoted as MIP@AgI–BiOINFs). Here, the unique nanoarchitectured hybrid of AgI–BiOINFs was first in situ synthesized via a facile successive ionic layer adsorption and reaction (SILAR) approach and then employed as a matrix to graft the recognition element of MIP. Such a newly designed PEC sensor exhibits high sensitivity and selectivity for the determination of PFOA. The PEC analysis is highly linear over the PFOA concentration ranging from 0.02 to 1000.0 ppb with a detection limit of 0.01 ppb ($S/N=3$). This value obtained by using the facile PEC sensor is comparable to the results obtained by using well-established liquid chromatography–tandem mass spectrometry (LC–MS/MS). Toward practical applications, this low-cost and sensitive assay was successfully applied to measure PFOA in real water samples.

1. Introduction

Perfluorooctanoic acid (PFOA) is a widely studied and environmentally prevalent member of a large class of xenobiotic compounds called perfluorochemicals (PFCs). It can be frequently found worldwide in surface waters and animal tissues (Lindstrom et al., 2011). Owing to its global ubiquity, ability to bioaccumulate in wildlife, extreme stability offered by the extremely strong carbon–fluorine bonds and difficulty to degrade, PFOA has aroused a tremendous environmental and health concern (Xu et al., 2013; Giesy and Kannan, 2001; Chen et al., 2013; Ohno et al., 2014). Therefore, rapid determination of PFOA residues has become highly desirable. The current available detection methods for PFOA include gas chromatography–mass spectrometry (GC–MS) (Huset et al., 2008; Scott et al., 2006), liquid chromatography–mass spectrometry (LC–MS) (Risha et al., 2005; Saito et al., 2010), and liquid chromatography–tandem mass spectroscopy (LC–MS/MS) (Young et al., 2013; Eriksen et al., 2011). However, these methods often require complicated pretreatment steps, expensive labor resources, and they are not applicable for in-situ rapid analysis. Therefore, a simple, easy-to-operate, cheap and sensitive analytical method for fast screening of PFOA residues is urgently desirable.

Recently, photoelectrochemical (PEC) sensors, a kind of sensing technique based on photoinduced electron transfer processes at electrode/interfaces, have received much interest (Zhao et al., 2014; Cooper et al., 1998; Kang et al., 2010; Yang et al., 2015). Benefiting from the efficient separation of excitation source (light) and detection signal (current), PEC sensors are becoming a promising analytical technique with remarkable sensitivity, inherent miniaturization and easy integration in a wide variety of analytical fields (Liang et al., 2006; Haddour et al., 2004; Sun et al., 2014; Chen et al., 2012; Lu et al., 2013; Gong et al., 2012). It should be noted that photoactive materials play a crucial role in the performance of PEC sensors. Owing to the strong oxidizing power, photostability, and environmental benignity, various titanium dioxide (TiO_2)-based visible-light-responsive photoactive composites (e.g., $CdSe_xTe_{1-x}$-sentisized TiO_2, metal-doped TiO_2, polymer-hybridized TiO_2 and CdTe-cosensitized TiO_2/CdS:Mn) for PEC sensing have been explored (Kang et al., 2010; Li et al., 2014; Wang et al., 2013; Fan, L.F., et al., 2014). Despite these advances, the relatively sophisticated fabrication methods as well as tedious coupling procedures have seriously hampered their applications.

In particular, PFOA is chemically inert with extremely strong carbon–fluorine bonds (C–F, 116 kcal mol^{-1}), making them

* Corresponding author.
E-mail address: jmgong@mail.ccnu.edu.cn (J. Gong).

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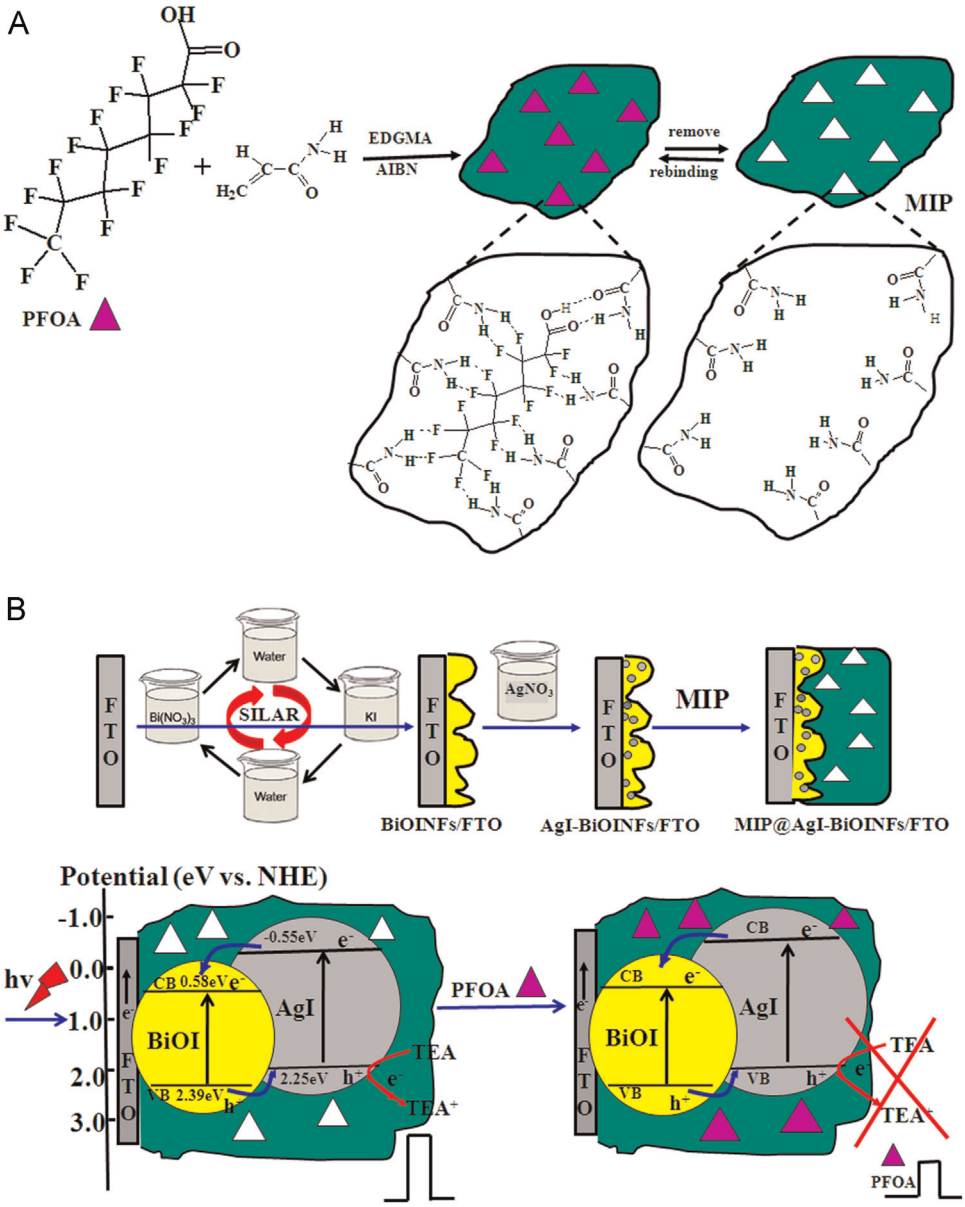
resistant to conventional advanced oxidation processes (Key et al., 1997; Niu et al., 2012). Since TiO_2 and even the powerful oxidants of hydroxyl radicals (•OH, $E^0 = +2.8$ V) show a poor reactivity with PFOA (Kutsuna et al., 2006), the detection of PFOA through a direct visible-light-responsive PEC strategy is hardly feasible. Therefore, three crucial issues should be addressed: (1) how to construct a high-performance visible-light-responsive PEC sensing platform in a simple fashion; (2) how to establish an indirect PEC transducer, which could be triggered by the introduced PFOA, i.e. igniting the separation/combination of the photogenerated electron–hole pairs, thus leading to the variance of photocurrent; (3) how to realize the highly selective detection of PFOA by PEC sensor? These remain a significant challenge.

Bismuth oxyiodide (BiOI) has a unique layered tetragonal structure, small band gap (~1.8 eV) and strong absorption in the visible-light region, extensively used as visible-light photocatalysts (Zhao, 2013a; Zhang et al., 2008). Meanwhile, various BiOI-based heterojunctions, e.g., TiO_2/BiOI (Zhang et al., 2009), C_3N_4/BiOI (Chang et al., 2014), and AgI/BiOI (Cheng et al., 2010, 2013) with enhanced performances have been achieved for photochemical applications. However, rational design of BiOI-based nanostructured probes for PEC analysis has been seldom reported (Zhao et al., 2013b; Peng et al., 2014). In this work, we present a facile approach to synthesize AgI nanoparticles–BiOI nanoflakes heterojunctions (labeled as AgI–BiOINFs), and demonstrate for the first time a simple indirect PEC sensing strategy for the detection of PFOA using AgI–BiOINFs hybrids integrated with the molecularly imprinted polymers (MIPs). As well known, MIPs, termed as "artificial antibodies", possess a specific ability of molecular recognition, widely used in separation and sensing (Wang et al., 2013; Chen et al., 2012; Haupt and Mosbach, 2000). In our work (as shown in Scheme 1), the controlled fabrication of the AgI–BiOINFs hybrid is realized via a facile successive ionic layer adsorption and reaction (SILAR) approach, where AgI nanoparticles are grown uniformly on the surface of three-dimensional (3D) crossed BiOI nanoflake arrays, providing an ideal matrix for subsequently grafting the recognition element of MIP. The smart integration of AgI–BiOINFs with MIP yields a novel MIP@AgI–



Scheme 1. Schematic illustration of the formation process of (A) the MIP, and (B) the SILAR deposition of AgI–BiOINFs films as well as the principle of PEC determination of PFOA using MIP@AgI–BiOINFs/FTO.