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# Enhanced effects of ionic liquid and gold nanoballs on the photoelectrochemical sensing performance of $WS_2$ nanosheets towards 2,4,6-tribromophenol

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ABSTRACT

Tungsten disulfide ($WS_2$) nanosheets were obtainable by exfoliation of its bulk crystals using ultrasonication in a N-methyl-pyrrolidinone (NMP) solution containing 1-vinyl-3-(3-aminopropyl)-imidazolium bromide (VAimBr) ionic liquid (IL). In addition, gold nanoballs (AuNBs) with controllable size and shape were synthesized using 1,3-di (3-bromopropyl)-imidazolium bromide ionic liquid as a functional monomer. AuNBs were self-assembled onto $WS_2$ nanosheet surface to form an AuNB/$WS_2$-IL nanocomposite. The AuNB/$WS_2$-IL nanocomposite was drop-coated onto a glassy carbon electrode surface to produce a new interface for immobilization of transthyretin (TTR) through a self-assembled interaction between cysteine residues of TTR and AuNBs. All materials and interfaces were fully characterized. The developed TTR-AuNBs/$WS_2$-IL/GCE electrode was found providing a very high-performance platform for the photoelectrochemical sensing of 2,4,6-tribromophenol (TBP) due to the strong affinity between TBP and TTR. With respect to our results, the photocurrent response of $WS_2$ nanosheets was significantly enhanced after the integration of AuNBs and VAimBr ionic liquid, and the enhancement is greatly beneficial for the photoelectrochemical sensing of TBP. Under optimized experimental conditions, the ratio $R_i$ [$R_i = \triangle i/i_0$] between the photocurrent variation ($\triangle i$) and the original photocurrent ($i_0$) shows good linear relationship ($R = 0.997$) to the logarithm of TBP concentration ($c$) in the range from 0.05 nmol $L^{-1}$ to 500 nmol $L^{-1}$. The limit of detection is calculated to be 0.023 nmol $L^{-1}$ ($S/N = 3$). The photoelectrochemical sensor was employed to determine the spiked TBP in the water samples collected from South-Lake Wuhan China. The excellent recoveries of 95.7% and 98.6% demonstrate that the TTR-AuNBs/$WS_2$-IL/GCE is suitable for practical use to determine trace TBP in real water samples.
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## 1. Introduction

2,4,6-Tribromophenol (TBP) is a newly used flame retardant for the production of polymers such as nylon 66, thermoplastic polyester, modified polyphenylene oxide, high impact polystyrene, and acrylonitrile butadiene styrene. In addition, TBP is an important raw material in the chemical industry. Its production is 4500–23000 tons in the USA in 2006 and has been considered to be a high production volume chemical in the EU in 2010 [1]. TBP is currently widely used for formulation of insecticide, antifungal agent (e.g. wood treatment), and a chemical intermediate for the production of other flame retardants. TBP can be synthesized by oxidizing phenol with bromine and also obtained as a by-product from the synthesis of 1,2-bis(2,4,6-tribromophenoxy)ethane and photo-degradation of tetrabromobisphenol A. Some marine microorganisms and seaweeds are also able to generate TBP [2–4].

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Nowadays, it has been reported that significant amounts of TBP are found various sources including surface water, drinking water, soil, rubbish percolate, sludge, marine microorganisms, even in human tissues and plasma probably due to environmental contamination or pollution [5]. TBP possesses some typical characteristics of persistent organic pollutants (POPs), such as degradation-resistant, biological accumulation, and biotoxicity etc. The recent investigations pointed out that feeding zebra fish with fodder containing TBP at the concentration of 3.3 mg $g^{-1}$ caused obvious reproduction toxicity effects [6]. For rats, high acute oral exposure to TBP results hypoactivity, salivation, nasal discharge, lacrimation, decreased motor activity, tremors, prostration, clonic convulsions, and death [7]. The limited oral repeated-dose toxicity studies of TBP in rats shows toxicity to liver and kidney, reduced neonatal viability and neonatal body weights, may interfere with thyroid hormone transport, estrogen metabolism and cellular $Ca^{2+}$ homeostasis. Therefore, to develop analytical methods with high selectivity, sensitivity, and fast response for trace TBP detection will be very significant for environmental protection and human health. Up to now, the determination technology for TBP mainly depends on chromatography coupled with electron capture detector or mass spectroscopy. Although the technique can give sensitive and accurate results, the requirements of expensive instruments and skillful technician limit their applications, especially for the in-situ detections and monitoring [8]. Electrochemical sensors possess certain intrinsic properties such as low-cost instrumentation, high sensitivity, high selectivity, and easy microminiaturization. They thus have been extensively studied for the determination of POPs including TBP [9–12]. The development of electrochemical sensor for TBP based on surface molecular imprinting technology has been reported and the sensor fabrication method is done by imprinting the core-shell nanoparticles (modified with (3-chloropropyl)trimethoxysilan and polyethylenimine as functional monomer), TBP (as a template), and ethylene glycol dimethacrylate (as a cross-linker). This imprinted sensor demonstrated high selective recognition ability and low detection limit for TBP [10]. Another example of electrochemical sensor based on molecularly imprinted nanofiber film method, using TBP as a template, β-cyclodextrin as functional monomer, and poly-vinylbutyral as an electro-spinning matrix, also exhibits good selectivity, reproducibility, high sensitivity, and low detection limit [9].

Photoelectrochemical sensing is a newly emerging strategy designed for complex system assay. In photoelectrochemical sensing, light is used as an excitation source whilst current is measured as the output detection signal. The separation between the sources of excitation (light) and detection (photocurrent) in the photoelectrochemical process offers high sensitivity with low background signal. The photoelectrochemical sensing technique has been demonstrated to be a very efficient tool in biosensing and bioanalytical applications. Semiconductors such as $TiO_2$ and quantum dots are commonly used as the photoactive materials for photoelectrochemical sensors development [13,14]. Unfortunately, the wide band gap nature of these materials, which absorb UV light and often leads to deactivation effects on some biomolecules [15,16]. In addition, the low energy conversion efficiency and photobleaching effects of the materials also hinder the further development of photoelectrochemical biosensors.

Recently, transition metal dichalcogenides have attracted great attention due to their native characteristics such as graphene-like layered structure, large specific surface area, and excellent electronic, optoelectronic and catalytic properties [17]. $WS_2$ is a typical layered transition-metal dichalcogenide. It consists of S-W-S layers which are stacked by one W atom and two S atoms through Van der Waals' force interaction [18]. When the 2D $WS_2$ nanosheets exfoliated from the bulk material, its indirect band gap will be transferred as a direct band gap (1–2 eV) and the photoelectric conversion efficiency will also be improved [19]. The layered structure of $WS_2$ is beneficial for the in-plane electron transport. Therefore, it has been widely used in the field of electrochemical catalysis, lithium-ion battery, supercapacitor, and biosensing recently [20–23].

In the present study, 1-vinyl-3-(3-aminopropyl)-imidazolium bromide ionic liquid was used as a critical auxiliary-reagent in N-methyl-pyrrolidinone to exfoliate bulk $WS_2$ crystals to produce monolayer (or a-few-layer) $WS_2$-IL nanosheets by ultrasonication. As the ionic liquid possesses excellent conductivity and biocompatibility, thus, it is used as an auxiliary exfoliation solvent and a functional reagent. It has been reported that ionic liquid can greatly improve the photoelectrochemical response of photoactive materials and enhance the sensing performances [24,25]. Another key material is the preparation of gold nanoballs (AuNBs) with controllably size and shape. The synthesis was done by using 1,3-di (3-bromopropyl)-imidazolium bromide ionic liquid as the functional monomer. AuNBs were then self-assembled onto $WS_2$-IL nanosheets through the reaction between the sulfur atom and the gold atom to form AuNBs/$WS_2$-IL nanocomposites [26]. To the best of our knowledge, there is no report on the exfoliation of $WS_2$ with ionic liquid to produce $WS_2$ nanosheets, and on the enhanced effects of ionic liquid and gold nanoballs on the photoelectrochemical response of $WS_2$ nanosheet. In addition, photoelectrochemical biosensor developed for TBP was also never been reported. Therefore, the photoelectrochemical response of $WS_2$-IL nanosheets and AuNBs/$WS_2$-IL nanocomposites were investigated to demonstrate the enhanced effects. In addition, AuNBs/$WS_2$-IL nanocomposites were also used to construct a photoelectrochemical interface for immobilizing transthyretin [TTR, a transport protein found in serum and cerebrospinal fluid for carrying thyroid hormone (thyroxine, T4)] to fabricate a biosensor for TBP. The chemical structure of TBP is very similar to that of thyroxine (Scheme S1). TBP thus also has high affinity interaction with TTR [27] and thus improving the sensing selectivity by the incorporation of TTR in the nanocomposites. The newly developed photoelectrochemical biosensor was successfully demonstrated in the determination of trace TBP in water samples from a lake in Wuhan China.

## 2. Experimental section

All reagents and apparatus are details in the Supporting Information.

### 2.1. Synthesis of VAimBr ionic liquid

The synthesis of 1-vinyl-3-(3-aminopropyl)-imidazolium bromide (VAimBr) ionic liquid was shown in Scheme S 2. The procedures were detailed as following: 3-Bromopropylamine hydrobromide (1.64 g, 0.007 mol) was dissolved in 50 mL of anhydrous acetonitrile, and N-vinyl-imidazole (2.82 g, 0.03 mol) was added. The reaction was protected under nitrogen and was kept at 55 °C for 12 h. Solvents were evaporated under vacuum to obtain a crude product after reaction. The crude product was re-dissolved in water and was extracted with toluene (3 × 20 mL) thoroughly. The pH value of the aqueous solution was adjusted to 9.0–10.0 by using $Na_2CO_3$ solution. Water was evaporated under vacuum, and the obtained solid product was purified by silica gel column chromatography using ethyl acetate/methanol (70:30, V/V) as eluent to give the target compound, 1-vinyl-3-(3-aminopropyl)-imidazolium bromide. VAimBr ionic liquid was characterized with $^1$H NMR (Fig. S 1) and HPLC-MS (Fig. S 2).

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