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Group-Targeting Detection of Total Steroid Estrogen Using Surface-Enhanced Raman Spectroscopy

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Supporting Information

ABSTRACT: Steroid estrogens, including 17β-estradiol (TE2), estrone (TE1), and ethinyl estradiol (TEE2), which are the strongest endocrine disruptors and coexist in the environment, seriously harm the health of organisms; thus, the monitoring of total steroid estrogens (TEs) has attracted growing attention. Herein, a method based on surface-enhanced Raman spectroscopy (SERS) group-targeting detection is established to detect TEs in natural water for the first time. The TEs response detection range and detection limit were 0.01−50 nM and 5 pM, respectively. An anti-interference ability was observed: even if coexisting interfering species were present in the system at 100-fold the concentration of estrogens, the detection error of the method was less than 0.276. In addition, the association constants between the aptamers and TE1, TE2, and TEE2 were similar, and therefore, the recognition of TE1, TE2, and TEE2 by the aptamers was consistent. Furthermore, the interaction sites A44, T72, and G69 between the aptamers and TE1, TE2, and TEE2 were investigated by molecular docking. On this basis, the estrogens in environmental water samples, including animal farm wastewater, maternity hospital wastewater, surface water from near an animal farm, and surface water from near a maternity hospital, were successfully determined.

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Estrogens, a kind of environmental endocrine disruptor, are a class of structurally similar steroidal compounds[1] and are considered to be the strongest endocrine disruptors.[2,3] Estrogens are mainly excreted by animals and humans and discharged from animal husbandry operations through incomplete removal in wastewater.[4,5] Estrogen exposure in natural groundwater and surface water occurs at the nanomolar level.[5] Estrogens have high estrogenic activity, as well as strong bioaccumulative toxicity; these traits give rise to endocrine dyscrasia and even carcinogenesis in humans and animals, even at nanomolar concentrations.[6] In particular, natural estrogens such as 17β-estradiol (TE2) and estrone (TE1) and synthetic estrogens such as ethinyl estradiol (TEE2) always coexist in the environment owing to their similar chemical structures.[7] Among these compounds, TE2 is considered to be the most active estrogen. Moreover, both TEE2 and TE1 have become the most sensitive endocrine disruptors among adolescents, resulting in a serious impact on the health of young people.[8] The estrogenic efficacy of TE2, TEE2, and TE1 is more than 3 orders of magnitude higher than that of most endocrine disruptors, such as nonylphenol and bisphenol A.[9] Consequently, the detection of total steroid estrogens (TEs) is highly desired due to the synergetic effects of such compounds on the environment. Monitoring TEs in the environment will avoid inaccurate assessments of water quality and the destruction of ecological systems.

To date, numerous methods of estrogen detection have been developed due to the high toxicity and health risks these compounds pose to human beings; these methods include high-performance liquid chromatography (HPLC),[10] high-performance thin layer chromatography−electrospray ionization mass spectrometry (HPTLC−ESI-MS),[11,12] and liquid chromatography−mass spectrometry (LC−MS),[13] which perform sequential measurements of individual estrogens, even though phenomena such as peak tailing and overlap occur in most methods. However, these analytical methods usually not only need to be combined with sample pretreatment, such as solid-phase extraction (SPE),[14] solid-phase microextraction (SPME),[15] liquid−liquid extraction (LLE),[16] derivatization of estrogens,[11,17] or the separation of estrogens by molecularly imprinted (MI) microspheres to concentrate and purify the sample,[10] but also involve time-consuming analysis and exploration of the complex testing conditions of the instrument. Therefore, TEs cannot be detected directly by using the above technologies, resulting in difficulties when

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A simple one-step pretreatment, highly sensitive and selective sensing of 17β-estradiol in environmental water samples using surface-enhanced Raman spectroscopy

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ABSTRACT

A highly sensitive and selective aptamer-based surface-enhanced Raman spectroscopic biosensing system was established for detecting trace amount of 17β-estradiol (E2) for the first time, and applied in the environmental samples based on a simple one-step pretreatment. Raman reporter molecule 4-mercaptobenzoic acid labelled gold-silver core-shell nanoparticles (Au@Ag CS NPs) and E2-aptamer endowed SERS with high sensitivity and selectivity. A wide linear range from 0.1 pM to 10 nM was obtained for the detection of E2, with a low detection limit of 0.05 pM. Additionally, this system showed excellent selectivity for E2, where the Raman intensity of E2 was greater than 3.97-fold that of 100-fold concentration of other interfering substances. The high binding affinity of the E2-aptamer towards E2 was further investigated by the UV–vis absorption measurements, whereas E2-aptamer showed no binding affinity to other interferents. Finally, E2 in the environmental water samples collected from the sewer and nearby river of local obstetric hospital were successfully determined by this system, which exhibited superior sensitivity. This work has provided a new detection biosensing system for trace determination of typical contaminants in the environment.

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1. Introduction

The most active nature estrogen 17β-estradiol (E2), as a typical environmental endocrine disrupting chemical (EDC) [1–3], possesses a very long residual period and low concentration in the environment. However, it brings many deleterious effects to the human and the aquatic organisms [4–6], due to its strong bioaccumulative toxicity [7], which causes disequilibrium in endocrine function and even results in cancers [6,8]. E2 in the environment is mainly derived from the excretion of animals and human, and the emissions from breeding industrials, then flows into the surface water through sewage and other methods, which impacts on the normal growth of aquatic organisms directly. Toxicological experiments have shown that the male fishes that exposed to E2 at a concentration of 3.68–184 pM synthesized vitellogenin in vivo [9]. The United States National Environmental Protection Agency proposed the maximum residue of E2 in surface water was 1.47 pM in 2012 [10], and Japan also increased the new regulations that E2 in drinking water was limited to 0.294 nM in 2015. Therefore, it cannot be ignored to detect E2 in the environment with low concentration and high toxicity. It is of great significance to protect the environment and human health by establishing a simple, rapid, efficient and sensitive method for the detection of E2.

To date, some new analytical methods such as high performance liquid chromatography (HPLC) [11,12], liquid chromatography combined with mass spectrophotometer (LC–MS) [13], immunoassay [14,15], colorimetric [16] and electrochemical [17–19] methods are used for the detection of E2. These methods have low detection limit of nM or pM for E2. However, for the conventional analytical methods like LC–MS and HPLC, complex pretreatments such as purification, concentration and extraction of the samples are required. Besides, it also reveals the shortcomings including exploring the complex detection conditions of the instrument, the difficulty and the longtime of analysis. Moreover, immunological analysis based on antibody-receptor, such as fluorescence immunoassay, and chemiluminescence immunoassay [20], show high sensitivity and sensitivity in E2 determination, but the biocomponents are expensive, and the requirements of environ-

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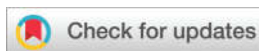

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Monitoring 2,3′,5,5′-tetrachlorobiphenyl with a rapid and sensitive environmental aptamer sensor†

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Polychlorinated biphenyl (PCB) detection in the environment is significant for both environmental protection and human health. Herein, a highly sensitive aptamer sensor has been established by employing a 2,3′,5,5′-tetrachlorobiphenyl (PCB72) targeting aptamer as a highly specific recognition element and a gold/silver (Au@Ag) nanocomposite as the surface-enhanced Raman spectroscopy (SERS) substrate for detecting environmental PCB72. The Au@Ag nanoparticles (NPs) exhibit a strong SERS enhancement and provide an efficient substrate for immobilizing the PCB72 aptamer and Raman signal labelled molecule, 4-mercaptobenzoic acid (4-MBA). The targeted PCB72 could competitively bind with the PCB72 aptamer, resulting in a few aptamers sticking to the Au@Ag NPs and the "hot spot" strengthening effect of the substrate. Under optimal conditions, this aptamer sensor exhibits great performance with high sensitivity, excellent selectivity and stability for the monitoring of PCB72, which shows an excellent linear correlation ranging from 1 to 1000 pg mL^{-1} with a limit of detection of 0.3 pg mL^{-1}. Furthermore, this aptamer assay exhibits high specificity and selectivity for PCB72 with the detection error of less than 0.27 for other PCBs and 0.21 for other interfering species, even if the coexisting interferents are 100-fold concentration in the system. Additionally, the recognition mechanism of the binding of aptamers to PCB72 is analyzed *via* UV-vis spectroscopy and molecular docking simulations, which suggest that PCB72 could insert into the aptamers. Furthermore, this method is successfully utilized for PCB72 detection in real water samples with a simple pre-treatment. In general, this work provides a new and effective method using an environmental aptamer sensor for rapid and sensitive PCB72 detection.

1. Introduction

As a class of persistent organic pollutants in the world, which is extremely insoluble in water while soluble in fat and organic solvents, polychlorinated biphenyls (PCBs) are easily enriched in human and animal fats. The main source of PCBs is from the discharged waste of factories, which could be absorbed and accumulated into mammals, thereby leading to bio-accumulative and toxic problems.[1,2] The standard levels of PCBs proposed by the Food and Drug Administration (FDA) in food is limited to 0.2–3 ppm.[3] Despite the adoption of restrictive rules, so far, a certain amount of PCBs has been detected in sediment,[4] food,[5] and seawater[6] because their biological, physical and chemical degradation is very difficult. Moreover, their accumulation and toxicity in organisms is harmful to both the environment and people's health.[1] So, the monitoring of PCBs in the environment and the evaluation of its toxicity are of great significance for the protection of the environment and human health.

For the quantification of PCBs, various methods have been used like gas and liquid chromatography-mass spectrometry.[7,8] However, these methods have some limitations that include complex sample preparation, expensive equipment, rigorous experimental environments, and high requirements of the operators.[9,10] To solve these problems, another strategy for measuring PCBs like a biological sensor, which can monitor PCBs without costly equipment, such as an enzyme-based biosensor or antibody-based biosensor,[11] have been recently proposed. However, the tedious and long preparation period restrict antibodies' universal use, especially for small molecules.[12] Hence, fabricating new approaches for PCB determination without using complex pre-treatment procedures is pressingly required.

Surface-enhanced Raman spectroscopy (SERS) possesses great advantage of ultra-high sensitivity that enablessingle

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