Molecularly imprinted ultrathin graphitic carbon nitride nanosheets—Based electrochemiluminescence sensing probe for sensitive detection of perfluorooctanoic acid
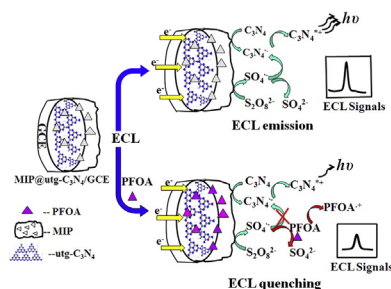
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HIGHLIGHTS

- A highly sensitive ECL sensor for rapid detection of PFOA developed.
- As-prepared sensor fabricated by MIP modified utg-C_3N_4 nanosheets.
- Unique ECL properties of MIP modified utg-C_3N_4 nanosheets explored.
- The first smart integration of utg-C_3N_4 with MIP yielding a novel ECL sensing probe.
- The resulting sensor exhibiting fine applicability for detection of PFOA in real samples.

GRAPHICAL ABSTRACT

ABSTRACT

Driven by the urgent demand for the determination of low level perfluorooctanoic acid (PFOA) present in environment, a novel electrochemiluminescence (ECL) sensor has been first developed for the detection of PFOA using the molecularly imprinted polypyrrole modified two-dimensional ultrathin g-C_3N_4 (utg-C_3N_4) nanosheets as a cathodic ECL emitter with $S_2O_8^{2-}$ as coreactant. The prepared molecularly imprinted polymer (MIP) functionalized utg-C_3N_4 nanosheets (MIP@utg-C_3N_4) exhibit a stable and significantly amplified ECL signal. It is found that the targets of PFOA could be efficiently oxidized by the electro-generated strong oxidants of SO_4^{-} (from the reduction of coreactant $S_2O_8^{2-}$), thus leading to a low yield of the excited utg-C_3N_4 (g-$C_3N_4^*$) and finally a decrease in ECL signal. Based on this, a highly sensitive and selective MIP@utg-C_3N_4-based signal-off ECL sensor is developed for sensing PFOA. Such a newly designed ECL sensor exhibits highly linear over the PFOA concentration in two ranges, from 0.02 to 40.0 ng mL^{-1} and 50.0–400.0 ng mL^{-1}. The detection limit (S/N = 3) is estimated to be 0.01 ng mL^{-1} (i.e. 0.01 ppb), 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, showing fine applicability for the detection of PFOA in real samples.

1. Introduction

Perfluorooctanoic Acid (PFOA), as a representative of per-fluorinated chemicals (PFCs), has been recognized as a widespread contaminant in various environmental matrices including water,

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air, wildlife, and humans [1–3]. 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 [4,5]. Recent studies have revealed that its toxicity and carcinogenicity might pose a great risk to human health and ecosystem. Currently, available detection methods for PFOA include gas chromatography-mass spectrometry (GC−MS) [6,7], liquid chromatography-mass spectrometry (LC-MS) [8−10], and liquid chromatography-tandem mass spectroscopy (LC-MS-MS) [11,12]. However, these methods often require complicated pretreatment steps and expensive labor resources. Recently, fluorous membrane ion-selective electrodes [13] and colorimetric sensor using mixed poly(ethylene glycol) and perfluorinated thiols modified gold nanoparticles [14] for the detection of PFCs have been reported, respectively, but limited by the laborious preparation procedures, cost and efficiency. Therefore, a simple, cheap and sensitive analytical method for fast prescreening of PFOA residues is urgently needed.

Electrochemiluminescence (ECL) is chemiluminescence triggered by electrochemical methods [15,16]. Owing to its versatility, simple instruments, good stability against photobleaching, low cost, and low background noise, ECL detection has received considerable attention [17−21]. During the past decades, a variety of ECL-emitting species, including Ru complex [22−25], luminol [26,27], and various semiconductors [28−33] have been developed and widely used in the areas of immunoassay, biowarfare agent detection, DNA biosensor, and food as well as water testing. Despite the outstanding achievements achieved, to meet the fast-developing detection requirements, intense research still focused on exploiting the innovative, stable, nontoxic, and highly efficient ECL luminophores.

Graphitic-phase carbon nitride (g-C_3N_4) is the most stable allotrope of carbon nitride, possessing a typical stacked two-dimensional structure [33,35]. In recent years, metal-free polymeric g-C_3N_4 has attracted worldwide research interest because of its unique electronic properties, low toxicity, low cost, and high stability [34−39]. It has been explored in a wide variety of applications including catalysis [40−44], degradation [45], and sensors [46−50]. For example, Wang et al. pioneered the applications of g-C_3N_4 in the photocatalysis [40]. Barman's group employed g-C_3N_4 for fluorescent detection of Hg^{2+} [46]. Sun's group fabricated the colorimetric sensors of H_2O_2 using photoluminescent g-C_3N_4 [47]. Lv's group developed a persistent luminescence probe based on g-C_3N_4 for imaging detection of biothiols [48]. Compared with its applications in catalysis and fluorosensor, however, there have been less attention paid to its ECL sensing applications. Only till recently have Xiao and coworkers reported the anodic/cathodic ECL behavior of g-C_3N_4 for the detection of rutin [51] and Cu^{2+} with $S_2O_8^{2-}$ as coreactant [52], respectively. Yet, bulk g-C_3N_4 materials used in these studies, with low specific surface area and poor solubility have strongly limited its further applications as ECL luminophore. Recently, g-C_3N_4 nanosheets with atomic-scale thickness have been facially exfoliated from bulk g-C_3N_4 and explored as fluorosensors due to offering a high surface-area-to-volume ratio and fully exposed surface active sites [53−57]. Recent theoretical investigations also revealed that ultrathin g-C_3N_4 nanosheets (utg-C_3N_4) exhibit unique electronic and optical properties [55]. Therefore, it would be of great importance to expand the potential applications of utg-C_3N_4-based luminopore in the fields of ECL. As known, PFOA is chemically inert with extremely strong carbon-−fluorine bonds, making them resistant to conventional advanced oxidation processes. Peroxydisulfate ion ($S_2O_8^{2-}$) was found to be an efficient photochemical oxidant for the decomposition of PFOA, because of the generated highly powerful oxidants of sulfate

radicals (SO$_4^{\cdot-}$, $E^0 = + 2.3$ eV) during the photolysis of $S_2O_8^{2-}$ [58]. Meanwhile, peroxydisulfate ion is a typical coreactant of cathodic g-C_3N_4 ECL. This inspires us for the first time to establish an utg-C_3N_4-based coreactant ECL system and explore its novel applications for the detection of PFOA.

Herein, a novel ECL luminophores based on utg-C_3N_4 nanosheets and molecularly imprinted polypyrrole as PFOA recognition element is to be fabricated. Molecularly imprinted polymer (MIP), possesses a specific ability of molecular recognition, and has been extensively used in separation and sensing [59,60]. The smart integration of utg-C_3N_4 and molecularly imprinted polypyrrole yields a functionalized utg-C_3N_4 nanosheet as a very effective cathodic ECL emitter for sensitive and selective detection of PFOA. The cathodic coreactant utg-C_3N_4 ECL system is conducted in 0.10 M potassium sulfate (Na$_2$SO$_4$) aqueous solution containing potassium peroxydisulfate (Na$_2$S$_2$O$_8$) as the coreactant. The electro-reduced utg-C_3N_4 can easily react with a coreactant of $S_2O_8^{2-}$ to produce an excited state, which thus subsequently decays back to its ground state, emitting strong luminescence. Since the generated intermediate, the powerful oxidant of sulfate radicals (SO$_4^{\cdot-}$, $E^0 = + 2.3$ eV) exhibits efficient oxidation ability toward PFOA. Upon the addition of PFOA, the cathodic utg-C_3N_4 ECL signal would be greatly influenced due to the consuming of SO$_4^{\cdot-}$. On the basis of the effect of PFOA on the ECL signal of utg-C_3N_4, a new rapid and sensitive utg-C_3N_4-based quenching ECL approach was developed for the determination of PFOA. To the best of our knowledge, it is the first example of investigating the ECL behavior of molecularly imprinted utg-C_3N_4 nanosheets. Furthermore, a highly sensitive and selective utg-C_3N_4-based coreactant ECL system was established for PFOA sensing. The proposed novel ECL system not only opened the field of development of novel ECL-emitting species but also pave the way to measure novel POPs in environment. The resulting utg-C_3N_4-based ECL system exhibits fine applicability for determination of PFOA in real samples.

2. Experimental section

2.1. Materials and instrumentation

Perfluorooctanoic acid (PFOA), perfluoropropioic acid (PFPA), perfluorovaleric acid (PFVA), perfluorohexanoic acid (PFHA), perfluoroheptanoic acid (PFHpA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluorooctane sulfonate (PFOS) and methyl parathion (MP) were obtained from Aladdin Industrial Co. (Shanghai, China). 2,4-dichlorophenoxyacetic acid (2,4-D) was obtained from Sigma−Aldrich Co. Pentachlorophenol (PCP) were obtained from Sinopharm Chemical Reagent Company. Melamine, sodium peroxydisulfate (AR grade), sodium sulfate (AR grade) and pyrrole were obtained from Treechem Co. (Shanghai, China). All other chemicals were of analytical grade and used as received without further purification. Phosphate buffer solutions (PBS, 0.1 M) with various pH values were prepared by mixing stock standard solutions of Na$_2$HPO$_4$ and NaH$_2$PO$_4$. All aqueous solutions were prepared with ultrapure water (resistivity ≥ 18 MΩ). All experiments were carried out at room temperature.

ECL studies were performed on a MPI-E multifunctional electrochemical and chemiluminescent analytical system (Xi'an, China). The voltage of the photo multiplier tube (PMT) was biased at 500 V during the whole processes. Electrochemical impedance spectra (EIS) were measured in the frequency range from 0.1 Hz−100 kHz with a signal amplitude of 5 mV on CHI 660D electrochemical workstation (CHI, USA) in 5 mM K$_3$Fe(CN)$_6$/K$_4$Fe(CN)$_6$ with 0.1 M KCl as the supporting electrolyte. A conventional three-electrode system was used for the electrolytic