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Electrochemical determination of methylmercury via modulating bandgap of sulfur doped graphitic carbon nitride

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ABSTRACT

Methylated mercury compounds are neurotoxins; they are ubiquitous in muddy sediments of water bodies under anaerobic conditions. A variety of coupled techniques such as capillary gas chromatography with inductively coupled plasma mass spectroscopy, or atomic fluorescence spectroscopy is used for detection of methylated mercury compounds. However, a sensitive analytical method for rapid screening of methylated mercury compounds is required. This work it was developed an electrochemical method for the detection of methylmercury in environmental samples using chemically modified Au electrodes via the bandgap modulation strategy. For the chemical modification, the sulfur-doped g-C₃N₄ was used as a starting material. The forbidden bandgap of the sulfur-doped g-C₃N₄ was regulated with urea and thiourea admixture fabricated by thermal polymerization at an optimal ratio (urea: thiourea = 3:1; hereafter UT-gCN (3:1). The UT-gCN (3:1) modified Au electrode was used for rapid detection of CH_3Hg^+ by differential pulse voltammetry (DPV) method operated at -0.80 V deposition potential, 800 s accumulation time in NaAc/HAc buffers (pH=5.0). The calibration curve of CH₃Hg⁺ showed linearity within concentration range 0–25 ppb CH_3Hg^+ with 0.52 μ A/ppb sensitivity and 0.175 ppb detection limit. The new electrochemical sensor is robust and interference-free to Cu^{2+} , Cd^{2+} , Pb^{2+} , Bi^{3+} , As^{3+} . The efficiency of the UT-gCN(3:1) sensor can be replenished by protonation with HCl. Present results indicate the potential applications of UT-gCN (3:1) modified Au electrodes in the rapid detection of methylmercury in environmental samples.

1. Introduction

Mercury is a persistent toxic pollutant that shows significant bioaccumulation and biomagnification [1–3]. The toxicity of mercury depends on its chemical speciation. In the environment, mercury occurs in different chemical forms, e.g. Hg^{0} , Hg^{2+} , and methylated mercury, and their relative toxicities are methylated mercury > Hg^{0} > Hg^{2+} [3,4]. Mercury contamination is a significant public health and environmental problem because methylmercury easily enters the bloodstream and affects the brain by cross-cutting the blood-brain barrier [5,6].

When released into the environment, it accumulates in organic-rich sediments where it converts into methylmercury and enters the food

chain [3,7,8]. Methylated mercury and mercury are transformed mutually in nature, and mercury-containing industrial waste is discharged into the water body along with wastewater[9]. Volatile mercury species present in the atmosphere can transport into soil and water by precipitation, then it can convert into methylated mercury by soil bacteria and desulfurization vibrio and other bacteria in the bottom mud of the water bodies [10]. Methylated mercury is converted into Hg^0 by a biochemical pathway. After it is released into the atmosphere from the water body, it is oxidized to Hg^{2+} by H_2O_2 in the atmosphere [11]. Hg^{2+} then returns to a water body with rainwater and is converted into CH_3Hg^+ , and then into $(CH_3)_2Hg$ by anaerobic microorganisms. Therefore, the availability of robust methodology for rapid detection of

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methylated mercury in environmental samples is at the forefront of research.

Recently, the methods for methylmercury detection have improved significantly. The combined use of elemental analysis instruments such as atomic emission spectroscopy (AES) [12], atomic fluorescence spectroscopy (AFS) [13], and inductively coupled plasma-mass spectrometry (ICP-MS)[14] with high-performance liquid chromatography (HPLC) [15] has become increasingly sophisticated in the determination of mercury in environmental samples [16]. However, these methods determine the total concentration of mercury; operations are complex and costly. However, the electrochemical techniques are inexpensive, and they can obtain low detection limits which are becoming increasingly prominent [17]. Besides, the electrochemical methods have the advantage of detecting analytes in situ, and chemical species identification is possible. Xu et al. made AuNPs-RGO modified glassy carbon electrode (GCE) to detect CH₃Hg⁺ in fish. Under optimal conditions, the CH₃Hg⁺ concentration shows a good linear relationship with 3 – 24 ppb CH_3Hg^+ ; the method sensitivity is 0.57 μ A/ppb, and the detection limit is 0.12 ppb [18]. Shi et al. used gold particles-deposited GCE by electrochemical vapor generation (ECVG) technology is used for CH₃Hg⁺ detection [19]. By this method, the detection limit for CH_3Hg^+ in liquids is 4.4 ng/L and the detection limit for CH_3Hg^+ in solids is 0.44 pg/mg. Zhang et al. used fluorescence spectroscopy with an atomic combination of electrolytic vapor generation technology(EVG) for the detection of mercury [20]. Research has shown that on cysteine, CH₃Hg⁺ is converted effectively into mercury vapor. Under the optimal conditions, the detection limit of CH₃Hg⁺ in an aqueous solution by the AFS-EVG method is 0.073 ppb [21].

Graphite carbon nitride (g-C₃N₄) has a unique band structure, excellent stability, and biocompatibility, which can provide a sensitive sensing platform for electrochemical detection of small biomolecules [22]. At present, g-C₃N₄ is widely used as a starting material for the detection of heavy metal ions [23]. This work developed a novel method for the detection of methylmercury in environmental samples using S-doped g-C₃N₄. The forbidden band gap of g-C₃N₄ is modulated with urea and thiourea composite to enhanced charge transfer efficiency and specific surface area, and to inhibit particulate aggregation [24,25]. The heterojunction structure of the composite was regulated by varying urea to thiourea ratio to the desired value. The composite was stripped and then protonated by HCl. During these processes, the bulk UT-gCN changed into porous ultra-thin nanosheets [26], providing more active sites for CH₂Hg⁺ adsorption. Besides, the bandgap of the UT-gCN was adjusted, and the catalysis and ionic conductivity improved [27], which would do good to the transformation of mercury species on the electrochemical sensing interface. Subsequently, the new composite was used to modify the Au electrode surface. The chemically modified Au electrode was used in the development of an analytical method for CH₃Hg⁺ detection by differential pulse voltammetry. All experimental parameters, e.g. deposition potential, accumulation time, etc. were optimized to yield enhanced sensitivity for CH₃Hg⁺ detection. The detection method robustness of was determined by evaluating sensor stability, reproducibility, and materials reactivation.

2. Materials and methods

2.1. Chemical materials

Methylmercury was obtained from Shanghai Aladdin Biochemical Reagent Co. Ltd (PR China). Analytical grade urea, thiourea, and other chemicals were purchased from Shanghai Wokai Reagent Co. Ltd (PR China). All chemicals were used without further purification. 0.1 M sodium acetate buffer solution was prepared by mixing a stock solution of 0.1 M HAc and 0.1 M NaAc. The working solutions of Hg²⁺, CH₃HgCl were prepared by serial dilution of respective stock solutions.

2.2. Apparatus

All electrochemical experiments were carried out on a high-precision electrochemical workstation (CHI660D, China). The three-electrode systems comprised an Au working electrode, a Pt counter electrode, and an Ag/AgCl reference. The X-ray photoelectron spectroscopy (ESCALAB250Xi, Thermo Scientific, USA) method was used to determine elemental oxidation states and surface composition. The morphology and microstructures of the new materials were examined using scanning electron and microscopic transmission methods (SEM, Quantum 200 FEG, FEI, USA). The crystal structure of the material was carried out using an X-ray diffractometer (XRD, D/MAX2500V, Rigaku Co., Japan). UV–visible spectrums of the samples were obtained under diffused reflectance mode within 200–800 nm using a UV–vis spectrometer (CARY5000, Agilent Technologies Inc., USA), and the Fourier transform infrared spectrums (FTIR) in transmission mode were taken using KBr pellets (Nicolet 67, Thermo Nicolet Co., USA).

2.3. Materials preparation

2.3.1. Preparation of U-gCN and T-gCN

The U-gCN or T-gCN was prepared via thermal polymerization by using urea or thiourea as the precursor at 550 °C. In a typical experiment, 16 g of urea (thiourea) pellets were ground into powder in an agate mortar, then put into a 30 ml alumina crucible with a loading density of 0.53 g/ml. After spreading uniformly, the alumina crucibles were sealed and placed in a muffle furnace at 550 °C for 2 h under the condition of air (heating rate 10 °C/ min). Afterward, the samples were cooled to room temperature under ambient conditions with a synthetic yield of about 3%. The samples were then powdered and designated as U-gCN (urea-g-C₃N₄) and T-gCN (thiourea-g-C₃N₄), separately.

2.3.2. Preparation of UT-gCN homogeneous heterojunction

UT-gCN homogeneous heterojunction materials were prepared as below. A known amount of urea (12, 16, 18, and 20 g) and thiourea (12, 8, 6, and 5 g) were dissolved in 60 ml distilled water and stirred for 1 h at 60 °C in a water bath. Then the mixed solution of urea and thiourea was dried in an oven at 60 °C for 12 h. The obtained solid composites were ground into powder in an agate mortar, transferred into two 30 ml alumina crucibles, and heated in a muffle furnace at 550 °C for 2 h under the condition of air [28]. Then, the samples were cooled to room temperature with a yield lower than 5%. Following this procedure, the urea and thiourea composites at 1:1, 2:1, 3:1 and 4:1 wt ratios were prepared and hereafter designated as UT-gCN (1: 1), UT-gCN (2: 1), UT-gCN (3: 1), and UT-gCN (4: 1).

2.4. Electrochemical detection

All electrochemical experiments were carried out in 10 ml of 0.1 M HAc-NaAc buffers. The gold electrode was first polished with 1 μ m, 0.3 μ m, and 0.05 μ m Al₂O₃ powder, and then washed with ethanol and deionized water in order. 2 mg of nano-materials were put into a test tube, and 4 ml of deionized water was added to prepare 0.5 g/L suspensions of U-gCN, T-gCN, UT-gCN (1: 1), UT-gCN (2: 1), UT-gCN (3: 1) and UT-gCN (4: 1). 5 μ L solution droplets were deposited on the Au surface using a pipette gun and dried at room temperature.

The material was stripped and protonated by HCl. 2 g of the composite material was put into 20 ml deionized water, stirred, and ultrasonically treated for 16 h. The ultrasonic frequency was 90 Hz, and the water was changed every 20 min to keep the water temperature below 25 °C. Then centrifuge at 10,000 rpm for 5 min, then put the solid in an oven and dry at 60 °C for 12 h to obtain the stripped composite material. The stripped material was put into HCl (37%) and stirred at room temperature for 3 h to obtain opaque dispersion. With the progress of protonation, yellow UT-gCN changed into white UT-gCN. Then washed with deionized water for three times, and then dried in an oven at 60 °C for 12 h to obtain the composite material after HCl protonation.

Electrochemical determination of CH_3Hg^+ , Hg^{2+} , and Sn^{2+} was carried out by differential pulse stripping voltammetry (DPV). A -0.80 V potential for 800 s was applied during the preconcentration step. After 20 s of equilibration, the respective voltammogram was recorded. Following experimental conditions were used; starting potential 0 V, end potential 1 V, transition potential 5 mV, amplitude 50 mV, pulse width 50 ms, sampling width 40 ms, pulse duration 100 ms. Before starting a new experiment, the electrode surface was cleaned at 0.80 V for 150 s. Before commencement of an experiment, both AU and modified Au electrodes were activated by performing a CV in 0.5 M H₂SO₄ (potential range: 0.2–1.6 V; scan rate: 100 millivolt seconds [29]) to remove oxides on the electrode surface (shown in Fig. S1).

2.5. Theoretical calculations

The density functional theory (DFT) calculations were carried out using B3LYP functional and 6–31 g (d, p) basis set (Gaussian 16, Revision C.01, Gaussian Inc., Wallingford, CT, USA).

3. Results and discussion

3.1. Characterization of the U-gCN/T-gCN homogeneous heterojunction

The morphology and chemical composition of U-gCN, T-gCN, and UT-gCN (3:1) isotype heterojunctions were examined by SEM/EDX and TEM microscopy (Fig. 1a–f). As shown in Fig. 1(a)–(c), all samples exhibit porous structures. In all cases, the particles are discrete, and within the substrate, the pore channels & layered microstructures are well discerned. The unique microstructures present on T-gCN and U-gCN inhibit the recombination of photo-excited charge carriers [30]. As shown in Fig. 1(d) and (e), the T-gCN composes dense layers (Fig. 1e) whereas U-gCN (Fig. 1d) contains thin nanosheets. However, UT-gCN (3:1) shows a different morphology (Fig. 1f), and the EDX data (Fig. S2) ensures uniform spatial distribution of both host (C and N) and dopants (S and O) elements [31,32].

The XPS survey spectrums (Fig. 2a) show that C, N, and O are present in all the samples (T-gCN, U-gCN, UT-gCN), whereas only in T-gCN and UT-gCN, S is present in small proportions. The XPS analysis of the UTgCN (3:1) homotoped heterojunction is shown in Fig. 2(b)–(e). The C1s spectrum of UT-gCN (3:1) (Fig. 2b) shows three characteristic peaks at 284.8 eV, 286.3 eV, and 288.1 eV. The features shown in the peak at 284.8 eV are due to the presence of amorphous carbon, the peak at 286.3 eV has ascribed the presence of C in C-NH₂ species [33], and the characteristic peak at 288.1 eV corresponds to C tri-nitrogen group C-(N)₃ present in the g-C₃N₄ lattice [34]. The N1s peak (Fig. 2.c) at 398.6 eV is assigned to the triazine ring (C = N-C). The weak peak at 400.6 eV is ascribed to an amino group (C-N-H) associated with hydrogen and tertiary nitrogen N-(C)₃ group. The peak at 404.3 eV is attributed to the charging effect in heterocycles [35].

Fig. 2(d) shows the characteristic O 1s peak at 532 eV, which corresponds to the H₂O adsorbed on the catalyst surface. Fig. 2(e) depicts the existence of S2p in UT-gCN (3:1). The peak at 163.9 eV is ascribed to S $2p_{3/2}$, which corresponds to N–S bonds result by the replacement of lattice C by S within the C–N bonding framework [36]. The peak at 168.5 eV is due to the presence of S species. Therefore, the results of the energy spectrum analysis show that the doped S atoms exist as N-S bonds through the lattice substitution of C atoms [14]. Fig. 2(f) shows that atomic ratios of UT-gCN (3:1) and a small amount of S is doped in the composite material, accounting for about 1.24%. Fig. S3 shows the constructed S-doped g-C₃N₄ model. Without doping, the heptazine rings are connected by a C–N bond to form a stable repeating structure. When S is doped in this way, the structure of the heptazine ring is deformed, but the whole structure remains in a ring state. The bond lengths of the three S-N bonds are 1.646, 1.791, and 1.575 Å.

Fig. 3(a) shows the X-ray diffractograms of co-condensed products, U-gCN, T-gCN, and UT-gCN. In the XRD pattern of g-C₃N₄, two primary diffraction peaks were observed around 12.6° and 27.7°. The diffraction peak at 12.6° is due to the planar packaging structure of the triazine rings that correspond to the crystal plane of g-C₃N₄. The intense diffraction peak around 27.7° corresponds to the interlayer stacking of aromatic rings that fit the crystal plane of g-C₃N₄. The inset in Fig. 3(a) shows that the diffraction angle (27.7°) of U-gCN is larger than T-gCN (27.4°), indicating that U-gCN (0.323 nm) has shorter interplanar spacing. The extra oxygen in urea can promote the condensation process of urea and make the crystal structure of g-C₃N₄ more stable [37]. At the same time, the diffraction angle (27.5°) of the UT-gCN peak is situated between the U-gCN and T-gCN, which confirms the shape of the U-gCN / T-gCN structures.

Fig. 3(b) displays FT-IR spectra of U-gCN, T-gCN, and UT- gCN. The incisive IR peak at 808 cm⁻¹ represents the breathing oscillations of the tri-s-triazine structure in g-C₃N₄. The presence of spectral signals



Fig. 1. SEM images of (a)U-gCN, (b)T-gCN, (c)UT-gCN(3:1) and TEM images of (d)U-gCN, (e)T-gCN, (f)UT-gCN(3:1).



Fig. 2. XPS spectra of (a)U-gCN,T-gCN, and UT-gCN survey, (b-e) C1s, N1s,O1s and S2p of UT-gCN (3:1). composite and (f) Atomic composition of UT-gCN (3:1).



Fig. 3.(. a) XRD (b)FT-IR spectra of U-gCN, T-gCN and UT- gCN.

corresponds to C–S, and C–O bonds provide indirect evidence for the successful synthesis of S-doped g- C_3N_4 composites. The IR peaks present in the 1200–1600 cm⁻¹ range are due to tensile vibrations of the C-N and C[–]N heterocyclic units of g- C_3N_4 [38]. The physical adsorption of CO₂ may cause the absorption curve at 1700 cm⁻¹ by the atmosphere, and hydroxyl and amino groups exist on the surface, and the apparent characteristic peak is near 3200 cm⁻¹ [14].

3.2. Electrochemical characterization

During the deposition process, when CH₃Hg⁺ is reduced to elemental mercury on the Au electrode surface, a peeling process may occur. Fig. 4.

shows the voltammogram obtained using a chemically modified Au electrode with U-gCN, T-gCN, or UT-gCN. The stripping currents generated by CH_3Hg^+ reduction on bare Au, U-gCN, and T-gCN modified electrodes are almost similar. However, Au modified electrode with UT-gCN shows an enhanced peak current upon CH_3Hg^+ reduction. Therefore, to determine optimal urea to thiourea ratio, composites UT-gCN (1:1), UT-gCN (2:1), UT-gCN (3:1), and UT-gCN (4:1) were used to modify the Au electrode. The highest peak current for CH_3Hg^+ is received with Au modified electrode with UT-gCN (3:1). Therefore, we used UT-gCN (3:1) modified Au electrode in the sensor development for CH_3Hg^+ detection.



Fig. 4. (a) The DPV responses for 15 ppb CH_3Hg^+ in HAc-NaAc (pH=5.0) on the bare gold electrode and different modified gold electrodes; (b) Comparison of the DPV responses for 15 ppb CH_3Hg^+ in HAc-NaAc (pH=5.0) on the modified gold electrodes with different proportions of U-gCN/T-gCN homogeneous heterojunction.

3.3. Optimization of experimental condition

To achieve the best performance for detection of CH_3Hg^+ by UT-gCN (3:1)modified electrode, following experimental conditions, such as electrolyte type, pH, preconcentration time and potential, stripping time, and potential, were optimized using 15 ppb CH_3Hg^+ . First, as shown in Fig. 5(a), we measured the peak current of 15 ppb CH_3Hg^+

reduction in three buffers: HAc-NaAc, citric acid, and PBS. The highest peak current for the CH₃Hg⁺ reduction is observed in the buffer system HAc-NaAc at pH 5.00. The position of the peak position for CH₃Hg⁺ reduction was also examined as a function of pH. When the solution pH is increased from 4 to 6, the CH₃Hg⁺ peak shifts towards a positive direction. The CH₃Hg⁺ reduction process believes in occurring two steps, e.g. CH₃Hg⁺ \rightarrow CH₃Hg \rightarrow Hg⁰; Hg⁰ is amalgamated with Au on the



Fig. 5. The influences of (a) Electrolyte, (b) pH, (c) preconcentration time, and (d) preconcentration potential on the peak current of 15 ppb CH₃Hg⁺ for UT-gCN(3:1) modified Au electrode.

electrode surface. The parameters used during preconcentration and deposition steps exert markedly on the magnitude of stripping current of the analyte. Therefore, we optimized experimental parameters such as time and applied potential used during preconcentration. As the preconcentration time has increased from 400 s to 1000 s at -0.80 V applied potential in the HAc-NaAc buffer, the peak current shows a gradual increase. However, after 800 s, there is a slight decline in the peak current due to electrode surface saturation by the analyte (Fig. 5c). Consequently, an optimal preconcentration time is chosen as 800 s. Finally, the variation of the analyte signal with the applied potential is examined in 15 ppb CH₃Hg⁺ of pH 5.00 HAc-NaAc at 800 s deposition time. The applied potential shows an optimal value at -0.80 V (Fig. 5d), and therefore which was taken in subsequent studies.

The scanning rate has a great influence on electrochemical sensing performance. The LSV results of 30 ppb CH_3Hg^+ in the buffer solution at different scanning rates (10 mv, 25 mv, 50 mv, 100 mv, 150 mv, 250 mv) were also studied (Fig. S6). It can be found that the peak current increases with the increase of scan rate, and the peak current has a linear relationship with the scanrate^{1/2}, indicating that the electrode surface is mainly controlled by diffusion. According to Laviron's theory [39]:

$$E_p = \frac{RT}{\alpha nF} \ln \frac{KsRT}{\alpha nF} - \frac{RT}{\alpha nF} \ln v$$

The electron transfer number can be calculated from the linear relationship between Ep and lnv: $E_p=0.01 lnv+0.376$. According to Laviron's half-peak width method, assuming $\alpha=0.5$, the electron transfer rate constant $K_s=73.8\ s^{-1}$, the electron transfer coefficient $\alpha=0.5$, and the electron transfer number n=2.76 can be obtained.

3.4. Analytical performance of chemically modified Au electrode with U-gCN/T-gCN

Under optimal experimental conditions, e.g. applied potential – 0.80 V, pH 5.00 NaAC/HAc, 800 s deposition time, the chemically modified Au electrode with UT-gCN (3:1) was used for the development of CH₃Hg⁺ detection method within 0–25 ppb CH₃Hg⁺ concentration window. Bare Au electrode was used as a control. As shown in Fig. 6, for both electrodes the variation of peak current with the CH₃Hg⁺ concentration shows an excellent linear relationship and the corresponding linear regression model for bare Au electrode (Fig. 6a), I_p (μ A) = 0.230 C (ppb) –0.054 R² = 0.998, n = 9. When compared to the Au electrode, the sensitivity of bulk UT-gCN modified Au electrode for CH₃Hg⁺ detection has shown about a two-fold increase as I_p (μ A) = 0.402 C

(ppb) $-0.152 \text{ R}^2 = 0.978$, n = 9 (Fig. S4a). As shown in Fig. S4b, the linear relationship (Ip (μ A) = 0.447 C(ppb) + 1.467 n = 9, R² = 0.994) re-established after stripping treatment shows better sensitivity than the data shown in Fig. S4(a).

The stripped material is protonated by HCl treatment to achieve better sensitivity. The protonated UT-gCN not only shows enhanced dispersibility and surface area but also adjusts the bandgap and ionic conductivity of the material [27]. As shown in Fig. 6(b), a good linear relationship between CH₃Hg⁺ concentration from 0 to 25 is observed, Ip (μ A) = 0.52 C (ppb)+ 0.915 (n = 9, R² =0.991), with sensitivity reaching 0.52 μ A/ppb, detection limit is 0.175 ppb. Table S1 lists some previously improved materials for the detection of CH₃Hg⁺ by different electrochemical methods. It can be seen that UT-gCN modified gold electrode has higher sensitivity and lower detection limit.

3.5. Bandgap modulation mechanism

The differential pulse voltammetry (DPV) was used to study the sensing capability of the modified electrode for CH_3Hg^+ . The electrochemical reduction mechanism of CH_3Hg^+ on the working electrode is described as follows [40]:

$$CH_{3}Hg^{+} + e^{-} \Leftrightarrow CH_{3}Hg^{-}$$
$$2CH_{3}Hg^{-} \Leftrightarrow (CH_{3}Hg)_{2}$$
$$(CH_{3}Hg)_{2} \Leftrightarrow (CH_{3})_{2}Hg + Hg^{0}$$
$$2CH_{3}Hg^{-} + H^{+} + e^{-} \Rightarrow CH_{4} + Hg^{0}$$

The reduction potential of methylmercury CH_3Hg^+ on the gold electrode supported by UT-gCN (3:1) is 0.63 V, which is lower than the reduction potential (0.67 V) on the bare gold electrode, which proves that the S-doped g-C₃N₄ load is beneficial to improve the catalytic activity of the substrate [21]. The catalytic mechanism of the nanocomposite can be obtained by DFT calculations [41,42], the initial charge of methylmercury is + 1.0 (Fig. 7a), under the influence of S-doped g-C₃N₄, the Mullikan charge of methylmercury ion decreases, and the methylmercury charge is + 0.985. The electron transfer between methylmercury and g-C₃N₄ is spontaneous[43].

The optimized structure of the catalyst is shown in Fig. 7(b). The variation of HOMO-LUMO energy gap values as a function S-doped g- C_3N_4 is given based on the optimized catalyst structure, the HOMO-LUMO energy gap was calculated. It can be seen that the energy gap is



Fig. 6. DPSV responses of increasing CH_3Hg^+ concentration and the calibration curve of the peak current with CH_3Hg^+ concentration on (a) the bare gold electrodes and (b) the HCl-protonated UT-gCN(3:1) modified gold electrode.



Fig. 7. (a) Optimized geometries of UT-gCN and CH₃Hg⁺ with Mulliken, (b)HOMO, and (c)LUMO of UT-gCN(3:1).

the smallest when S is doped. Generally speaking, the smaller the HOMO-LUMO gap, the better the conductivity. Due to the increased specific surface area of S-doped g- C_3N_4 and very good electron transport properties, the UT-gCN(3:1) modified Au electrode should have a larger electroactive area when compared to AuNPs modified electrodes. The deposited CH_3Hg^+ on Au surface can be reduced efficiently on UT-gCN (3:1) modified electrode.

To verify the bandgap modulation mechanism, the optical properties of U-gCN, T-gCN, and UT-gCN(3:1) samples before and after adsorption of methylmercury were characterized by UV–vis diffuse reflectance spectroscopy (DRS). As shown in Fig. 8(a), compared with the band edge of U-gCN, UT-gCN(3:1) has a redshift, it may be that the doping of S leads to capture more light energy to generate more photoinduced electron-hole charges [36]. The incorporation of the S atom into the $g-C_3N_4$ matrix has a significant impact on the closely related band structure and electronic properties, which is related to the light absorption of semiconductors. As shown in Table 1, according to Kubelka-Munk formula [44], the bandgap widths of U-gCN, T-gCN, and UT-gCN (3:1) adsorbed with methylmercury are calculated to be 2.71 eV, 2.62 eV, and 2.45 eV, respectively [45], and the band gaps of U-gCN, T-gCN and UT-gCN(3:1) before and after adsorption with CH₃Hg⁺ are narrower than those before adsorption, and the band gaps



Fig. 8. (a)UV-vis DRS, (b)Plots of $(\alpha h\nu)^{1/2}$ vs photon energy before adsorption and (c)UV-vis DRS, (d)Plots of $(\alpha h\nu)^{1/2}$ vs photon energy after adsorption of U-gCN, T-gCN and UT-gCN(3:1).

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Table 1

Band gap of U-gCN, T-gCN and UT-gCN(3:1).

Samples	Before adsorption/eV	After adsorption/eV
U-gCN	2.82	2.71
T-gCN	2.67	2.62
UT-gCN(3:1)	2.73	2.45

of UT-gCN(3:1) are narrower than those of U-gCN and T-gCN before and after adsorption. Moreover, the band gaps of U-gCN and T-gCN changed a little before and after adsorption with methylmercury. Adsorption of S-doped $g-C_3N_4$ and CH_3Hg^+ can better adjust the bandgap and improve the conductivity. In Fig. 7(d), it can be concluded that the bandgap of UT-gCN(3:1) is the narrowest, which is consistent with the results calculated by density functional theory (DFT), indicating that S doping can indeed adjust the bandgap and improve the conductivity.

3.6. Interference study

It is necessary to eliminate possible interferences to determine CH₃Hg⁺ accurately. According to the electrochemical reduction mechanism of CH_3Hg^+ , the inorganic Hg^{2+} has a significant influence on the determination of CH₃Hg⁺ due to overlapping stripping currents. We adopted two methods to eliminate the effects of Hg²⁺ on CH₃Hg⁺ detection. One approach is blocking Hg²⁺ by adding DTPA as a complexant [8]. The mercury-DTPA complex is not reduced on the Au electrode under the potential used for methylmercury detection. The second method is the addition of ${\rm SnCl}_2$ to reduce ${\rm Hg}^{2+}$ in the presence of CH_3Hg^+ selectively. As shown earlier, $SnCl_2$ can only reduce Hg^{2+} and does not affect CH₃Hg⁺. As shown in Fig. 9, both methods can eliminate inorganic Hg²⁺ effectively. Besides, the chemical interferences due to metal ions of Cu²⁺, Cd²⁺, Pb²⁺, Bi^{3+,} and As³⁺ on CH₃Hg⁺ detection are also examined (Fig. 10). Usually, changes in peak currents within the 5% range are acceptable [46]. It can be found that the addition of metal ions in multiple proportions does not change the analyte signal of CH₃Hg⁺ more than 5%. Therefore, the metal ions common in natural water samples do not interfere significantly with the signal of CH₃Hg⁺.

3.7. Evaluation of reproducibility and stability

The stability and reproducibility of the UT-gCN (3:1) modified Au sensor for CH_3Hg^+ detection was also examined. Fig. 11(a) shows the DPV responses of 10 ppb CH_3Hg^+ sample measured using five UT-gCN (3:1) modified Au electrodes. The relative standard deviation of the five-electrode experiments is 2.31% indicating good signal

reproducibility. Fig. 11(b) shows the DPV response of UT-gCN(3:1) modified Au electrode in 10 ppb CH_3Hg^+ solution measured in 5 consecutive days. The relative standard deviation is 3.61%. The Au electrodes modified with UT-gCN(3:1) are robust to multiple productions and repeated usage.

3.8. Natural water sample analysis

To assess possible interference from the matrix elements in natural water, we collected two samples in Hu Bin pond (Hefei University of Technology, China). We took one water sample at the water's edge near the teaching area and the other one at the water's edge near the living area, and the water quality data are shown in Table S2. DPV method analyzed the methyl mercury in water samples with UT-gCN(3:1) modified U electrode, and the data are shown in Table 2. Samples were mixed in 0.1 M HAc-NaAc buffer (pH5) at a ratio of 1:9 before electrochemical detection. In any sample, a signal corresponds to CH₃Hg⁺ cannot be obtained, which indicates no pollution with CH₃Hg⁺ or Hg^{2+} . In a subsequent experiment, CH_3Hg^+ was added into the diluted lake water samples at 5, 10, and 15 ppb. The CH₃Hg⁺ spiked recoveries were measured, as shown in Table 2. In both samples, the CH₃Hg⁺ spiked recoveries and relative standard deviations are within 91.2-101.2% and 2.2%-3.8%, respectively (Table 2). The data show the new method of CH₃Hg⁺ detection is not affected by the matrix constituents in natural water samples. The new CH₃Hg⁺ method can efficiently be used in methylmercury monitoring of environmental samples [47].

4. Conclusions

We fabricated S-doped g-C₃N₄ with homotypic heterojunction using urea and thiourea at a 3:1 ratio to modify the Au electrode for detection of methylated mercury. The new electrochemical method of CH₃Hg⁺ detection uses differential pulse voltammetry. It is robust and possesses excellent reproducibility. The chemical interference from Cu²⁺, Cd²⁺, Pb²⁺, Bi^{3+,} and As³⁺ for methylated mercury detection is negligible in our method. The spiked recoveries of methylated mercury in natural water samples are between 91.2% and 101.2% with 2.2%–3.8% relative standard deviation (RSD). The newly developed UT-gCN (3:1) sensor has the potential application in the determination of methylated mercury in environmental samples.

CRediT authorship contribution statement

Xing Chen: Conceptualization, Supervision, Writing - review & editing, Funding acquisition. Xiaotong Sun: Methodology, Formal



Fig. 9. (a) Voltammograms of 15 ppbCH₃Hg⁺, 15 ppb CH₃Hg⁺ with 15 ppb Hg²⁺, and 15 ppb CH₃Hg⁺ with 15 ppb Hg²⁺ and 0.1 M DTPA (b) Voltammograms of 15 ppb CH₃Hg⁺, 15 ppb CH₃Hg⁺ with 15 ppb Hg²⁺, and 15 ppb CH₃Hg⁺ with 15 ppb Hg²⁺ and 0.1 M SnCl₂ on the UT-gCN(3:1) modified Au electrode.

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Fig. 10. DPV responses toward 15 ppb CH_3Hg^+ on the UT-gCN(3:1) modified Au electrode after adding different concentrations of (a) Cu^{2+} (b) Cd^{2+} (c) Pb^{2+} (d) Bi^{3+} and (e) As^{3+} .



Fig. 11. (a) DPV responses of five UT-gCN(3:1) modified gold electrodes toward 10ppb CH_3Hg^+ . (b) DPV responses of UT-gCN(3:1) modified gold electrodes toward 10ppb CH_3Hg^+ in the successive five days.

Table 2

Determination of spiked CH_3Hg^+ in real samples (number of samples assayed =3).

Samples	CH ₃ Hg ⁺ added (ppb)	CH ₃ Hg ⁺ found (ppb)	RSD (%)	Recovery (%)
Sample 1	5	5.05	2.5	101
	10	9.12	3.8	91.2
	15	14.86	2.2	99.1
Sample 2	5	5.06	2.6	101.2
	10	10.02	3.5	100.2
	15	14.82	2.4	98.8

analysis, Investigation, Writing - original draft. **Min-Shu Cui:** Formal analysis, DFT calculation. **Yao Liu:** Methodology, Investigation, Formal analysis. **Kangping Cui:** Formal analysis. **Rohan Weerasooriya:** Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2021.105510.

References

- O. Abollino, A. Giacomino, M. Malandrino, S. Marro, E. Mentasti, Voltammetric determination of methylmercury and inorganic mercury with an homemade gold nanoparticle electrode, J. Appl. Electrochem. 39 (11) (2009) 2209–2216.
- [2] K.N. Bridges, C.G. Furin, R.F. Gerlach, Subsistence fish consumption in rural Alaska: using regional monitoring data to evaluate risk and bioavailability of dietary methylmercury, Sci. Total Environ. 736 (2020), 139676.
- [3] C. Baird, M. Cann, Environmental Chemistry, 5th edition. 2012.
- [4] H. Xu, J. Wu, W. Luo, Q. Li, W. Zhang, J. Yang, Dendritic cell-inspired designed architectures toward highly efficient electrocatalysts for nitrate reduction reaction, Small 16 (30) (2020), 2001775.
- [5] P. Grandjean, Methylmercury toxicity and functional programming, Reprod. Toxicol. 23 (3) (2007) 414–420.
- [6] N. Shirai, T. Suzuki, M. Yamashita, Y. Yokoyama, Health risk of methylmercury intake and health benefit of fish consumption, Nippon Suisan Gakkaishi 79 (5) (2013) 890–905.
- [7] C.R. Hammerschmidt, M.S. Gustin, J. Bennett, Mercury biogeochemical cycling and processes: implications for human and ecosystem health, Sci. Total Environ. 496 (2014) 635, 635-635.
- [8] M. Korolczuk, I. Rutyna, New methodology for anodic stripping voltammetric determination of methylmercury, Electrochem. Commun. 10 (7) (2008) 1024–1026.
- [9] M.C. Bisinoti, W.F. Jardim, Behavior of methylmercury in the environment, Quim. Nova 27 (4) (2004) 593–600.
- [10] E.G. Brunke, C. Walters, T. Mkololo, L. Martin, C. Labuschagne, B. Silwana, F. Slemr, A. Weigelt, R. Ebinghaus, V. Somerset, Mercury in the atmosphere and in rainwater at Cape Point, South Africa, Atmos. Environ. 125 (2016) 24–32.
- [11] X. Lu, W. Gu, L. Zhao, M. Farhan Ul Haque, A.A. DiSpirito, J.D. Semrau, B. Gu, Methylmercury uptake and degradation by methanotrophs, Sci. Adv. 3 (2017), 1700041.
- [12] J. Mo, Q. Li, X. Guo, G. Zhang, Z. Wang, Flow injection photochemical vapor generation coupled with miniaturized solution-cathode glow discharge atomic emission spectrometry for determination and speciation analysis of mercury, Anal. Chem. 89 (19) (2017) 10353–10360.
- [13] J. Gomez-Ariza, F. Lorenzo, T. Garcia-Barrera, Comparative study of atomic fluorescence spectroscopy and inductively coupled plasma mass spectrometry for mercury and arsenic multispeciation, Anal. Bioanal. Chem. 382 (2) (2005) 485–492.
- [14] T. Luo, Y. Wang, M. Li, W. Zhang, H. Chen, Z. Hu, Determination of major and trace elements in alloy steels by nanosecond and femtosecond laser ablation ICP-MS with non-matrix-matched calibration, At. Spectrosc. 41 (1) (2020) 11–19.
- [15] L. Pereira, T.A. Maranhão, V.L.A. Frescura, D.L.G. Borges, Multivariate assessment of extraction conditions for the fractionation analysis of mercury in oily sludge samples using cold vapor atomic fluorescence spectrometry, J. Anal. At. Spectrom. 34 (9) (2019) 1932–1941.
- [16] S.L.C. Ferreira, V.A. Lemos, L.O.B. Silva, A.F.S. Queiroz, A.S. Souza, E.G.P. da Silva, W.N.L. dos Santos, C.F. das Virgens, Analytical strategies of sample preparation for the determination of mercury in food matrices - a review, Microchem. J. 121 (2015) 227–236.
- [17] Y.Y. Lin, Y. Peng, J.W. Di, Electrochemical detection of Hg(II) ions based on nanoporous gold nanoparticles modified indium tin oxide electrode, Sens. Actuators B-Chem. 220 (2015) 1086–1090.
- [18] Y. Xu, W. Zhang, J. Shi, X. Zou, Y. Li, T. Haroon Elrasheid, X. Huang, Z. Li, X. Zhai, X. Hu, Electrodeposition of gold nanoparticles and reduced graphene oxide on an electrode for fast and sensitive determination of methylmercury in fish, Food Chem. 237 (2017) 423–430.
- [19] W.C. Zu, Z.H. Wang, Ultra-trace determination of methylmercuy in seafood by atomic fluorescence spectrometry coupled with electrochemical cold vapor generation, J. Hazard. Mater. 304 (2016) 467–473.
- [20] M.T. Shi, X.A. Yang, L.M. Qin, W.B. Zhang, Highly efficient electrocatalytic vapor generation of methylmercury based on the gold particles deposited glassy carbon electrode: a typical application for sensitive mercury speciation analysis in fish samples, Anal. Chim. Acta 1025 (2018) 58–68.
- [21] W.B. Zhang, X.A. Yang, Y.P. Dong, J.J. Xue, Speciation of inorganic- and methylmercury in biological matrixes by electrochemical vapor generation from an L-Cysteine modified graphite electrode with atomic fluorescence spectrometry detection, Anal. Chem. 84 (21) (2012) 9199–9207.
- [22] A. Thomas, A. Fischer, F. Goettmann, M. Antonietti, J.O. Müller, R. Schlögl, J. M. Carlsson, Graphitic carbon nitride materials: variation of structure and

morphology and their use as metal-free catalysts, J. Mater. Chem. 18 (41) (2008) 4893-4908.

- [23] M. Wang, R. Fu, C. Jin, Z. Li, J. Sun, P. Yu, M. You, The facile fabrication of g-C3N4 ultrathin nanosheets with higher specific surface areas for highly sensitive detection of trace cadmium, Measurement 140 (2019) 548–556.
- [24] H. Qin, W. Lv, J. Bai, Y. Zhou, Y. Wen, Q. He, J. Tang, L. Wang, Q. Zhou, Sulfurdoped porous graphitic carbon nitride heterojunction hybrids for enhanced photocatalytic H₂ evolution, J. Mater. Sci. 54 (6) (2019) 4811–4820.
- [25] Q. Fan, J. Liu, Y. Yu, S. Zuo, B. Li, A simple fabrication for sulfur-doped graphitic carbon nitride porous rods with excellent photocatalytic activity degrading RhB dye, Appl. Surf. Sci. 391 (2017) 360–368.
- [26] Y. Liu, G.L. Wen, X. Chen, R. Weerasooriya, Z.Y. Hong, L.C. Wang, Z.J. Huang, Y. C. Wu, Construction of electrochemical sensing interface towards Cd(II) based on activated g-C₃N₄ nanosheets: considering the effects of exfoliation and protonation treatment, Anal. Bioanal. Chem. 412 (2) (2020) 343–353.
- [27] X. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J.M. Carlsson, K. Domen, M. Antonietti, A metal-free polymeric photocatalyst for hydrogen production from water under visible light, Nat. Mater. 8 (1) (2009) 76–80.
- [28] Y. Wang, M. Qiao, J. Ly, G. Xu, Z. Zheng, X. Zhang, Y. Wu, g-C₃N₄/g-C₃N₄ isotype heterojunction as an efficient platform for direct photodegradation of antibiotic, Fuller. Nanotub. Carbon Nanostruct. 26 (4) (2018) 210–217.
- [29] M. Avramov-Ivic, S. Petrovic, P. Zivkovic, D. Mijin, K. Drljevic, A study of the catalytic role of a gold electrode in the electrochemical activation of four macrolide antibiotics in sodium bicarbonate solution, Chem. Ind. Chem. Eng. Q. 16 (2) (2010) 111–116.
- [30] Y. Wang, C. Jiang, Y. Le, B. Cheng, J. Yu, Hierarchical honeycomb-like Pt/NiFe-LDH/rGO nanocomposite with excellent formaldehyde decomposition activity, Chem. Eng. J. 365 (2019) 378–388.
- [31] R. Zhu, Y. Zhang, X. Fang, X. Cui, J. Wang, C. Yue, W. Fang, H. Zhao, Z. Li, In situ sulfur-doped graphitic carbon nitride nanosheets with enhanced electrogenerated chemiluminescence used for sensitive and selective sensing of l-cysteine, J. Mater. Chem. B 7 (14) (2019) 2320–2329.
- [32] M. Amiri, H. Salehniya, A. Habibi-Yangjeh, Graphitic carbon nitride/chitosan composite for adsorption and electrochemical determination of mercury in real samples, Ind. Eng. Chem. Res. 55 (29) (2016) 8114–8122.
- [33] T. Liu, J. Li, Z. Khai Lim, H. Chen, S. Hu, Z. Yuan, J. Guo, Simultaneous removal of dissolved methane and nitrogen from synthetic mainstream anaerobic effluent, Environ. Sci. Technol. 54 (12) (2020) 7629–7638.
- [34] F. Dong, Z. Zhao, T. Xiong, Z. Ni, W. Zhang, Y. Sun, W.K. Ho, In situ construction of g-C₃N₄/g-C₃N₄ metal-free heterojunction for enhanced visible-light photocatalysis, ACS Appl. Mater. Interfaces 5 (21) (2013) 11392–11401.
- [35] C. Bai, J. Bi, J. Wu, Y. Han, X. Zhang, Enhanced photocatalytic hydrogen evolution over a heterojunction composed of silver cyanamide and graphitic carbon nitride, New J. Chem. 42 (19) (2018) 16005–16012.
- [36] L. Jiang, X. Yuan, G. Zeng, X. Chen, Z. Wu, J. Liang, J. Zhang, H. Wang, H. Wang, Phosphorus- and sulfur-codoped g-C₃N₄: facile preparation, mechanism insight, and application as efficient photocatalyst for tetracycline and methyl orange degradation under visible light irradiation, ACS Sustain. Chem. Eng. 5 (7) (2017) 5831–5841.
- [37] H. Wang, Q. Lu, M. Li, H. Li, Y. Liu, H. Li, Y. Zhang, S. Yao, Electrochemically prepared oxygen and sulfur co-doped graphitic carbon nitride quantum dots for fluorescence determination of copper and silver ions and biothiols, Anal. Chim. Acta 1027 (2018) 121–129.
- [38] A. Mohammad, M.E. Khan, M.H. Cho, Sulfur-doped-graphitic-carbon nitride (S-g-C₃N₄) for low cost electrochemical sensing of hydrazine, J. Alloy. Compd. 816 (2020), 152522.
- [39] E. Laviron, L. Roullier, General expression of the linear potential sweep voltammogram for a surface redox reaction with interactions between the adsorbed molecules: applications to modified electrodes, J. Electroanal. Chem. Interfacial Electrochem. 115 (1) (1980) 65–74.
- [40] H. Lin, J. Xie, Z. Zhang, S. Wang, D. Chen, Perovskite nanoparticles@N-doped carbon nanofibers as robust and efficient oxygen electrocatalysts for Zn-air batteries, J. Colloid Interface Sci. 581 (2021) 374–384.
- [41] L.H. Kang, M.Y. Zhu, Y. Zhao, A DFT study of acetylene hydrogenation catalyzed by S-doped Pd-1/g-C₃N₄, Catalysts 9 (11) (2019) 887.
- [42] G. Giovannetti, et al., Substrate-induced band gap in graphene on hexagonal boron nitride: Ab initio density functional calculations, Phys. Rev. B 76 (7) (2007).
- [43] X. Zhang, Z. Chen, Y. Ma, N. Zhang, D. Wei, H. Zhang, H. Zhang, Response of partial nitrification sludge to the single and combined stress of CuO nanoparticles and sulfamethoxazole antibiotic on microbial activity, community and resistance genes, Sci. Total Environ. 712 (2020), 135759.
- [44] J.R.A. Collado, Calculation of the atomic spin densities and energy band gaps of carbon high-spin aromatic (pi) large macromolecular systems, J. Chem. Phys. 129 (15) (2008).
- [45] F. Lyu, Y. Sun, Q. Yang, B. Tang, M. Li, Z. Li, M. Sun, P. Gao, L.H. Ye, Q. Chen, Thickness-dependent band gap of α-In₂Se₃: from electron energy loss spectroscopy to density functional theory calculations, Nanotechnology 31 (31) (2020), 315711.
- [46] H. Devnani, D.S. Rajawat, S.P. Satsangee, Black rice modified carbon paste electrode for the voltammetric determination of Pb(II), Cd(II), Cu(II) and Zn(II), Proc. Natl. Acad. Sci. India Sect. A-Phys. Sci. 84 (3) (2014) 361–370.
- [47] A. Mardegan, P. Scopece, F. Lamberti, M. Meneghetti, L.M. Moretto, P. Ugo, Electroanalysis of trace inorganic arsenic with gold nanoelectrode ensembles, Electroanalysis 24 (4) (2012) 798–806.