



Article

Co-Deposition of Bimetallic Au-Pt with L-Cysteine on Electrodes and Removal of Copper by Iron Powder for Trace Aqueous Arsenic Detection

Wei-Zhi Zhang ¹, Kan Wang ², Ning Bao ³ and Shou-Nian Ding ^{1,*}

¹ School of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189, China; zhangweizhi@seu.edu.cn

² Nanjing Tengsen Analytical Instruments Co., Ltd., No. 99, Wan'an North Road, Jiangning District, Nanjing 211103, China; wangk@tengya.com

³ School of Public Health, Nantong University, 9 Seyuan Rd., Nantong 226019, China; ningbao@ntu.edu.cn

* Correspondence: snding@seu.edu.cn

Abstract: Much progress has been made in the determination of As (III), while numerous electrochemical sensors based on metal nanomaterials with significant sensitivity and precision have been developed. However, further research is still required to achieve rapid detection and avoid interference from other metal ions (especially copper ions). In this study, bimetallic AuPt nanoparticles are electrochemically modified with screen printing electrodes. What's more, L-cysteine also self-assembles with AuNPs through Au-S bond to enhance the electrochemical performance. To overcome the interference of Cu (II) in the sensing process, the reduced iron powder was chosen to remove Cu (II) and other oxidizing organics in aqueous solutions. The lowest detectable amount is 0.139 ppb, a linear range of 1~50 ppb with superlative stability by differential pulse anodic stripping voltammetry. Fortunately, the reduced iron powder could eliminate the Cu (II) with no effect on the As (III) signal.

Keywords: bimetallic Au-Pt; differential pulse anodic stripping voltammetry; reduced iron powder; Cu (II)



Citation: Zhang, W.-Z.; Wang, K.; Bao, N.; Ding, S.-N. Co-Deposition of Bimetallic Au-Pt with L-Cysteine on Electrodes and Removal of Copper by Iron Powder for Trace Aqueous Arsenic Detection. *J. Compos. Sci.* **2024**, *8*, 327. <https://doi.org/10.3390/jcs8080327>

Academic Editor: Prashanth Konda Gokuldoss

Received: 4 July 2024

Revised: 8 August 2024

Accepted: 16 August 2024

Published: 18 August 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Over the past few years, hazardous metallic ions pollution caused by industrial emissions has worsened, which threatens food and drinking water safety. These metal ions can accumulate in humans via the trophic transfer, leading to serious health issues [1–3]. Of these, arsenic (III) (As (III)) contamination is one of the most damaging problems [4,5]. The World Health Organization (WHO) has established maximum allowable concentration about As (III) at 10 parts per billion (ppb) in potable water [6]. Therefore, developing a new device to precisely sensing of the As (III) in potable water and food is vital.

It is well known that some large-scale testing instruments like atomic fluorescence spectrometry (AFS), atomic absorption spectrometry (AAS) as well as inductively coupled plasma mass spectrometry (ICP-MS) can be utilized to As determination [7–10]. However, the high expensive price, bulky volume, and time-consuming analysis affect the scope of application of these instruments.

Electrochemical sensing methods have been widely used to detect chemical and biological substances, demonstrating the benefits of excellent selectivity, high sensitivity, rapid detection and economy [11]. Anodic stripping voltammetry is an efficient strategy for As (III) electroanalysis, and different electrochemical methods have been developed based on it such as cyclic voltammetry (CV), cathodic stripping voltammetry (CSV), square wave anodic stripping voltammetry (SWASV) and differential pulse anodic stripping voltammetry (DPASV) [12,13]. ASV detects according to the subsequent stages: 1 electrodeposition:

An electrochemical reduction of As^{3+} to As^0 is performed on the electrode surface.; 2 The electrodeposited As^0 undergoes anodic oxidation to As^{3+} , which is then dissolved into the electrolyte [14]. The electrochemical device can detect heavy metal ions as a result of the particular oxidation potential of them. However, this method has poor selectivity when applied in complex matrices since the interfering ions can co-deposit with the target ion. To overcome this problem, different strategies and electrode modification materials have been developed to enhance the analytical performance, while the biomolecules that selectively interact with the desired analyte provide the selectivity [15]. Electrochemical detection often employs screen-printed carbon electrodes (SPCEs) because of their advantages of inexpensive, high reproducibility, and simple construction [16]. An SPCE modified with nanoparticles becomes a practical strategy to detect the harmful metal ions selectively and sensitively. Many new modification methods have been developed to promote the detectability of As (III). An AuNP/polyaniline sensor with an $0.4 \mu\text{g L}^{-1}$ detection limit for arsenic was developed by Chowdhury et al. [17]. Besides gold nanomaterials, silver-based electrochemical sensors were also developed for the specific detection of As (III). S. Prakash had prepared silver nanoparticles with chitosan (CT)-modified glassy carbon electrode (GCE) for the detection of As (III) by differential-pulse anodic dissolution voltammetry (DPASV), a broad linear z , advanced sensitivity, and the LOD was 1.20 ppb [18]. It was reported that the electrodes were modified with amino acids such as N-acetyl-L-cysteine (NAC) mixed self-assembled monolayers (SAMs) to enhance accuracy and precision of As (III) detection [19]. All these methods have enabled the rapid detection of arsenic ions. However, all the Au-based electrode's electrochemical sensors have an insurmountable drawback, which is the electrical signal of As (III) and is interfered with by other metal ions such as Cu (II) present in the aqueous solutions [20].

Hence, we devoted ourselves to developing a unique electrochemical sensor for arsenic determination based on metallic composite Au-Pt nanoparticles and L-cysteine. It has been proved that the cathodic reaction can be enlarged by electrochemical hydrogen reaction, while the Pt sites of bimetallic Au-Pt electrode are more likely to facilitate the hydrogen evolution reaction, and the Au sites can further the anodic stripping of As (0) [21]. Therefore, as shown in Figure 1, the introduction of Pt could enhance the As (III) analysis performance of Au-based sensors. L-cysteine could bind to the Au nanoparticles on the SPCE via the Au-S bond, which could facilitate the preconcentration of As on active sites on SPCEs and inhibit the oxidation of gold nanoparticles during the anodic stripping process [16]. Differential pulses anodic stripping voltammetry was utilized for arsenic detection. We also explored the interference of copper ions and developed an advanced method to eliminate the interference of Cu (II) by using the reduced iron powder to remove copper ions from the solution.

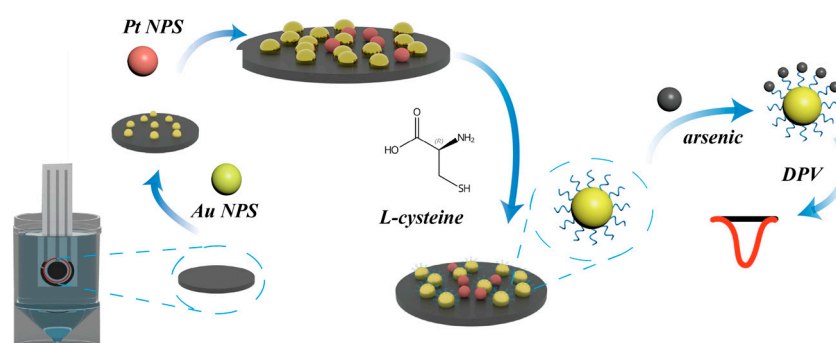


Figure 1. The deposition process of bimetallic Au-Pt NPs and L-cysteine.

2. Materials and Methods

A 1% (w/w) solution of chloroauric acid was prepared in our laboratory. Chloroplatinic acid hexahydrate was bought through Ron's Chemical Reagent Co. (Chengdu, China). L-Cysteine was purchased from Energy Chemistry Company (Shanghai, China). Sulfuric

acid was purchased from Yonghua Chemical Co. (WuXi, China), and 100 mg/L of arsenic standard solution was obtained from the National Center for Reference Materials Copper (II) sulfate pentahydrate was purchased from Sinopharm Group Chemical Reagent Co. (Shanghai, China). All solutions were prepared with deionized water.

An electrochemical station (CH Instruments 660E, Shanghai, China) was employed for Electrochemical analysis experiments. All the electrochemical experiments were executed in a disposable screen-printed carbon electrochemical cell (SPEC) with a carbon working electrode (2.8 mm diameter), an Ag/AgCl pseudo-reference electrode, and a carbon counter electrode. The SPEC was obtained from Nanjing Tensgen Analytical Instrument Co., Ltd. (Nanjing, China). There was a device with an SPEC connector and 1 mL plastic sample cell, which can also autorotate with the sample cell during the electrodeposition procedure.

A 1 mL sample cell containing an electrolyte solution and an As (III) standard solution was prepared, and the screen-printed carbon electrodes were dipped in it. The electrolyte solution contains 0.7 mM of chlorauric acid, 1.4 μ M of Chloroplatinic acid, and 1.6 mM of L-cysteine in 50 mM H₂SO₄. The deposition potential of the working electrode was set at -0.9 V (vs. Ag/AgCl reference electrode), while the deposition time was 1200 s under stirring (150 rpm) conditions.

The differential pulse anodic stripping voltammetry (DPASV) method was performed after electrodeposition. The scan window was between -0.4 and 0.6 V and additional detection parameters included: the increased potential: 0.02 V/s; the pulse width: 0.02 s; sample width: 0.02 s; amplitude: 0.05 V; pulse period: 0.3 s; Quite Time: 30 s.

3. Results and Discussion

This part can be organized with minor headings. It should deliver a brief and exact summary of the experimental outcomes, their analysis, and the conclusions that can be inferred from the experiments.

3.1. Cyclic Voltammetry of Electrodes

Figure 2a shows the cyclic voltammetry of bare electrodes, Au nanoparticle, Pt nanoparticle, Au NPs/L-cysteine, and Au-Pt NPs/L-cysteine in 0.5 M of H₂SO₄. There are no redox signals on the bare electrode. The reduction peak of Au was at 0.5 V on Au NPs/SPCE, and when the L-cysteine was co-deposited with Au (III), the reduction current decreased significantly, which was caused by L-cysteine which can slow down the formation rate of gold nanoparticles. The Au redox peak was at 1.0 V, and the maximum current rose because L-cysteine could increase the effective areas of electrode [16]. On the Pt NPs/SPCE, the redox peaks of Pt were at 0.3 V and 0.16 V [21], respectively. The characteristic value of Pt was minimal due to the limited quantity of electrode-positied Pt NPs in the experiments, which made it obvious to find the characteristic peak of Pt on Au-Pt NPs/c-cysteine/SPCE curves.

The electrodes with Au NPs, Pt NPs, and L-cysteine modification were evaluated with cyclic voltammetry. The solution in the experiment contained 0.1 M of L⁻¹ KCl and 5 mM of L⁻¹ [Fe (CN)₆]^{3-/4-}. The potential limits extended between -0.2 and 0.4 V with a sweep speed of 0.1 V/s. As Figure 2b shows, the incorporation of platinum nanoparticles results in an enhancement of both the anodic and cathodic currents of the Au NPs/L-cysteine-modified electrode, which indicates that the effective area of the electrode was increased with the modification of Pt NPs. Therefore, the performance of Au-Pt NPs/L-cysteine SPCE was better in the As (III) determination in water-based solutions.

The following is the hypothesized mechanism for the enhanced DPASV electrochemical signal of As (III) on Au-Pt/L-cysteine. The Pt site has a lower overpotential for hydrogen evolution and a higher capacity for pre-enrichment with cathodic reduction of As (0) monolayers (up to three arsenic (0) atoms per platinum atom compared to two arsenic (0) atoms per gold atom), while the gold site has a preferable thermodynamics and kinetics for As (III) determination by ASV. The electrochemical generation of atomic and molecular hydrogen on Pt sites may facilitate the electrocatalytic reduction of trivalent arsenic ions to

zero-valent arsenic at platinum sites and an adjacent gold site. Bimetallic interface zones in the Au-Pt nanocomposite demonstrate some combined characteristics of both platinum and gold in order to result in cathodic arsenic metal pre-enrichment, associated with electronic interactions closely associated bimetallic sites. Then, the electrodeposition of arsenic on gold sites can be enhanced by Pt sites [22]. What is more, the attachment of L-cysteine on Au-NPs significantly enhances the electrode's active area, thus increasing the oxidation current peak values [23].

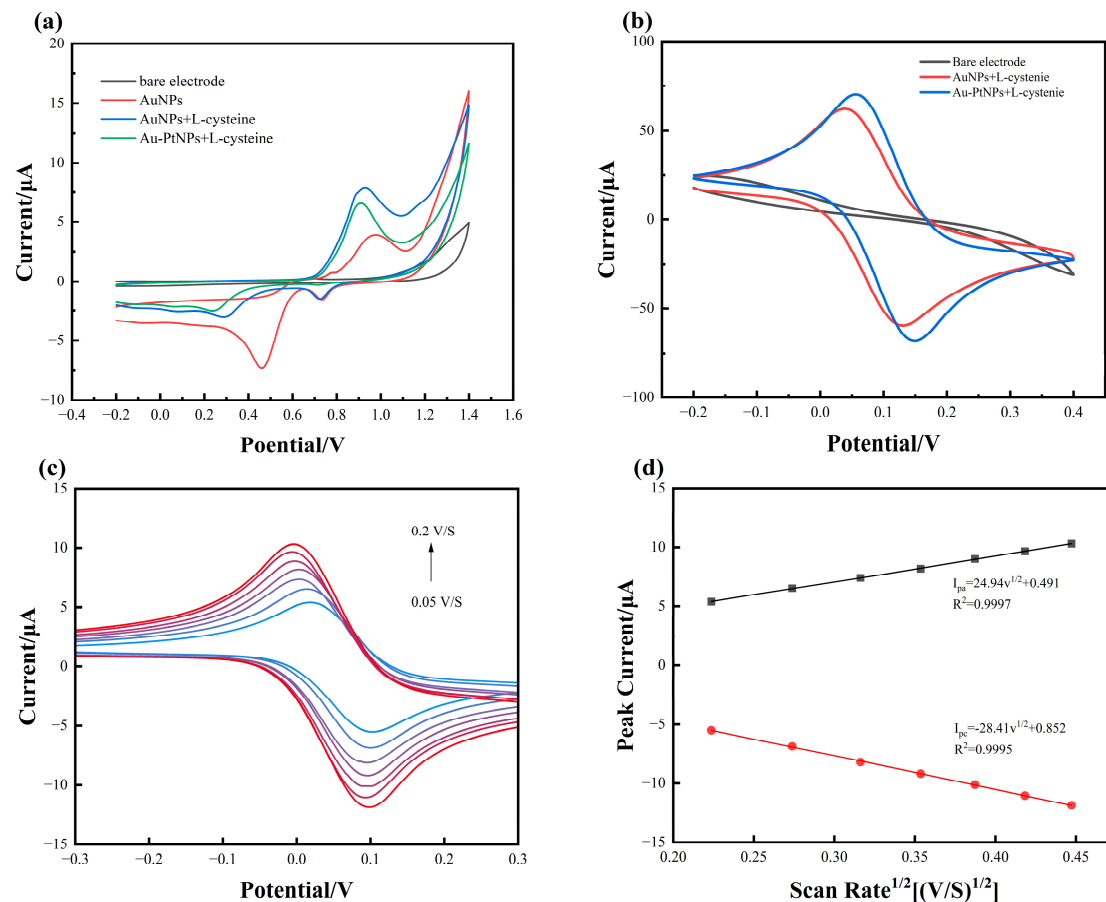


Figure 2. Electrochemical characterization of the electrode. (a) Cyclic voltammetry for bare electrode, AuNPs electrode, AuNPs/L-cysteine electrode, and Au-Pt NPs/L-cysteine electrode in 0.5 M of H₂SO₄. (b) Cyclic voltammograms for bare SPCE, AuNPs/L-cysteine electrode, and Au-Pt NPs/L-cysteine electrode in 0.1 M of KCl and 5 mM of [Fe(CN)₆]³⁻. (c) Cyclic voltammograms of Au-Pt NPs/L-cysteine electrode with multiple sweep speeds. (d) Linear relationship between the square root of the scan speeds and the maximum current values.

3.2. SPCE's Active Region Evaluation

The active areas of the advanced electrode can be estimated by the Randles–Sevcik equation [24,25]. The CV measurement was conducted in 5 mM of L⁻¹ [Fe(CN)₆]^{3-/4-} and 0.1 M of KCl, with multiple sweep speeds. The relationship between the current and the potential (from −0.3 V to 0.3 V) as a function of various sweeping rates (between 0.015 and 0.2 V/s) is demonstrated in Figure 2. It shows that the maximum current values exhibited a strong linear correlation with the square root of the sweep speeds, which means that the oxidation–reduction process of electrolytes on the modification of SPEs was almost relied on linear distribution process. Consequently, productive exposed area was determined utilizing the Randles–Sevcik equation:

$$I_p = 2.69 \times 10^5 n^{2/3} A D^{1/2} v^{1/2} C_0$$

where I_p is the maximum amperometric value (A), n is the sum of electron transfers ($n = 1$), A is the electrochemical active region of the working electrode (cm^2), D is the diffusion constant of a solution contains 5 mM of $\text{K}_3\text{Fe}(\text{CN})_6$ and 0.1 M of KCl ($6.3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$), v is the sweep speed (V s^{-1}), and C_0 is electrolyte concentration (mol cm^{-3}). Therefore, the electrochemical effective region of the electrode can be calculated from the slope of the $I_p-v^{1/2}$, and the bare electrode's active area is 0.002 cm^2 , the effective surface region of the electrode containing Au NPs and L-cysteine is 0.033 cm^2 and the active region of the electrode containing Au-Pt NPs/L-cysteine is 0.035 cm^2 . The electrochemical performance improved when the active region increased due to the modification of the electrode with platinum nanoparticles and L-cysteine.

3.3. Optimization of Experimental Results

3.3.1. Electrolyte

In this experiment, we obey the rules that have been reported, which explain the optimal parameters of the molar concentration ratio of $\text{H}_2\text{PtCl}_6/\text{HAuCl}_4$ is 1:500 [21]. The impact of varying electrolyte concentrations on the electrochemical detection of $20 \mu\text{g L}^{-1}$ arsenic was examined through the manipulation of chloroplatinic acid quantities (ranging from 0 to 1.0 mM) and L-cysteine concentrations (ranging from 0.5 mM to 3.2 mM) within the solution. As shown in Figure 3a, the maximum amperage rose until it reached the maximum at 0.7 mM and then it began to decrease with the concentration rise, which was caused by excessive chloroplatinic acid that has the impedance to the stripping of arsenic [16]. Figure 3b demonstrates that the concentration of L-cysteine can significantly reduce the peak current.

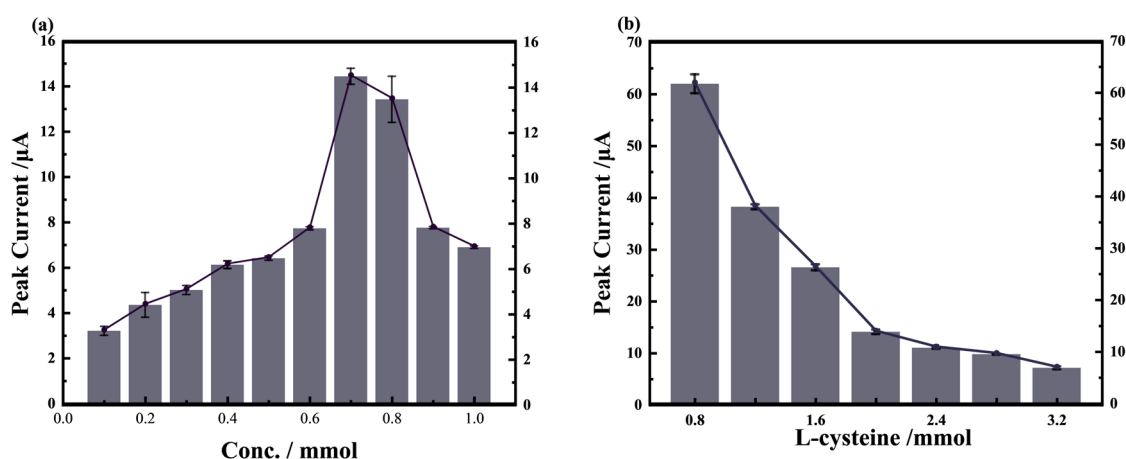


Figure 3. Effect of (a) chloroplatinic acid concentration and (b) L-cysteine concentration on the maximum current of arsenic peeling.

The observed phenomenon can be attributed to the interaction between L-cysteine and gold nanoparticles (Au NPs), wherein binding of L-cysteine onto the Au NPs hinders the stripping process. Notably, when the concentration of L-cysteine reached 2.0 mM, a significant reduction in the detected current originating from the Au NPs was observed, indicating the concealment of the Au NPs (Figure S1). Therefore, to obtain the best current effect from arsenic, the optimal concentrations of the components were determined to be 0.7 mM for chloroauric acid and 2.0 mM for L-cysteine. The concentration of sulfuric acid was chosen at 50 mM ($\text{pH} = 1$). The error bars presented in Figure 3 and the accompanying graph denote the standard deviation. A greater length of the error bars indicates a larger standard deviation within the data set, reflecting greater variability in the measurements.

3.3.2. Electrodeposition Potential and Time

To find out the optimal electrodeposition potential, the effect of electrodeposition potential in the range of $-0.5 \sim -1.1 \text{ V}$ on detecting the maximum value of As (III) was

conducted (Figure 4). As shown in Figure 4a, the maximum value rose and arrived at the top when the potential was -0.9 V, and then with the increase of potential current response of As (III) was dropped, which may be because excessive negative potential could result in chaos in redox reactions on the electrode. At low potential, the reduction in H^+ ions hinders electron transfer on active surface, resulting in a decrease in enrichment efficiency, which is primarily attributed to the occurrence of the hydrogen evolution phenomenon [26]. Figure 4b explains the relationship between electrodeposition time and peak current of the electrochemical fingerprint of As (III). The current value rose significantly with the increase in deposition time, while when the time reached 1200 s, it tended to be stable. Therefore, the optimal arguments of deposition potential and time were -0.9 V and 1200 s.

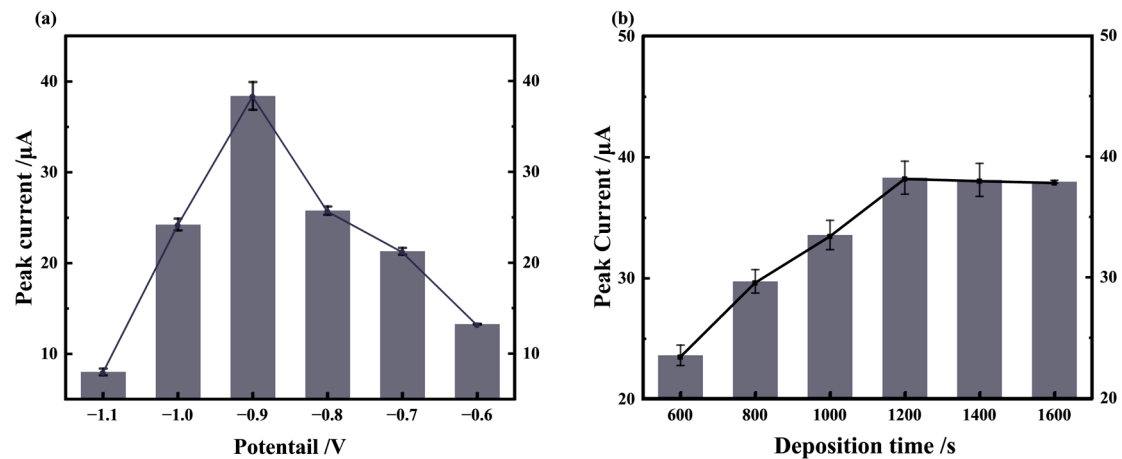


Figure 4. The maximum current values of arsenic stripping were influenced by (a) deposition potential and (b) deposition time.

3.4. Quantitative Analysis of As (III)

The electrochemical sensor for arsenic detection was conducted at Au-PtNPs and L-cysteine co-deposited SPEC. various concentrations (0, 1, 3, 5, 7, 10, 20, 30, 40, 50 $\mu\text{g L}^{-1}$) of As (III) were measured in optimal conditions to explore the line relationship between the concentration of As (III) and maximum current confirmed its line limits. In addition, the analysis limit of the SPEC was also calculated by the data from the experiments (Figure 5).

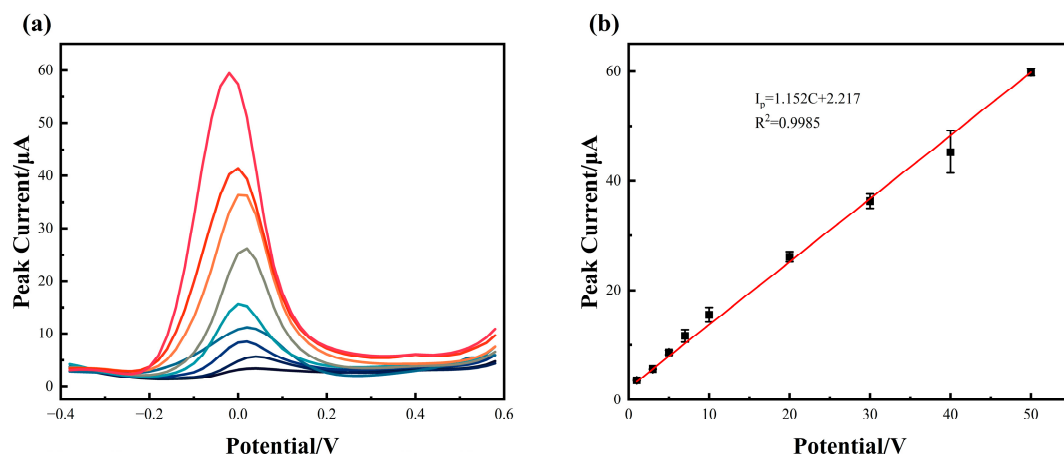


Figure 5. (a) DPASV curves of Au-Pt NPs/L-cysteine in various arsenic (1, 3, 5, 7, 10, 20, 30, 40, 50 $\mu\text{g L}^{-1}$) and 50 mM H_2SO_4 solution (b) two linear stand curves about the linear relationship between stripping peak current values and arsenic concentration were obtained from (a).

As is shown in Figure 5a, in a 50 mM H_2SO_4 solution, a direct proportional relationship was observed between the concentration of arsenic and the signal acquired through Differential Pulse Anodic Stripping Voltammetry (DPASV). Specifically, as arsenic concentration increased, a corresponding rise in the anodic stripping current was observed at a consistent deposition potential. The Figure 5b graphical representation also illustrated linear regression equations within the concentration ranges of 0 to 50 $\mu\text{g L}^{-1}$, indicating a strong and favorable linear correlation. The linear regression equations had slopes, which because the speed of reduction was affected by the concentration of As (III), the higher concentration would lead to a lower reduction speed, resulting in a lower slope [27]. The detection limit (LOD) calculation is performed using the formula $3\sigma/k$. The k represents the slope of the linear curve, and σ denotes the standard deviation of current value obtained from the blank sample. The LOD in the experiment for As (III) determination was 0.139 ppb, which proved that the modified SPEC with gold nanoparticles, platinum nanoparticles, and L-cysteine had a broad linear range and low LOD for As (III) determination. The outstanding detection performance of the electrochemical sensor we developed is more than that previously reported.

3.5. Interference from Copper Ion

As we all know, Cu (II) could cause a huge impact on the determination of As (III) through ASV analysis with Au nanoparticles. The main reason is that divalent copper ion could compose intermetallic compound Cu_3As_2 with arsenic ion in the course of preconcentration stage [28]. Figure 6c represents the interference of copper in the determination of As (III) with Au-Pt NPs/L-cysteine SPEC. There was a huge peak current when Cu (II) existed in the solution, which was almost 30 times more than the standard peak current value of As (III) stripping voltammetry. Therefore, this device could not detect the arsenic ions accurately.

To overcome this problem, some researchers try to use shield agents to prevent the interference of copper (II), such as EDTA. However, EDTA and other common masking agents (MA) will complex As (III) when shielding Cu (II) [29]. A new masking agent was also used to complex Cu (II) in the experiment (Figure 6). As Figure 6a shows, when the As (III) concentration was 10 ppb, there was no variation in the maximum amperage of arsenic anodic stripping, while the solution contained a higher concentration (50 ppb) in Figure 6b, the stripping peak current decreased significantly, which means that the masking agents complex As (III) when shielding Cu (II). Therefore, the masking agent could only be used when the As (III) concentration was low. However, researchers cannot know the concentration of the solution to be measured, which greatly limits the use of masking agents in the detection of arsenic ions.

Because the disadvantages of masking agents have been reported, we are trying to find a new method to solve the problem caused by copper ions. We find that Fe was a desirable reducer that could reduce the copper ion in solution and exist with arsenic ion and remove the organic oxides from the solution [30]. It has been reported that enhancing the signal of electroanalysis As (III) by co-deposit with iron group ions firstly uses reduced iron powder to shield the interference of Cu (II) [29] in neutral solution. In this study, this method was applied in an acidic solution to explore whether it was still possibly useful in practical As (III) electroanalysis. As Figure 6c,d show, there was no significant change in the anodic stripping maximum amperage of As (III), and the anodic stripping current pattern of As (III) was broader after Cu (II) removal by reducing iron powder, which did not affect the qualitative detection of As (III). Therefore, using the practical strategies for As (III) electroanalysis in Au-Pt NPs/L-cysteine modified SPEC is practicable.

Since the concentration of copper is inferior to 20 ppb in natural water [31], the applicability of the experimental results obtained under this condition was wider applied. Figure 7 presents the various concentrations of As (III) that were measured in optimal conditions and 20 ppb Cu (II) existed. An obvious concentration gradient trend could be

found in the Figure 7a,b, which means that the Au-Pt/L-cysteine could realize the As (III) determination with 20 ppb Cu (II) existed after the pretreatment.

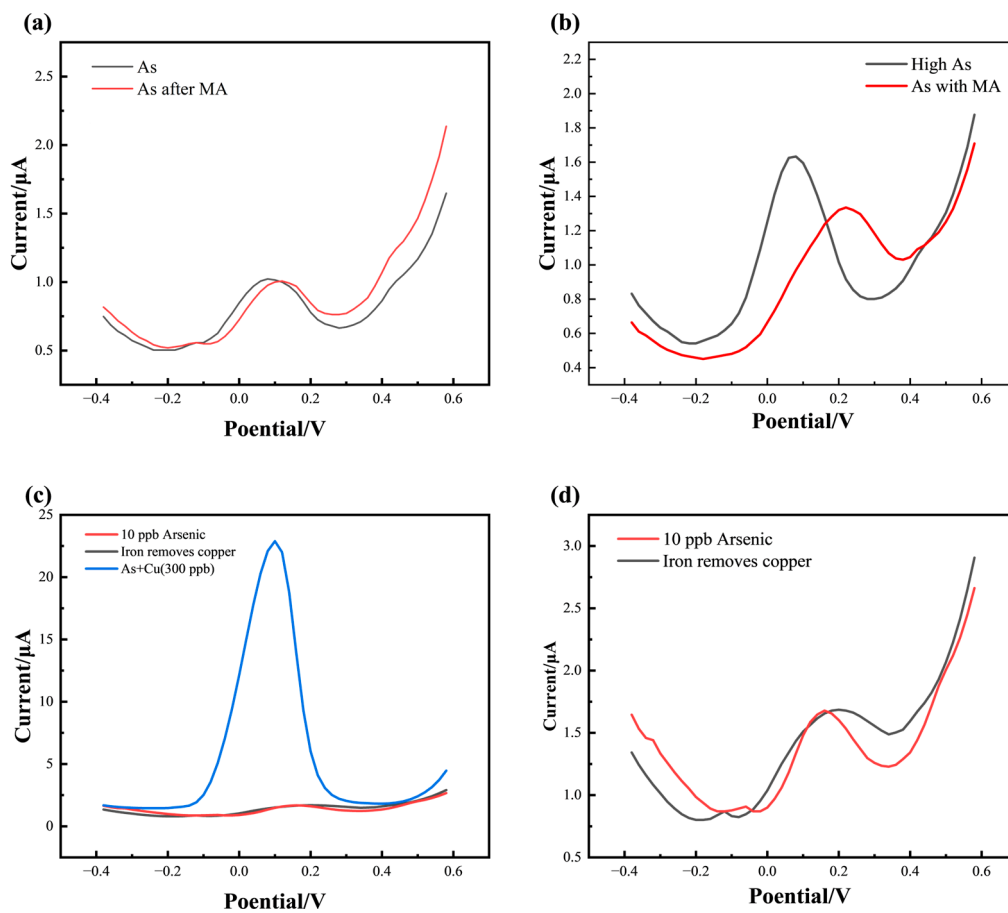


Figure 6. Effect of masking agent on arsenic ion signal at different As (III) concentrations. (a) 10 µg L⁻¹ As (III) solution (b) 50 µg L⁻¹ As (III) solution. (c,d) represent the effect of copper ions on the arsenic electrical signal during detection and the shielding effect of the introduction of reducing iron powder on copper.

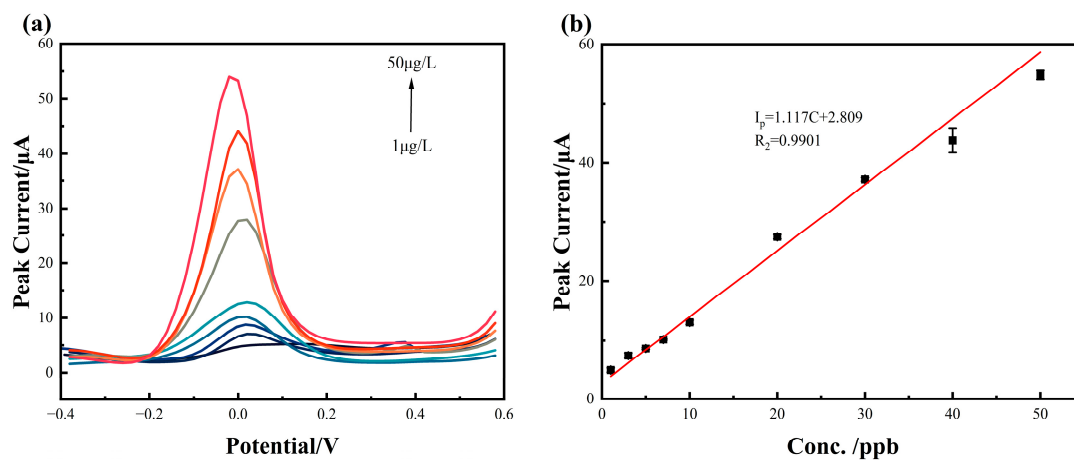


Figure 7. The electrochemical sensor for As (III) determination after copper removal by reducing iron powder (a) DPASV curves of Au-Pt NPs/L-cysteine in various arsenic concentrations (1, 3, 5, 7, 10, 20, 30, 40, 50 µg L⁻¹) and 50 mM H₂SO₄ solution. (b) The linear standard curves about the linear relationship between stripping peak current values and arsenic concentration were obtained from (a).

The experimental findings revealed a notable increase in the values of stripping apex current as the arsenic ratio increased. Moreover, a linear regression equation was observed, indicating a strong linear relationship within the concentration range of 0 to 50 $\mu\text{g L}^{-1}$. The LOD also for the concentration of As (III) was quantified to be 0.144 parts per billion (ppb). These results signify that the determination system exhibits a broad linear scope and a minimal detection threshold in order to obtain the accurate quantification of As (III), despite copper ions existing.

Table 1 enumerates various methods for arsenic ion detection. In comparison, the sensor suggested in this project demonstrates competitive advantages concerning detection limit, linear range, and simplicity of electrode modification. The bimetallic system offers a simpler alternative to traditional nanomaterial systems for sensor applications, aligning more closely with the requirements for rapid field detection and potentially reducing process costs. Additionally, compared to monometallic systems, the bimetallic approach selectively introduces a second metal, thereby enhancing the catalytic properties for arsenic ion detection.

Table 1. Comparison with other sensors.

Ref.	Method	Material	Linear Range	LOD (ppb)
[30]	SWASV	$\text{Fe}^{2+}/\text{Fe}^{3+}$ (GCE)	1–15 ppb	0.487
[32]	CV	AuNPs (SPCE)	0.075–30 ppb	0.11
[33]	SWASV	FePt (GCE)	1–15 ppb	0.8
[21]	LSASV	AuPt (GCE)	0.005 to 3.0 μM	0.28
[34]	SWASV	AuNPs/ α - MnO_2 (CGE)	1–10 ppb	0.019
[35]	SWASV	Fe_3O_4 NPs/AuNPs (GCE)	1–100 ppb	0.22
[36]	LSASV	Buckypaper modified by GNP	0.75–750 ppb	0.75 ppb
This work	DPV	AuPt/L-cysteine	1–50 ppb	0.139

The sensor is designed with portability and rapid detection in mind, primarily targeting areas where large instruments are impractical, such as measuring arsenic ion content in food, particularly rice. Additionally, it is suitable for detecting arsenic ions in water quality. Overall, this sensor addresses the need for swift detection in scenarios where large instruments are not feasible.

3.6. Other Ions' Interference

We have tested some metal ions normally found in aqueous solutions for the specificity examination. Ag (I), Fe (III), Mn (II), Ba (II), Co (II), Cr (VI), and Pb (IV), with a concentration 20-fold surpassing As (III), were mixed with the cells containing 20 $\mu\text{g L}^{-1}$ of As (III) solution. Figure 8 shows that the As (III) stripping peak current was not significantly altered by the addition of interfering ions, except Cu (II), which indicates that most ions do not affect the detection of As (III). As we know, Ag (I) was also a severe interference factor in the detection of As (III) [16], and Au-Pt NPs/L-cysteine modified SPEC could eliminate interference from the silver ion. The effect of copper ions could be removed by the reduction in iron powder. Hence, the developed electrochemical sensor demonstrated a remarkable capability to selectively detect As (III) despite mixing with other interfering ions, highlighting its significant potential for accurate As (III) detection in aqueous solutions.

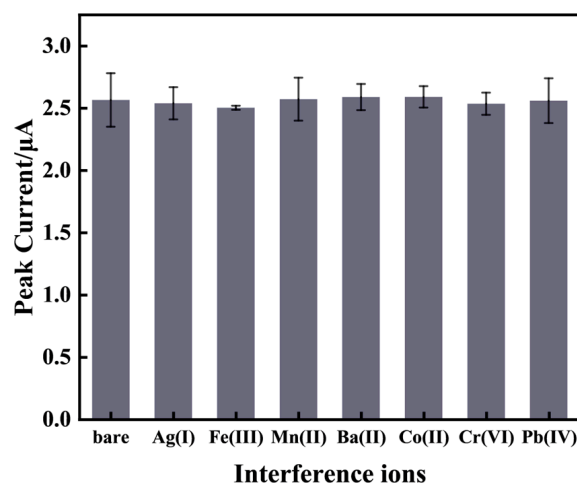


Figure 8. Selectivity study for the modified electrode. The level of other ions was 20-fold surpassing target substance.

4. Conclusions

In summary, the bimetallic nanoparticles Au-Pt NPs co-deposited with L-cysteine on an SPCE for quick and responsive detection of As (III). The easy treatment and rapid detection inspire the wider application of electrochemical sensors in the analysis of arsenic. Moreover, the electrochemical measurement device designed in this work also overcame the interference of copper by using reduced iron powder, and the result demonstrated that extra Fe^{2+} would not affect the electrical signal of As (III). This method could show a significant linear range with a determination both before and after treatment. The electrochemical sensor shows a potential to achieve rapid and accurate As (III) sensing in aqueous solutions.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/jcs8080327/s1>, Figure S1: A screen-printed electrode and a matched connector.

Author Contributions: Conceptualization, methodology, writing—original draft preparation, data analysis W.-Z.Z.; conceptualization, data analysis, resource K.W.; investigation, writing—review, data analysis N.B.; writing—review and editing, supervision S.-N.D. All authors have read and agreed to the published version of the manuscript.

Funding: The authors gratefully acknowledge the financial support from the National Natural Science Foundation of China (22174015).

Data Availability Statement: The data that support the findings of this study are available from the corresponding author upon reasonable request.

Conflicts of Interest: Author Kan Wang was employed by the company Nanjing Tengsen Analytical Instruments Co., Ltd. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

References

1. Cai, L.; Ying, D.; Liang, X.; Zhu, M.; Lin, X.; Xu, Q.; Cai, Z.; Xu, X.; Zhang, L. A Novel Cationic Polyelectrolyte Microsphere for Ultrafast and Ultra-Efficient Removal of Heavy Metal Ions and Dyes. *Chem. Eng. J.* **2021**, *410*, 128404. [CrossRef]
2. Gianì, F.; Mastro, R.; Trovato, M.A.; Malandrino, P.; Russo, M.; Pellegriti, G.; Vigneri, P.; Vigneri, R. Heavy Metals in the Environment and Thyroid Cancer. *Cancers* **2021**, *13*, 4052. [CrossRef] [PubMed]
3. He, Q.; Silliman, B.R. Climate Change, Human Impacts, and Coastal Ecosystems in the Anthropocene. *Curr. Biol.* **2019**, *29*, R1021–R1035. [CrossRef] [PubMed]
4. Zhang, X.; Yang, H.; Sun, R.; Cui, M.; Sun, N.; Zhang, S. Evaluation and Analysis of Heavy Metals in Iron and Steel Industrial Area. *Environ. Dev. Sustain.* **2022**, *24*, 10997–11010. [CrossRef]
5. Shankar, S.; Shanker, U.; Shikha. Arsenic Contamination of Groundwater: A Review of Sources, Prevalence, Health Risks, and Strategies for Mitigation. *Sci. World J.* **2014**, *2014*, 304524. [CrossRef] [PubMed]

6. World Health Organization. *Guidelines for Drinking-Water Quality: First Addendum to the Fourth Edition*; WHO: Geneva, Switzerland, 2017; ISBN 978-92-4-155001-7.
7. Balcaen, L.; Bolea-Fernandez, E.; Resano, M.; Vanhaecke, F. Inductively Coupled Plasma—Tandem Mass Spectrometry (ICP-MS/MS): A Powerful and Universal Tool for the Interference-Free Determination of (Ultra)Trace Elements—A Tutorial Review. *Anal. Chim. Acta* **2015**, *894*, 7–19. [[CrossRef](#)] [[PubMed](#)]
8. Omeje, K.O.; Ezema, B.O.; Okonkwo, F.; Onyishi, N.C.; Ozioko, J.; Rasqa, W.A.; Sardo, G.; Okpala, C.O.R. Quantification of Heavy Metals and Pesticide Residues in Widely Consumed Nigerian Food Crops Using Atomic Absorption Spectroscopy (AAS) and Gas Chromatography (GC). *Toxins* **2021**, *13*, 870. [[CrossRef](#)] [[PubMed](#)]
9. Zou, H.; Zhou, C.; Li, Y.; Yang, X.; Wen, J.; Song, S.; Li, C.; Sun, C. Speciation Analysis of Arsenic in Edible Mushrooms by High-Performance Liquid Chromatography Hyphenated to Inductively Coupled Plasma Mass Spectrometry. *Food Chem.* **2020**, *327*, 127033. [[CrossRef](#)]
10. Gudlavalleti, R.H.; Bose, S.C.; Verma, S.K.; Khatri, P.; Scaria, J.; Dhewa, S.; Chaubey, V.K. A Novel Fluorometric Bio-Sensing-Based Arsenic Detection System for Groundwater. *IEEE Sens. J.* **2017**, *17*, 5391–5398. [[CrossRef](#)]
11. Krishnan, S. Review—Electrochemical Sensors for Large and Small Molecules in Biofluids. *J. Electrochem. Soc.* **2020**, *167*, 167505. [[CrossRef](#)]
12. Guo, Z.; Yang, M.; Huang, X.-J. Recent Developments in Electrochemical Determination of Arsenic. *Curr. Opin. Electrochem.* **2017**, *3*, 130–136. [[CrossRef](#)]
13. Hung, D.Q.; Nekrassova, O.; Compton, R.G. Analytical Methods for Inorganic Arsenic in Water: A Review. *Talanta* **2004**, *64*, 269–277. [[CrossRef](#)] [[PubMed](#)]
14. Liu, Z.-G.; Huang, X.-J. Voltammetric Determination of Inorganic Arsenic. *TrAC Trends Anal. Chem.* **2014**, *60*, 25–35. [[CrossRef](#)]
15. Rapini, R.; Marrazza, G. Electrochemical Aptasensors for Contaminants Detection in Food and Environment: Recent Advances. *Bioelectrochemistry* **2017**, *118*, 47–61. [[CrossRef](#)] [[PubMed](#)]
16. Wang, W.; Yi, Z.; Liang, Q.; Zhen, J.; Wang, R.; Li, M.; Zeng, L.; Li, Y. In Situ Deposition of Gold Nanoparticles and L-Cysteine on Screen-Printed Carbon Electrode for Rapid Electrochemical Determination of As (III) in Water and Tea. *Biosensors* **2023**, *13*, 130. [[CrossRef](#)] [[PubMed](#)]
17. Chowdhury, A.-N.; Ferdousi, S.; Islam, M.M.; Okajima, T.; Ohsaka, T. Arsenic Detection by Nanogold/Conducting-Polymer-Modified Glassy Carbon Electrodes. *J. Appl. Polym. Sci.* **2007**, *104*, 1306–1311. [[CrossRef](#)]
18. Prakash, S.; Chakrabarty, T.; Singh, A.K.; Shahi, V.K. Silver Nanoparticles Built-in Chitosan Modified Glassy Carbon Electrode for Anodic Stripping Analysis of As (III) and Its Removal from Water. *Electrochim. Acta* **2012**, *72*, 157–164. [[CrossRef](#)]
19. Chen, L.; Zhou, N.; Li, J.; Chen, Z.; Liao, C.; Chen, J. Synergy of Glutathione, Dithiothreitol and N-Acetyl-L-Cysteine Self-Assembled Monolayers for Electrochemical Assay: Sensitive Determination of Arsenic (Iii) in Environmental and Drinking Water. *Analyst* **2011**, *136*, 4526. [[CrossRef](#)] [[PubMed](#)]
20. Song, Y.; Swain, G.M. Total Inorganic Arsenic Detection in Real Water Samples Using Anodic Stripping Voltammetry and a Gold-Coated Diamond Thin-Film Electrode. *Anal. Chim. Acta* **2007**, *593*, 7–12. [[CrossRef](#)] [[PubMed](#)]
21. Bu, L.; Liu, J.; Xie, Q.; Yao, S. Anodic Stripping Voltammetric Analysis of Trace Arsenic (III) Enhanced by Mild Hydrogen-Evolution at a Bimetallic Au–Pt Nanoparticle Modified Glassy Carbon Electrode. *Electrochem. Commun.* **2015**, *59*, 28–31. [[CrossRef](#)]
22. Huang, Z.; Liu, Y.; Xie, F.; Fu, Y.; He, Y.; Ma, M.; Xie, Q.; Yao, S. Au-Supported Pt–Au Mixed Atomic Monolayer Electrocatalyst with Ultrahigh Specific Activity for Oxidation of Formic Acid in Acidic Solution. *Chem. Commun.* **2012**, *48*, 12106. [[CrossRef](#)] [[PubMed](#)]
23. Arihara, K.; Ariga, T.; Takashima, N.; Arihara, K.; Okajima, T.; Kitamura, F.; Tokuda, K.; Ohsaka, T. Multiple Voltammetric Waves for Reductive Desorption of Cysteine and 4-Mercaptobenzoic Acid Monolayers Self-Assembled on Gold Substrates. *Phys. Chem. Chem. Phys.* **2003**, *5*, 3758. [[CrossRef](#)]
24. Anu Prathap, M.U.; Srivastava, R.; Satpati, B. Simultaneous Detection of Guanine, Adenine, Thymine, and Cytosine at Polyaniline/MnO₂ Modified Electrode. *Electrochim. Acta* **2013**, *114*, 285–295. [[CrossRef](#)]
25. Anu Prathap, M.U.; Srivastava, R. Tailoring Properties of Polyaniline for Simultaneous Determination of a Quaternary Mixture of Ascorbic Acid, Dopamine, Uric Acid, and Tryptophan. *Sens. Actuators B Chem.* **2013**, *177*, 239–250. [[CrossRef](#)]
26. Lin, T.-H.; Lin, C.-W.; Liu, H.-H.; Sheu, J.-T.; Hung, W.-H. Potential-Controlled Electrodeposition of Gold Dendrites in the Presence of Cysteine. *Chem. Commun.* **2011**, *47*, 2044. [[CrossRef](#)]
27. Dong, X.; Li, M.; Feng, N.; Sun, Y.; Yang, C.; Xu, Z. A Nanoporous MgO Based Nonenzymatic Electrochemical Sensor for Rapid Screening of Hydrogen Peroxide in Milk. *RSC Adv.* **2015**, *5*, 86485–86489. [[CrossRef](#)]
28. Dai, X.; Compton, R.G. Gold Nanoparticle Modified Electrodes Show a Reduced Interference by Cu (II) in the Detection of As (III) Using Anodic Stripping Voltammetry. *Electroanalysis* **2005**, *17*, 1325–1330. [[CrossRef](#)]
29. Cai, X.; Xia, R.-Z.; Ye, J.-J.; Huang, C.-C.; Yang, Y.-F.; Zhang, L.-K.; Liang, B.; Yang, M.; Lin, C.-H.; Li, P.-H.; et al. Practical Strategy for Arsenic (III) Electroanalysis without Modifier in Natural Water: Triggered by Iron Group Ions in Solution. *Anal. Chem.* **2023**, *95*, 4104–4112. [[CrossRef](#)]
30. Wang, B.; Deng, C.; Ma, W.; Sun, Y. Modified Nanoscale Zero-Valent Iron in Persulfate Activation for Organic Pollution Remediation: A Review. *Environ. Sci. Pollut. Res.* **2021**, *28*, 34229–34247. [[CrossRef](#)] [[PubMed](#)]
31. Xie, F.; Yu, M.; Yuan, Q.; Meng, Y.; Qie, Y.; Shang, Z.; Luan, F.; Zhang, D. Spatial Distribution, Pollution Assessment, and Source Identification of Heavy Metals in the Yellow River. *J. Hazard. Mater.* **2022**, *436*, 129309. [[CrossRef](#)] [[PubMed](#)]

32. Udayan, A.P.M.; Kachwala, B.; Karthikeyan, K.G.; Gunasekaran, S. Ultrathin Quasi-Hexagonal Gold Nanostructures for Sensing Arsenic in Tap Water. *RSC Adv.* **2020**, *10*, 20211–20221. [[CrossRef](#)] [[PubMed](#)]
33. Moghimi, N.; Mohapatra, M.; Leung, K.T. Bimetallic Nanoparticles for Arsenic Detection. *Anal. Chem.* **2015**, *87*, 5546–5552. [[CrossRef](#)] [[PubMed](#)]
34. Meng, Y.; Xing, C.; Tian, J.J.; Zheng, G.; Jin, H.L.; Xing, J.H. Electrochemical Detection of Trace Arsenic(III) by Nanocomposite of Nanorod-Like α -MnO₂ Decorated with ~5 Nm Au Nanoparticles: Considering the Change of Arsenic Speciation. *Anal. Chem.* **2016**, *88*, 9720–9728. [[CrossRef](#)]
35. Sawan, S.; Hamze, K.; Youssef, A. The Use of Voltammetry for Sorption Studies of Arsenic (III) Ions by Magnetic Beads Functionalized with Nucleobase Hydrazide Derivatives. *Electroanalysis* **2021**, *7*, 1789–1799. [[CrossRef](#)]
36. Andrea, B.; Daniel, M. Arsenic (III) Detection in Water by Flow-through Carbon Nanotube Membrane Decorated by Gold Nanoparticles. *Electrochim. Acta* **2019**, *318*, 496–503. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.