

Page 1 of 28

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4 1 **Enabling Emergency Response to Arsenic Contamination:**

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6 2 **Simultaneous and Rapid Identification of Arsenic Speciation by**

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9 3 **Machine Learning-Driven Fluorescent Sensor Array**

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ABSTRACT

The rapid identification of arsenic speciation is critical for assessing its toxicity and guiding emergency response during water contamination events, yet it remains a significant challenge for current analytical methods. Herein, a novel machine learning-driven fluorescent sensor array was designed for the differentiation of four arsenic speciation, including arsenite (As^{III}), arsenate (As^{V}), monomethylarsonic acid (MMA^{V}), and dimethylarsinic acid (DMA^{V}). Wherein, two Fe-based luminescent metal-organic frameworks ($\text{NH}_2\text{-MIL-88 (Fe)}$ and OH-MIL-88 (Fe)) were synthesized by functionalizing MIL-88 (Fe) with 2-amino-terephthalic acid and 2-hydroxy-terephthalic acid, respectively, both of which presented promising fluorescence behavior. Remarkably, varying arsenic species differentially regulated the fluorescence intensity of $\text{NH}_2\text{-MIL-88 (Fe)}$ and OH-MIL-88 (Fe) , which was further analyzed by pattern recognition methods to develop a fluorescence sensor array for rapid, simultaneous identification of four arsenic species and their mixtures. Furthermore, machine learning algorithm was employed to integrate with fluorescent sensor array to establish a stepwise prediction model to precisely identify and predict four arsenic speciation, which was successful applied in actual water samples. Thus, our findings presented a robust, rapid, and intelligent platform for arsenic speciation, offering a powerful tool for water quality assessment and emergency response.

Keywords: speciation analysis, rapid detection, arsenic, array sensor, metal-organic frameworks

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Synopsis

This study highlighted an innovative machine learning-assisted fluorescent sensor array for the first time to identify multiple arsenic speciation in actual water samples.

Graphic abstract



INTRODUCTION

Arsenic contamination of water sources poses a significant global public health threat, with the frequency and severity of sudden pollution incidents underscoring an urgent need for advanced rapid response strategies ¹⁻⁴. The toxicity, mobility, and environmental fate of arsenic are intrinsically governed by its chemical speciation ⁵. Notably, the inorganic As demonstrates greater toxicity than organic As species including pentavalent dimethylarsenous acid (DMA^V) and monomethylarsinic acid (MMA^V) ⁶, and inorganic trivalent arsenicals (As^{III}) are more toxic than inorganic pentavalent arsenicals (As^V) ⁷. Consequently, measurements of total arsenic concentration are inadequate for accurate risk assessment, which also cannot inform the specific remediation strategies and public health advisories required during emergency response ⁸. More importantly, in the critical first hours following a contamination event, the rapid identification of the dominant arsenic species is far more consequential for initiating appropriate emergency countermeasures than the precise quantification of total arsenic at ultra-trace levels after protracted analysis. Thus, this exigency highlights a pressing demand to develop analytical methodologies capable of high-throughput and rapid arsenic speciation for establish the rapid emergency response to fight against the arsenic contamination accidents ⁹.

Established laboratory techniques ¹⁰, such as atomic absorption spectrometry ^{11, 12} and high performance liquid chromatography with inductively coupled plasma mass spectrometric ¹³⁻¹⁵, provide excellent sensitivity and accuracy for speciation analysis ¹⁰. However, their application in emergency scenarios is impeded by centralized instrumentation, prolonged analysis times, and complex sample preparation ¹⁶. Besides, current sensing approaches employing the “lock-and-key” principle demonstrated restricted capability, enabling the detection of merely one or two arsenic species with rapid response ^{17, 18}, such as As^{III} ^{19, 20}, As^V ²¹⁻²³, or As^{III} and As^V ²⁴⁻²⁶, and lacking the multiplexing capacity for multiple speciation.

Fortunately, sensor arrays become a potential tool for disease diagnosis ^{27, 28}, food safety ^{29, 30}, and environmental monitoring ³¹⁻³³, etc. In particular, fluorescent sensor arrays have emerged as promising platforms in sensing field, offering three key advantages: fast response, exceptional sensitivity, and multiplex detection capability ³⁴⁻³⁶, whereas their applications for

identifying arsenic speciation have not been reported. In addition, traditional fluorescent sensor arrays have meet the following challenges: (i) sensor arrays often incorporate multiple discrete sensing units, resulting in increased manufacturing expenses, intricate synthesis protocols, and time-consuming processes ³⁷; (ii) the discrimination of similar targets is susceptible to concentration interference ³⁸. For example, a low concentration of analytes with strong inhibition can produce the same effect to another high concentration of targets with weak inhibition. To address the above issues, employing a basic material functionalized with various groups as sensing units can simplify sensor arrays by using similar synthesis methods ³⁹, avoiding complex procedures ³² while generating effective cross-reactive probes ⁴⁰. Simultaneously, machine learning has emerged as a robust data processing platform, demonstrating exceptional capabilities in cluster analysis, regression modeling, and predictive analytics ^{41, 42}, thereby significantly improving sensor arrays' performance in accurate identification of multi-targets ^{28, 43, 44}. Consequently, we hypothesized that machine learning-assisted fluorescent sensor array could achieve the cost-effective, rapid, and intelligent identification of various arsenic speciation in arsenic contamination accident.

This study presented a novel machine learning-supported fluorescent sensor array based on two luminescent metal-organic frameworks (LMOFs, NH₂-MIL-88 (Fe) and OH-MIL-88 (Fe)) derived from MIL-88 (Fe) with different ligands, enabling simultaneous recognition of four arsenic species, including arsenite (As^{III}), arsenate (As^V), monomethylarsonic acid (MMA^V), and dimethylarsinic acid (DMA^V) (**Scheme 1**). Specifically, two LMOFs exhibited differential fluorescence responses to various arsenic species due to distinct interactions, generating characteristic fluorescence fingerprints for each arsenic speciation. The developed sensor array successfully differentiated all four arsenic species and their mixtures through pattern recognition analysis. Notably, with the support of a stepwise prediction model, the proposed sensor array achieved accurate classification and concentration prediction of arsenic speciation, showing good performance in real environmental waters. This work established a robust, rapid, and intelligent platform that holds significant promise for improving emergency response capabilities against arsenic contamination incidents.

MATERIALS AND METHODS

Fabrication of Fluorescent Sensor Array for Arsenic Speciation Identification

The fluorescent sensor array was fabricated by two Fe-based LMOFs (NH₂-MIL-88 (Fe) and OH-MIL-88 (Fe)), four arsenics (As^{III}, As^V, MMA^V, and DMA^V), and five replicates. Wherein, 100 μ L of NH₂-MIL-88 (Fe) and OH-MIL-88 (Fe) were separately added into the 5 columns (5 replicates) and 5 rows (blank and 4 arsenics), and then 100 μ L of different arsenic speciation solutions was added into the corresponding rows for incubating 2 min at room temperature. The fluorescence intensities of the Fe-LMOFs mixed with arsenic speciation were acquired at λ_{em} =435 nm, with λ_{ex} =350 nm for NH₂-MIL-88 (Fe) and λ_{ex} =317 nm for OH-MIL-88(Fe). Then, normalized fluorescence intensities (F/F_0) were obtained, where F indicated the measured intensity upon arsenic interaction and F_0 reflected the original intensity of the untreated Fe-LMOFs. The acquired fluorescence data (2 Fe-LMOFs $\times$ 4 arsenic species $\times$ 5 replicates) were then processed by linear discriminant analysis (LDA) and hierarchical cluster analysis (HCA) for arsenic speciation identification. In addition, the developed fluorescent sensor array also enabled the discrimination of individual arsenic species with varying concentrations and their mixtures via a similar approach.

Machine Learning-Assisted Fluorescent Sensor Array for Arsenic Speciation

Support vector machine (SVM), as one of the representative supervised learning algorithms, could divide data points of different categories by finding an optimal hyperplane and work by finding a function that fits the data to predict continuous values^{38, 45}. In this study, SVM was employed to establish a unified stepwise prediction model to combining with fluorescent sensor array. Then, a total of 160 data points were obtained by testing four arsenic species (As^{III}, As^V, MMA^V, and DMA^V) at eight different concentrations (1-50 μ g/mL) with five replicates each. The original dataset was divided into a training set (n=128) and a testing set (n=32). Following, both training and testing sets were processed through the stepwise prediction model, which facilitated concurrent qualitative identification and accurate quantitative analysis of various arsenic species.

RESULTS AND DISSCUSSION

Characterization of NH₂-MIL-88 (Fe) and OH-MIL-88 (Fe)

NH₂-MIL-88 (Fe) was obtained by the coordination interaction of Fe³⁺ and NH₂-BDC through a facile solvothermal method (**Figure 1a**). Wherein, NH₂-MIL-88 (Fe) exhibited a typical octahedral morphology in TEM and SEM images (**Figure 1b and 1c**), and the typical size distribution centered at 205.8 nm (**Figure S1**). Then, the generated NH₂-MIL-88 (Fe) was further assessed by the corresponding element mapping. As shown in **Figure 1d**, the characteristic elements of C, N, O, and Fe were obviously observed in individual NH₂-MIL-88 (Fe) nanoparticle, indicating the successful preparation of NH₂-MIL-88 (Fe). Similarly, the preparation of OH-MIL-88 (Fe) was similar to NH₂-MIL-88 (Fe), just replacing NH₂-BDC by OH-BDC (**Figure 1e**). Characterized by TEM images (**Figure 1f**), OH-MIL-88 (Fe) presented a typical quasi-spherical morphology with a size of about 2.45 μ m (**Figure S2**), similar results were also verified in SEM images (**Figure 1g**). Meanwhile, the corresponding element mapping was presented in **Figure 1h**, and the presence of C, N, O, and Fe elements in OH-MIL-88 (Fe) nanoparticles verified their successful preparation.

Then, the preparation of the NH₂-MIL-88 (Fe) and OH-MIL-88 (Fe) were further characterized. As shown in **Figure S3**, NH₂-MIL-88 (Fe) exhibited distinct and broad peak within the 300-400 nm range, which was attributed to the LMCT process by the transition of excited electrons from ligands to empty orbits of Fe³⁺ ⁴⁶. Meanwhile, OH-MIL-88 (Fe) presented an obvious absorption peak at 315 nm. Moreover, the XRD patterns of the NH₂-MIL-88 (Fe) and OH-MIL-88 (Fe) were depicted in **Figure 1i**. Wherein, NH₂-MIL-88 (Fe) exhibited six characteristic peaks at 9.23°, 10.36°, 13.01°, 16.61°, 18.46° and 19.01°, which were assigned to the crystal face of (002), (101), (102), (103), (200), and (201). All observed peaks matched well with the previously reported NH₂-MIL-88 (Fe) ²³. Meanwhile, OH-MIL-88 (Fe) exhibited matching crystallographic planes in its XRD patterns. Following, the FTIR spectra of NH₂-MIL-88(Fe) and OH-MIL-88 (Fe) were further studied (**Figure 1j**), which exhibited a C-H stretching vibration (benzene ring) at 767 cm⁻¹, along with prominent bands at 1575 cm⁻¹ and 1380 cm⁻¹, representing asymmetric and symmetric tensile vibration patterns of the coordinating carboxyl groups, respectively. These features indicated the incorporation of a dicarboxylic acid linker in the Fe-LMOFs. Meanwhile, we could observe the presence of a characteristic peak at 527 cm⁻¹ in two LMOFs, which was thought to be

associated with the Fe-O vibration. Besides, the peaks at 1245 cm^{-1} can be attributed to the characteristic C-N stretching, indicating the presence of aromatic amines. These results indicated the assembly of $\text{NH}_2\text{-BDC}$ and OH-BDC on two Fe-MOFs. In addition, the wide band in the range of $3200\text{-}3500\text{ cm}^{-1}$ in $\text{NH}_2\text{-MIL-88 (Fe)}$ represented the N-H stretching vibration absorption in $-\text{NH}_2$ group, while the characteristic peak at 1657 cm^{-1} was attributed to the bending vibration of N-H, indicating the modification of $\text{NH}_2\text{-BDC}$ on MIL-88 (Fe) ⁴⁷. For OH-MIL-88 (Fe) , a sharp characteristic peak representing the O-H stretching vibration of free hydroxyl groups could be seen at 3675 cm^{-1} , implying the combination of OH-BDC and MIL-88 (Fe) . In conclusion, all these results suggested that successful preparation of $\text{NH}_2\text{-MIL-88 (Fe)}$ and OH-MIL-88 (Fe) .

Following, XPS spectra was employed to further analyze the surface chemical information two LMOFs, and the full-survey spectrum of $\text{NH}_2\text{-MIL-88 (Fe)}$ and OH-MIL-88 (Fe) was described in (**Figure 1k**). Wherein, the noticeable signals of C, N, O, and Fe could be observed, and the elemental contents of Fe in $\text{NH}_2\text{-MIL-88 (Fe)}$ and OH-MIL-88 (Fe) were 23.35% and 22.02% (**Table S1**), represented the successful preparation of two Fe-based LMOFs. **Figure S4** summarized the Fe 2p high-resolution XPS spectra of $\text{NH}_2\text{-MIL-88 (Fe)}$ and OH-MIL-88 (Fe) , which were related to the typical peaks of Fe $2p_{3/2}$ (712 eV) and Fe $2p_{1/2}$ (725 eV), respectively. These two peaks could be fitted to several peaks of 711.6, 714.5, 725.4 and 729.9 eV, which were usually designated as the presence of Fe^{III} . Another peak centered on 718.25 eV was the satellite peak of Fe^{III} . The same results were also observed on OH-MIL-88 (Fe) ⁴⁸. Furthermore, O1s spectrum in $\text{NH}_2\text{-MIL-88 (Fe)}$ could be deconvoluted into three peaks at 530.4, 531.89 and 533.18 eV (**Figure S5a**), which are assigned to Fe-O bands, BDC linker carboxylic acid groups (C=O) and surface hydroxyl groups (-OH). The same results were also observed on OH-MIL-88 (Fe) (**Figure S5b**). Additionally, Brunauer-Emmett-Teller (BET) measurements revealed that $\text{NH}_2\text{-MIL-88 (Fe)}$ exhibited a surface area of $1010.3\text{ m}^2/\text{g}$, significantly higher than that of OH-MIL-88 (Fe) ($112.2\text{ m}^2/\text{g}$), whereas $\text{NH}_2\text{-MIL-88 (Fe)}$ had smaller pore size (2.66 nm) compared to OH-MIL-88 (Fe) (12.0 nm) (**Figure S6 and Figure S7**). Meanwhile, the average zeta potentials of $\text{NH}_2\text{-MIL-88 (Fe)}$ and OH-MIL-88 (Fe) were 30.13 and 20.31 mV, respectively (**Figure S8**). All these results

revealed the form of NH₂-MIL-88 (Fe) and OH-MIL-88 (Fe).

Luminescent property of NH₂-MIL-88 (Fe) and OH-MIL-88 (Fe)

Following, the fluorescence properties of NH₂-MIL-88 (Fe) and OH-MIL-88 (Fe) were further studied. Shown in **Figure S9**, the synthesized NH₂-MIL-88 (Fe) and OH-MIL-88 (Fe) presented optimal excitations at 350 nm and 317 nm, respectively. Interestingly, NH₂-MIL-88 (Fe) and OH-MIL-88 (Fe) showed the similar fluorescence emission, which located at 435 nm. Then, fluorescence lifetime analysis and stability tests were conducted to assess the luminescent behavior of NH₂-MIL-88 (Fe) and OH-MIL-88 (Fe). **Figure S10** and **Table S2** showed that the average fluorescence lifetimes were 9.03 ns for NH₂-MIL-88 (Fe) and 7.19 ns for OH-MIL-88 (Fe), confirming the excellent luminescent characteristics of two Fe-based LMOFs. In addition, both NH₂-MIL-88 (Fe) and OH-MIL-88 (Fe) demonstrated stable fluorescence properties when exposed to different pH environments (**Figure S11a**). Meanwhile, two Fe-based LMOFs could retain 85% of original fluorescence intensities after the long storage (**Figure S11b**), suggesting excellent fluorescent stability. Collectively, these results demonstrated the excellent luminescent properties of both NH₂-MIL-88 (Fe) and OH-MIL-88 (Fe).

Fluorescent Sensor Array for Discrimination of Multiple Arsenic Speciation

Following, NH₂-MIL-88 (Fe) and OH-MIL-88 (Fe) were employed as sensing elements for designing a novel fluorescent sensor array for the rapid discrimination of four arsenic speciation, including As^{III}, As^V, MMA^V, and DMA^V (**Figure 2a**). Wherein, four arsenic speciation at 5 µg/mL all increased the fluorescence intensities of NH₂-MIL-88 (Fe), meanwhile, As^V, MMA^V, and DMA^V also could enhance the fluorescence performance of OH-MIL-88 (Fe) (**Figure 2b**). Interestingly, the fluorescence intensities of OH-MIL-88 (Fe) observably decreased with the addition of As^{III} (**Figure 2c**). And Fluorescence response patterns visualized in radar plots (**Figure 2d**) and heat map (**Figure 2e**) confirmed the excellent performance of sensor array for identifying As^{III}, As^V, MMA^V, and DMA^V. Subsequently, the collected fluorescence patterns were subjected to LDA and HCA for data processing. **Figure 2f** demonstrated the accurate classification of four arsenic species (As^{III}, As^V, MMA^V, and DMA^V) into their respective groups without misclassification, and the

LDA results revealed distinct, non-overlapping distributions for As^{III} , As^{V} , MMA^{V} , and DMA^{V} (**Figure 2g**). In addition, the repeatability ($n=8$) of the sensor array for the detection of multiple arsenic speciation was further assessed. And the results of heatmap indicated that the proposed sensor array exhibited good repeatability for the identification of multiple arsenic speciation (**Figure S12**). Besides, the developed sensor array was employed for further discriminating four arsenic speciation with other concentrations. The results recorded in **Figure S13-S19** exhibited entire correct classification of As^{III} , As^{V} , MMA^{V} , and DMA^{V} at 1, 2, 10, 20, 30, 40, and 50 $\mu\text{g/mL}$. These findings demonstrated that the developed fluorescent sensor array enabled accurate discrimination of four arsenic species.

Sensing Mechanisms of Fluorescence Sensor Array for Arsenic Speciation

To investigate the underlying principle of the sensor array for arsenic speciation detection, we selected $\text{NH}_2\text{-MIL-88 (Fe)}$ as a representative, and revealed the interaction between As^{III} and As^{V} with $\text{NH}_2\text{-MIL-88 (Fe)}$. By comparing the fluorescence lifetime, we found that both As^{III} and As^{V} could improve the fluorescence lifetime of $\text{NH}_2\text{-MIL-88 (Fe)}$ (**Figure 3a** and **Table S3**). We speculate that As^{III} and As^{V} may bond with Fe^{3+} in $\text{NH}_2\text{-MIL-88 (Fe)}$ to form Fe-O-As coordination, and regulate the coordination field effect of Fe^{3+} , which promote the transfer of excited state electrons from organic ligands (2-amino terephthalic acid) to Fe centers, delaying electron-hole recombination and prolonging fluorescence lifetime. Following, the interaction of As^{III} and As^{V} with $\text{NH}_2\text{-MIL-88 (Fe)}$ was further studied through a series of characterizations, including elemental mapping, zeta potential, FTIR and XPS spectra. Shown in **Figure 3b** and **S20**, the characteristic element of As was obviously observed in the elemental mapping of $\text{NH}_2\text{-MIL-88 (Fe)}$ with the addition of As^{III} and As^{V} , indicating the combination of $\text{NH}_2\text{-MIL-88 (Fe)}$ and As. Meanwhile, the introduction of As did not transform the morphology of $\text{NH}_2\text{-MIL-88 (Fe)}$. Moreover, the zeta potentials of $\text{NH}_2\text{-MIL-88 (Fe)}$ decreased from 30.73 mV to 19.23 and 24.17 mV after reacting with As^{III} and As^{V} , respectively, indicating the interaction of As^{III} and As^{V} with $\text{NH}_2\text{-MIL-88 (Fe)}$ (**Figure S21**). In the XPS full spectrum (**Figure 3c**) and high-resolution fine As 3d spectra (**Figure 3d**), the characteristic peaks of As 3d were located at 45.6 and 45.9 eV in $\text{NH}_2\text{-MIL-88 (Fe)+As}^{\text{III}}$ and $\text{NH}_2\text{-MIL-88 (Fe)+As}^{\text{V}}$ respectively, verifying that As^{III} and As^{V} were

undoubtedly loaded into the NH₂-MIL-88 (Fe). Meanwhile, after the reaction of NH₂-MIL-88 (Fe) with As^{III} and As^V, a new peak at 531.4 eV corresponding to As-O appeared in O 1s spectra of NH₂-MIL-88 (Fe)+As^{III} and NH₂-MIL-88 (Fe)+As^V (**Figure 3e**), indicating the interaction of As^{III} and As^V with NH₂-MIL-88 (Fe). Furthermore, XPS analysis revealed a positive shift in the Fe 2p binding energy (**Figure 3f**), consistent with strong coordination between arsenate species and the Fe³⁺-μ₃-oxo clusters in NH₂-MIL-88 (Fe). Additionally, the FTIR spectra of NH₂-MIL-88 (Fe) (**Figure S22**) revealed a new peak at 828 cm⁻¹ upon the addition of As^{III} and As^V, corresponding to the symmetric and asymmetric stretching vibrations of As-O in the As-O-Fe bond, which was in agreement with the XPS results. In conclusion, the enhancement of fluorescent intensity of NH₂-MIL-88 (Fe) induced by As^{III} and As^V was attributed to the formation of Fe-O-As coordination by the interaction between As^{III} and As^V with NH₂-MIL-88 (Fe).

Quantitative Analysis and Mixtures differentiation of Arsenic Speciation

Then, the quantitative detection of different arsenic speciation (As^{III}, As^V, MMA^V, and DMA^V) was further investigated. Firstly, the reaction time and probe concentration were assessed to achieve optimal performance. When the reaction time tended to 2 min, the relative fluorescence intensity (F/F_0) of NH₂-MIL-88 (Fe) and OH-MIL-88 (Fe) to four arsenic speciation maintained stable (**Figure S23a and S23b**), thus the optimal reaction time was employed as 2 min. Furthermore, the fabricated sensor array successfully discriminated among the four arsenic species at a 1:1 ratio between NH₂-MIL-88 (Fe) or OH-MIL-88 (Fe) and the arsenic species (**Figure S23c and S23d**). Based on the above conditions, the capacity of the developed sensor array for the discrimination of varying concentrations of individual arsenic species was examined. As shown in **Figure 3g and 3h**, As^{III} with different concentrations was accurately classified into its respective groups without misclassification or overlap, confirming the ability of the fluorescent sensor array to effectively differentiate different concentrations of As^{III}. Furthermore, there was a good linear relationship between factor 1 values from the LDA and As^{III} concentrations in the range of 1-50 μg/mL (**Figure 3i**), and the limit of detection (LOD) for As^{III} was determined to be approximately 0.33 μg/mL using the 3σ/k method. Besides, the quantitative results for other three arsenic

speciation (As^{V} , MMA^{V} , and DMA^{V}) were obtained in **Figure S24**, and the calculated LODs were 0.12, 0.28, and 0.23 $\mu\text{g/mL}$, respectively (**Table S4**).

Subsequently, the performance of the developed sensor array in discriminating the mixtures of arsenic species was evaluated. Firstly, the mixtures of As^{III} and MMA^{V} with varying ratios ($\text{As}^{\text{III}}/\text{MMA}^{\text{V}}=10:0$, 8:2, 6:4, 4:6, 2:8, and 0:10, total concentration is 10 $\mu\text{g/mL}$) were prepared and detected by the fluorescent sensor array. **Figure 3j** demonstrated that LDA analysis successfully distinguished $\text{As}^{\text{III}}/\text{MMA}^{\text{V}}$ mixtures at different molar ratios, a result supported by the accurate categorical classification of HCA results (**Figure S25**). Moreover, the binary mixtures (As^{III} and As^{V}) at varying ratios ($\text{As}^{\text{III}}/\text{As}^{\text{V}}=10:0$, 8:2, 6:4, 4:6, 2:8, and 0:10) were also distinguished by the developed sensor array (**Figure S26**). Additionally, the ternary mixtures (As^{III} , As^{V} , and MMA^{V}) at different molar ratios ($\text{As}^{\text{III}}/\text{As}^{\text{V}}/\text{MMA}^{\text{V}}=1:0:0$, 0:1:0, 0:0:1, 8:1:1, 1:8:1, 1:1:8, 6:2:2, 2:6:2, and 2:2:6, total concentration is 10 $\mu\text{g/mL}$) were further investigated, and the results demonstrated that the sensor array maintained excellent discrimination performance for ternary mixtures of arsenic speciation (**Figure 3k** and **S27**). Furthermore, the quaternary mixtures (As^{III} , As^{V} , DMA^{V} , and MMA^{V}) at different molar ratios ($\text{As}^{\text{III}}/\text{As}^{\text{V}}/\text{DMA}^{\text{V}}/\text{MMA}^{\text{V}}=1:1:1:1$, 1:0:0:0, 0:1:0:0, 0:0:1:0, 0:0:0:1, 6:2:1:1, 2:6:1:1, 1:1:6:2, and 1:1:2:6, total concentration is 10 $\mu\text{g/mL}$) were effectively differentiated by the achieved sensor array (**Figure 3l** and **S28**). Following, the quantitative analysis of the arsenic speciation mixture was further assessed, and the intensity of six two-component groups, three three-component groups and one four-component groups were measured with ratios of 1:1. The regression equation was fitted after HCA and LDA. As depicted in **Figures S29-S31**, a strong linear correlation was observed at concentrations of 1-50 $\mu\text{g/mL}$ across samples, and the quantitative results were presented in **Table S4**. Consequently, the results confirmed that the sensor array was capable of detecting the mixtures of arsenic species. Additionally, the anti-interference performance was examined by introducing multiple interfering ions into the sensor array system, including cations (Na^+ , Mg^{2+} , Zn^{2+} , Fe^{2+} , Hg^{2+} , Pb^{2+} , Cr^{3+} , Ag^+ , and Co^{2+}) and anions (CO_3^{2-} , SO_4^{2-} , Cl^- , Br^- and NO_3^-). **Figure S32** demonstrated the complete separation between all interfering substances and arsenic species, highlighting the exceptional anti-interference capability. Although the

proposed sensor array still had some shortcomings in terms of sensitivity, our findings revealed significant improvements over previous studies for arsenic speciation analysis (**Table S5**): (a) multi-targets capability: the fluorescent sensor array could achieve the identification of four arsenic speciation, and its recognition ability was significantly superior to that of other sensors. (b) rapid response: our sensor achieved the detection of arsenic speciation within 2 minutes, showing enormous contribution for initiating the correct emergency response in arsenic contamination; (c) simplicity: compared with the complexity of instrumental methods, the simplicity of our sensor was more suitable for rapid, on-site decision-making during emergencies. These findings confirmed the robust capability of the developed sensor array for the quantitative analysis of arsenic speciation and differentiation of their mixtures, laying a good foundation for the detection of arsenic speciation in arsenic contamination.

Machine Learning-Assisted Fluorescent Sensor Array for Identifying Arsenic Speciation

The qualitative discrimination of arsenic species was frequently compromised by concentration interference effects. For example, a high concentration of arsenic speciation with a weak enhanced effect may generate the similar fluorescent responses to another arsenic speciation with low concentration with a strong enhanced effect. Therefore, it is a great challenge to accurately identifying different arsenic speciation by the proposed sensor array.

In this study, support vector machine (SVM) was employed to establish a stepwise prediction model to improve the recognition performance of the proposed fluorescent sensor array. Firstly, a dataset (n=160) of four arsenic speciation × eight concentrations (1-50 µg/mL) × five parallels was constructed, which was divided into training sets (80%, n=128) and test sets (20%, n=32) (**Figure S33**), and the specific database was listed in **Table S6**. Then, the corresponding classification model and regression model of arsenic speciation was established, which was shown in **Figure 4a**. The workflow involved the initial species identification based on sensor array response patterns (enhancement/inhibition effects), followed by category information extraction. The system then automatically initiated the

relevant regression model to predict concentration, ultimately providing simultaneous species and concentration outputs. As depicted in **Figure 4b-4e**, the accuracies of the training set and the test set are 96.09% and 96.88%, respectively, and the SVM model maintained good accuracy over 15 experimental replicates (**Figure S34**), confirming its robust stability. To avoid the potential overlap between the training and test set distributions caused by random partitioning, this study further employed the more robust k-fold stratified cross-validation method for model training and evaluation. The results showed that the model achieved an average accuracy of over 90% across the five validation runs, and the corresponding step chart and confusion matrix were presented in **Figure S35**. Meanwhile, the stepwise prediction model was used to further distinguish four arsenic species (As^{III} , As^{V} , DMA^{V} , and MMA^{V}) at a single concentration (1, 2, 5, 10, 20, 30, 40, and 50 $\mu\text{g/mL}$) and their multiple mixtures. As shown in **Figures S36 and S37**, SVM model exhibited accurate differentiation of As^{III} , As^{V} , DMA^{V} , and MMA^{V} at a single concentration. Meanwhile, the stepwise prediction model also showed good performance in identifying binary (**Figures S38 and S39**), ternary (**Figures S40**), and quaternary arsenic speciation (**Figures S41**), and the specific database was listed in **Table S7**. These results demonstrated that the proposed machine learning-assisted fluorescent sensor array can accurately distinguish different arsenic speciation and their mixtures qualitatively. Furthermore, the integration of stepwise prediction model and the developed sensor array was applied to accomplish the quantitative detection of arsenic speciation. Following, according to the established regression prediction model, we analyzed the fitting effect of the arsenic speciation in the concentration range of 1-50 $\mu\text{g/mL}$. The good fitting results were showed in **Figure 4f-4i**, **Figure S42**, and **Table S8**. Besides, the quantitative modeling and prediction for mixed arsenic species were also tested. Meanwhile, we used the established regression prediction model to analyze the fitting effect of the mixed arsenic speciation in the concentration range of 1-50 $\mu\text{g/mL}$, and the results were provided in **Figure S43-44** and **Table S8**. Meanwhile, the specific database was listed in **Table S9**. Therefore, the stepwise prediction model-supported fluorescent sensor array could achieve the qualitative and quantitative prediction of different arsenic speciation.

Actual Sample Analysis

The practicability of our proposed sensor array can be accessed by testing actual water samples, wherein ten water samples (S1-S10) were collected from Grand Canal and Yangtze River in Zhenjiang city (**Figure 5a** and **Table S10**). To verify the feasibility of the sensor array for real water samples, ten water samples (S1-S10) and four labeled samples (L1-L4) were tested, and the detection results were showed in **Figure 5b** and **5c**. Wherein, no arsenic speciation was detected in all ten real samples, but different arsenic speciation was observed in the four labeled samples. To further investigated the applicable performance of the machine learning-assisted sensor array, eight random actual water samples selected from ten water samples (S1-S10) were spiked different arsenic speciation (As^{III} , As^{V} , DMA^{V} , and MMA^{V}) with different concentration (5 and 20 $\mu\text{g/mL}$), respectively, which were determined by the proposed fluorescent sensor array, and processed by the stepwise prediction model. **Figure 5d** demonstrated perfect discrimination (100% accuracy) of all four arsenic species across eight spiked water samples, confirming its exceptional classification capability. Furthermore, quantitative results presented in **Figure 5e** demonstrated close agreement with spiked values, showing recoveries ranging from 94.9% to 106%. It implied that combining machine learning with sensor arrays enabled considerable practical application for accurate identification and prediction of arsenic speciation, providing a powerful tool for environmental monitoring.

ENVIRONMENTAL IMPLICATIONS

In this study, a stepwise prediction model-driven fluorescent sensor array based on $\text{NH}_2\text{-MIL-88 (Fe)}$ and OH-MIL-88 (Fe) was designed for accurate identification and prediction of four arsenic speciation, including arsenite (As^{III}), arsenate (As^{V}), monomethylarsonic acid (MMA^{V}), and dimethylarsinic acid (DMA^{V}). The approach addresses the critical bottleneck in responding to sudden arsenic contamination events-the lack of rapid, on-site speciation analysis, providing a rapid and sensing platform for the identification and prediction of multiple arsenic speciation. Although our sensor array has certain limitations in terms of sensitivity, the unique value of rapid detection in on-site emergency response is sufficient to prove that the proposed method is reasonable. In the future, the sensitivity of the provided

platform can be gradually improved without sacrificing the core advantages of speed and portability. In conclusion, our findings provided an emerging sensing strategy for the identification of multiple arsenic speciation, particularly valuable in resource-limited settings, carving a promising way for emergency response in water pollution incidents.

ASSOCIATED CONTENT

Supporting Information

Characterization of NH₂-MIL-88 (Fe) and OH-MIL-88 (Fe); assessment of fluorescence property for NH₂-MIL-88 (Fe) and OH-MIL-88 (Fe); HCA and LDA plot for the identification of four arsenic speciation at different concentrations; mechanism exploration of NH₂-MIL-88 (Fe) for detecting As^{III} and As^V; optimization of the fluorescence array sensor; quantitative analysis of sensor array for arsenic speciation; evaluation of sensor array for the mixtures of arsenic speciation; anti-interference ability of sensor array; accuracy of SVM model; predicted results for different arsenic speciation and their mixture by SVM; regression results for different concentrations of arsenic speciation (PDF).

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

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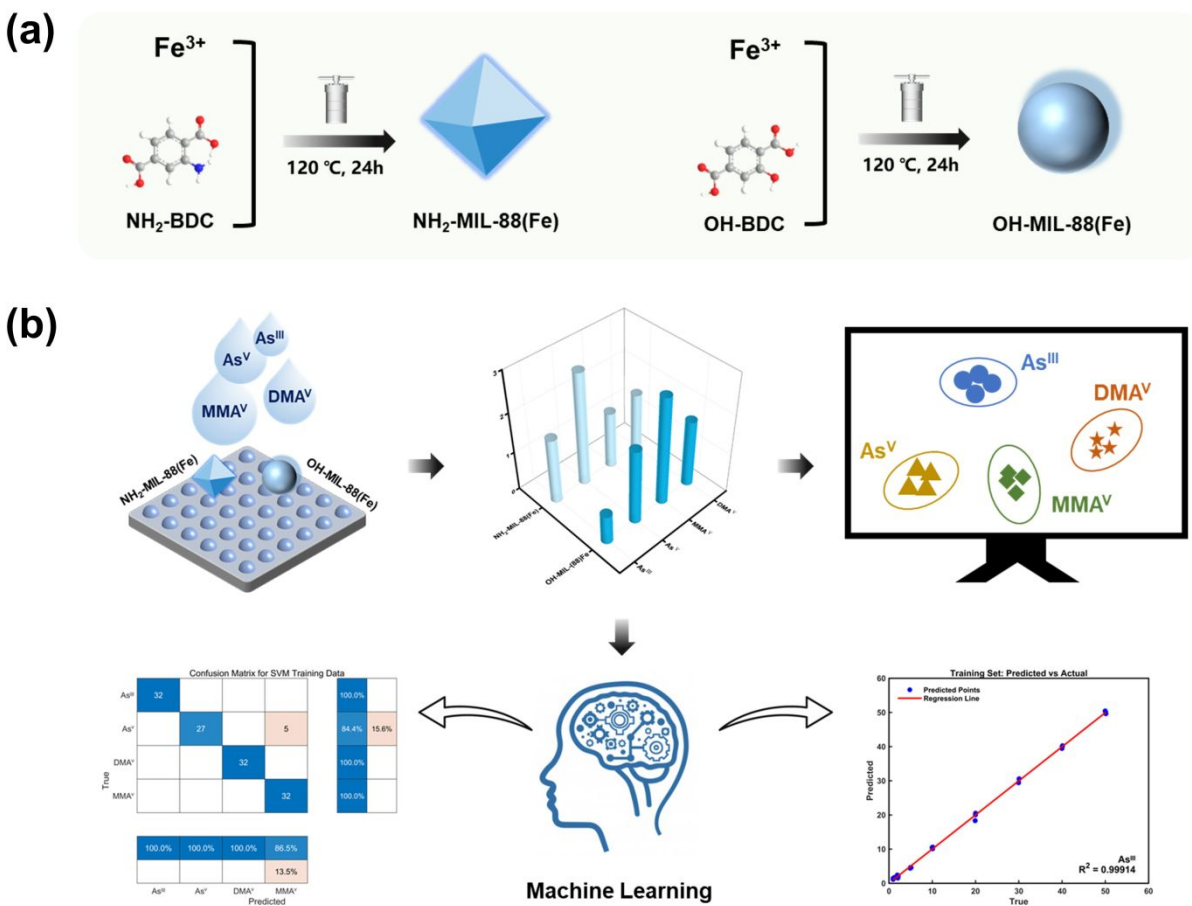
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Scheme 1. (a) Schematic representation of the synthesis for $\text{NH}_2\text{-MIL-88 (Fe)}$ and OH-MIL-88 (Fe) . (b) The development of fluorescence sensor array with machine learning algorithms for the discrimination of four arsenic speciation.

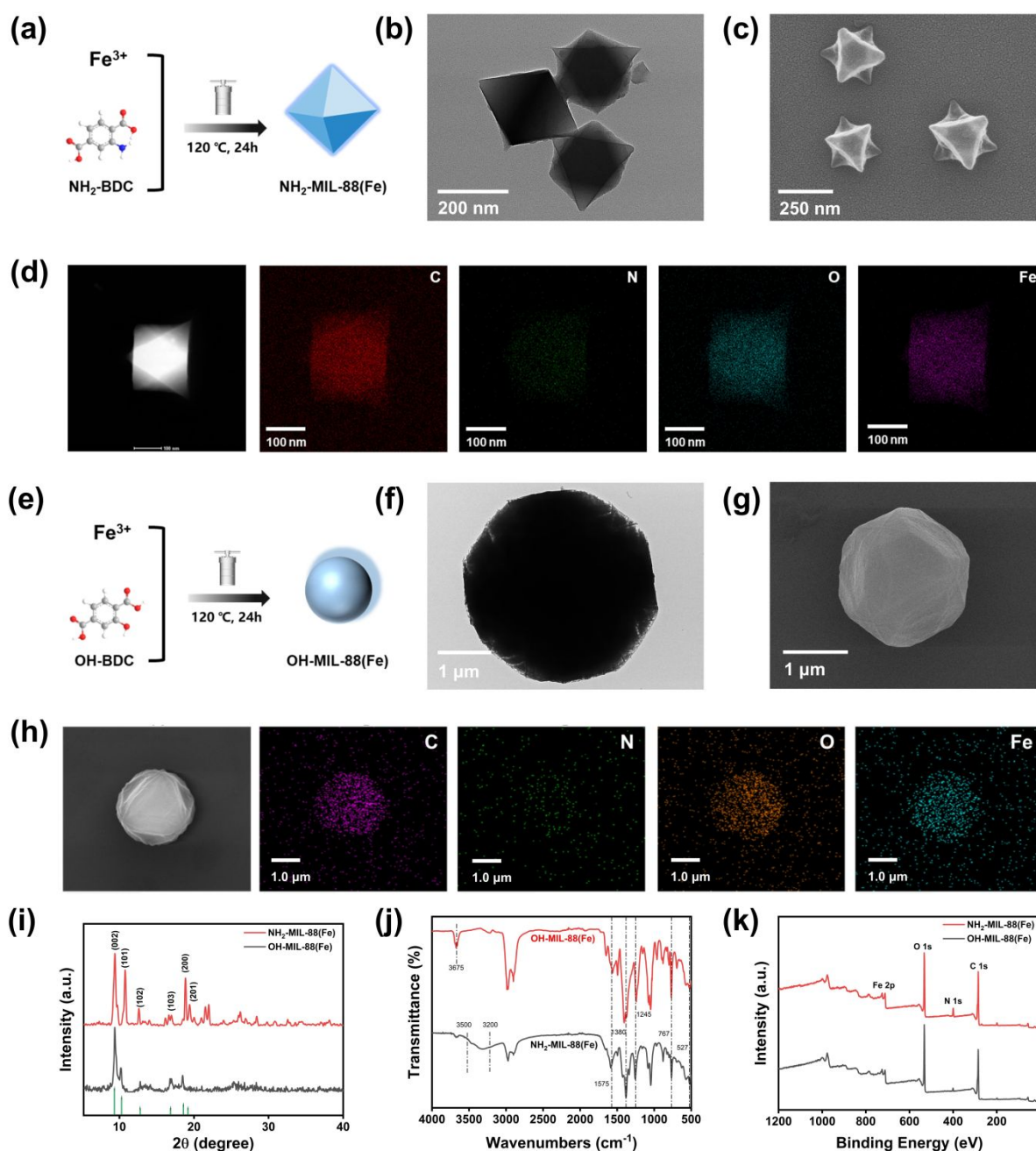


Figure 1. (a) Schematic diagram of the synthesis of NH₂-MIL-88(Fe). (b) TEM and (c) SEM images of NH₂-MIL-88(Fe). (d) HAADF and the corresponding mapping (C, N, O, and Fe) of NH₂-MIL-88(Fe). (e) Schematic diagram of the synthesis of OH-MIL-88(Fe). (f) TEM and (g) SEM images of OH-MIL-88(Fe). (h) HAADF and the corresponding mapping (C, N, O, and Fe) of OH-MIL-88(Fe). (i) XRD patterns, (j) FT-IR spectra, and (k) XPS of NH₂-MIL-88(Fe) and OH-MIL-88(Fe).

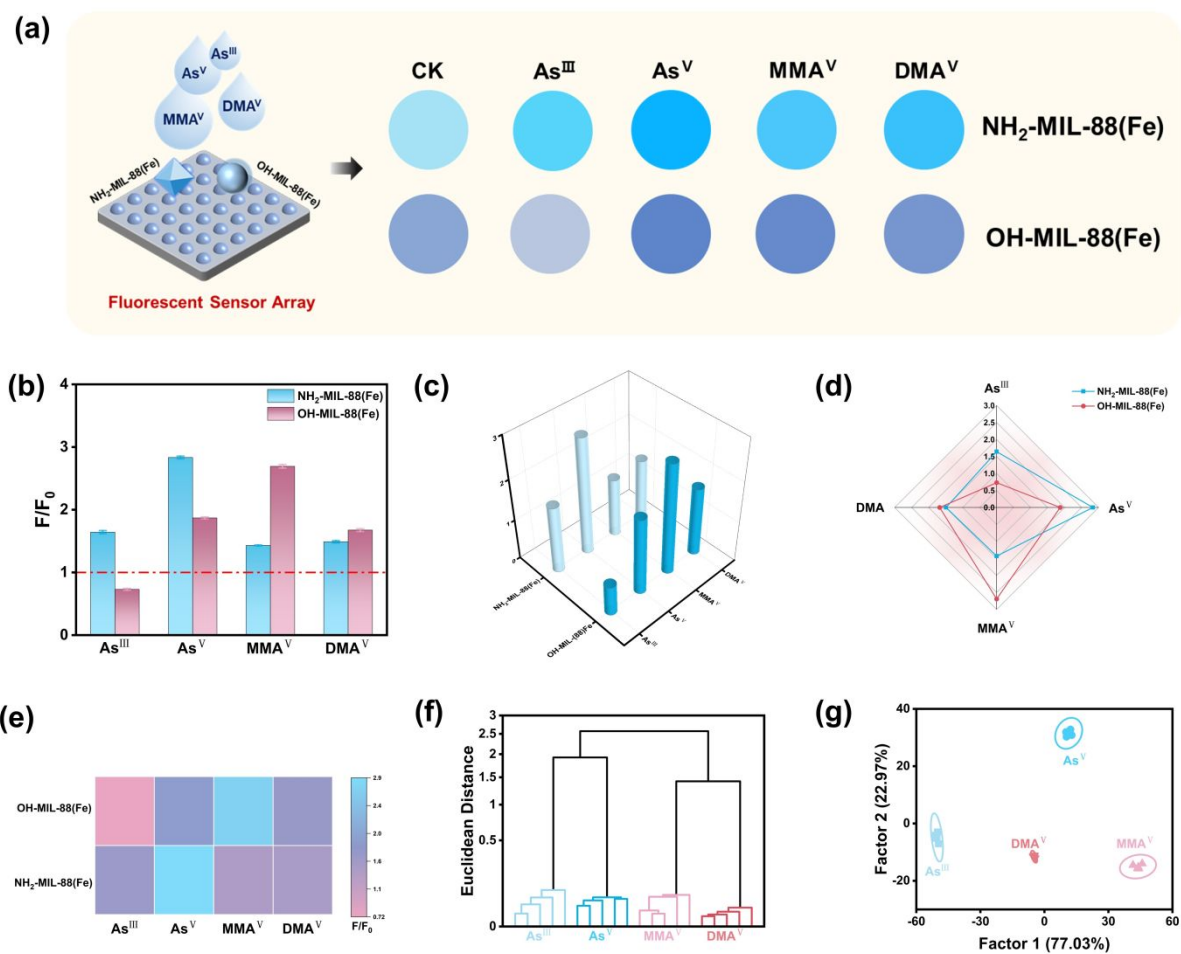


Figure 2. (a) Construction of the fluorescent sensor array based on $\text{NH}_2\text{-MIL-88(Fe)}$ and OH-MIL-88(Fe) for arsenic speciation detection. (b, c) Fluorescent intensity ratio (F/F_0) responses and (d) radar plot of $\text{NH}_2\text{-MIL-88(Fe)}$ and OH-MIL-88(Fe) to four arsenic speciation (As^{III} , As^{V} , MMA^{V} , and DMA^{V}) at $5\text{ }\mu\text{g/mL}$. (e) Visualized heat map generated from fluorescence patterns of fluorescence sensor array. (f) HCA and (g) LDA plot for the identification of four arsenic speciation at $5\text{ }\mu\text{g/mL}$ derived from the fluorescence-response patterns.

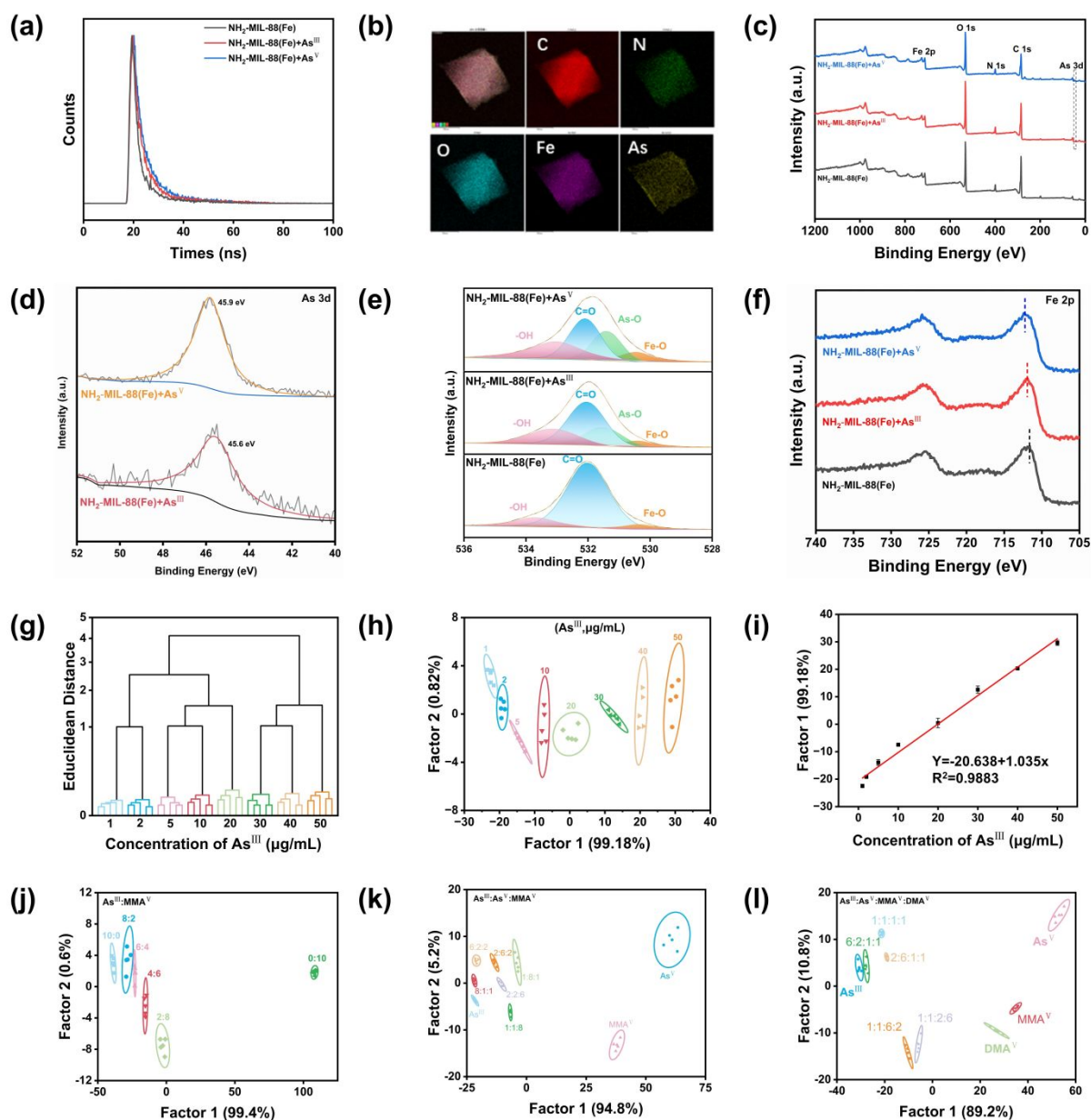


Figure 3. (a) Fluorescence lifetime of $\text{NH}_2\text{-MIL-88 (Fe)}$ in the presence of As^{III} and As^{V} . (b) EDS mapping images of $\text{NH}_2\text{-MIL-88 (Fe)}$ with the addition of As^{III} . (c) Full XPS spectra of $\text{NH}_2\text{-MIL-88 (Fe)}$, $\text{NH}_2\text{-MIL-88 (Fe)+As}^{\text{III}}$, and $\text{NH}_2\text{-MIL-88 (Fe)+As}^{\text{V}}$. (d) XPS spectra of As 3d for $\text{NH}_2\text{-MIL-88 (Fe)+As}^{\text{III}}$ and $\text{NH}_2\text{-MIL-88 (Fe)+As}^{\text{V}}$. XPS spectra of (e) O 1s and (f) Fe 2p for $\text{NH}_2\text{-MIL-88 (Fe)}$, $\text{NH}_2\text{-MIL-88 (Fe)+As}^{\text{III}}$, and $\text{NH}_2\text{-MIL-88 (Fe)+As}^{\text{V}}$. (g) HCA and (h) LDA plot for fluorescence response patterns toward different concentrations of As^{III} . (i) Linear relationships between factor 1 and various concentrations of As^{III} . LDA plot for fluorescence response patterns toward (j) binary mixtures (As^{III} and MMA^{V}), (k) ternary mixtures (As^{III} , As^{V} , and MMA^{V}), and (l) quaternary mixtures (As^{III} , As^{V} , DMA^{V} , and

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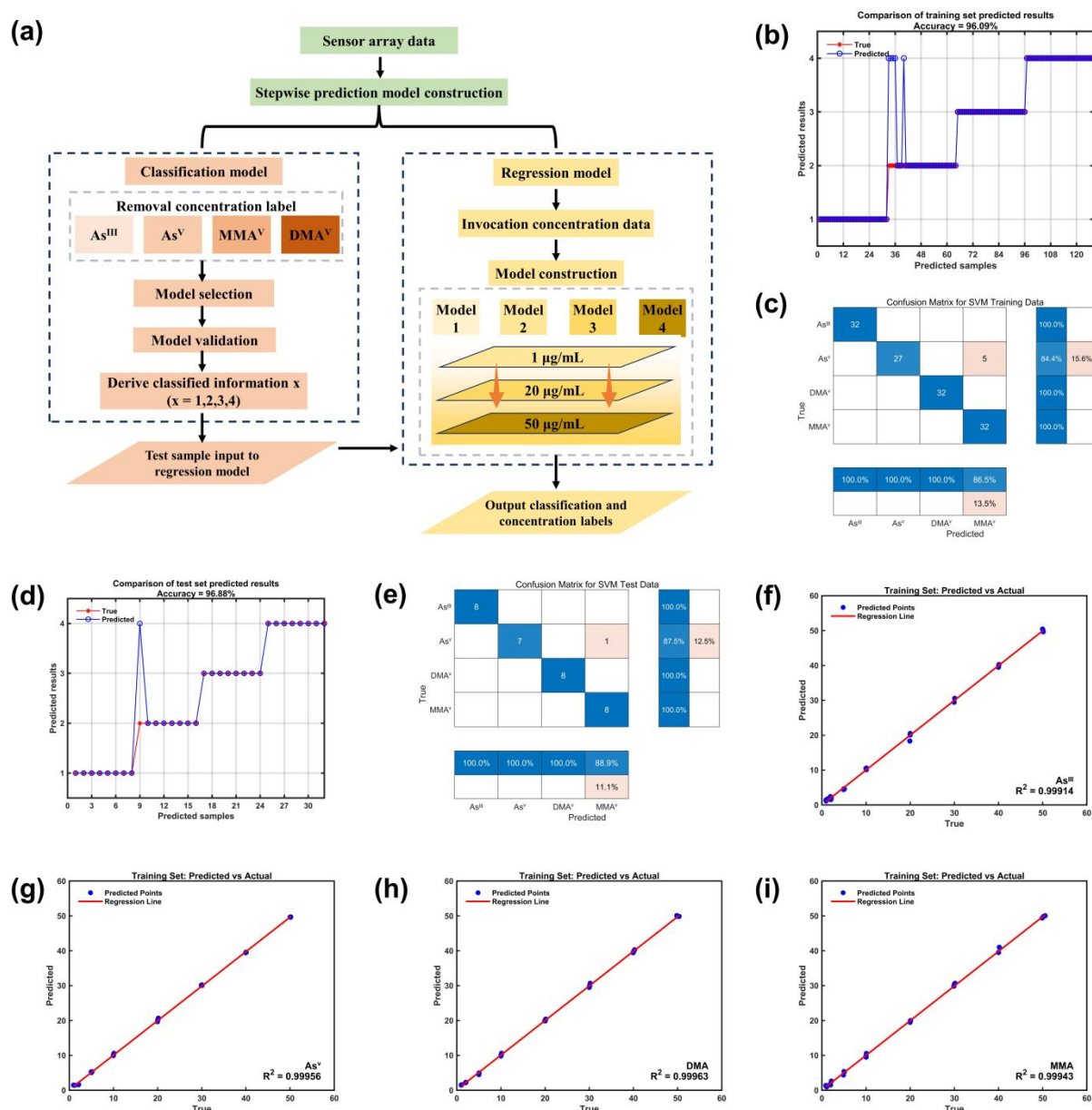


Figure 4. (a) Stepwise prediction models based on classification and regression algorithms by SVM for qualitative and quantitative arsenic speciation recognition. (b) Comparison of training set predicted results. (c) Confusion matrix for training data. (d) Comparison of test set predicted results. (e) Confusion matrix for testing data. Regression analysis of (f) As^{III} , (g) As^{V} , (h) DMA^{V} , and (i) MMA^{V} by using SVM.

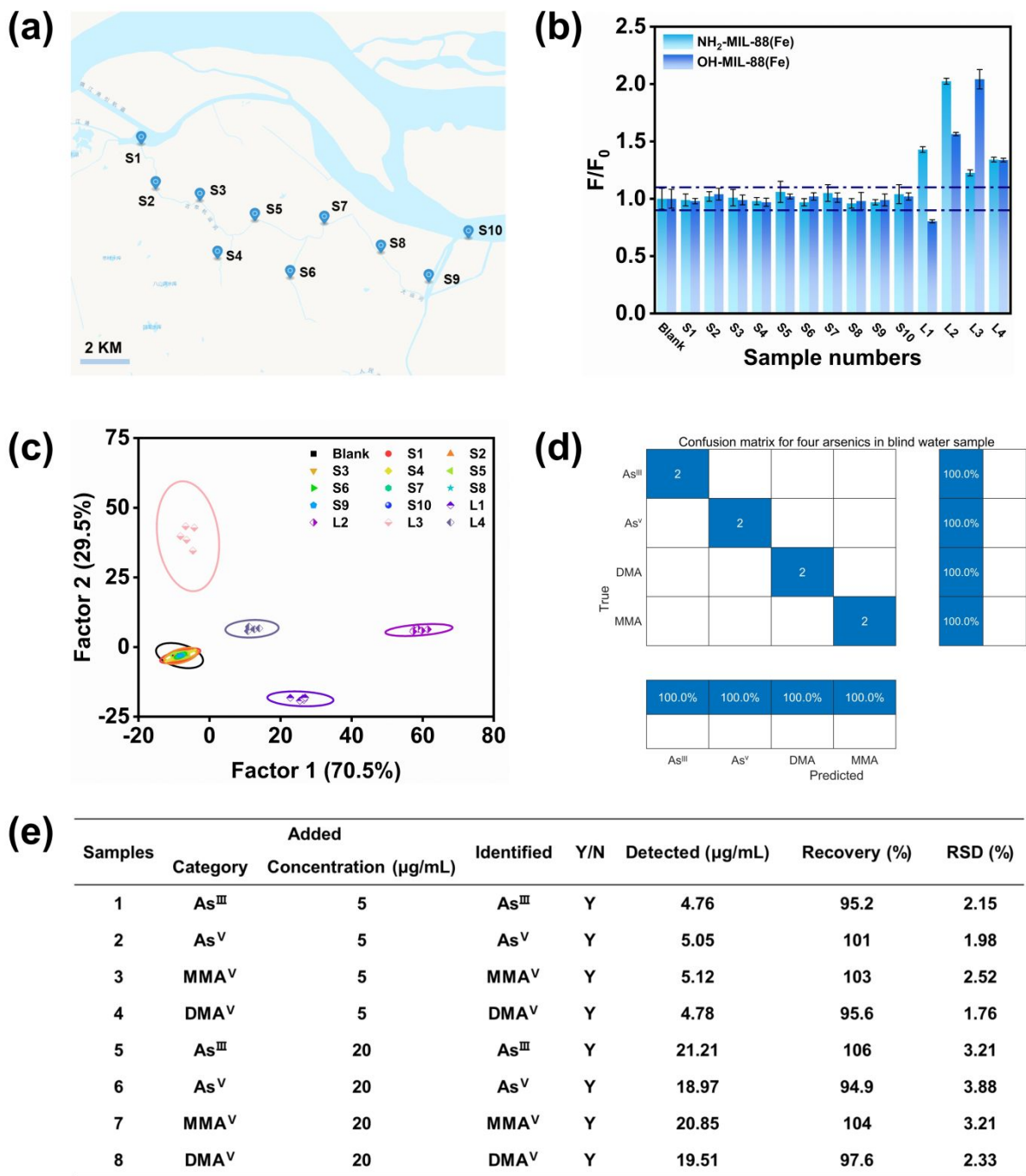


Figure 5. (a) The map of actual water samples (S1-S10) collected from Grand Canal and Yangtze River in Zhenjiang city. (b) Fluorescent intensity ratio (F/F_0) responses of arsenic speciation in ten actual water samples (S1-S10) and four labeled water samples (L1-L4) detected by the proposed sensor array. (c) LDA plot for the identification of arsenic speciation in ten actual water samples (S1-S10) and four labeled water samples (L1-L4) derived from the fluorescence-response patterns. (d) Confusion matrix for the arsenic speciation in blind water sample. (e) Table showing the results of arsenic speciation analysis.

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Enabling emergency response to arsenic contamination: simultaneous and rapid identification of arsenic speciation by a machine learning-driven fluorescent sensor array

Wei, Dali; Fan, Yunxiang; Wu, Bohan; Shen, Yuxuan; Deng, Chunmeng ...

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